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CK-12 Chemistry - Basic

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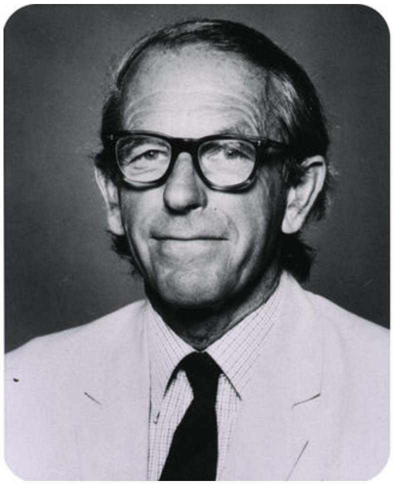
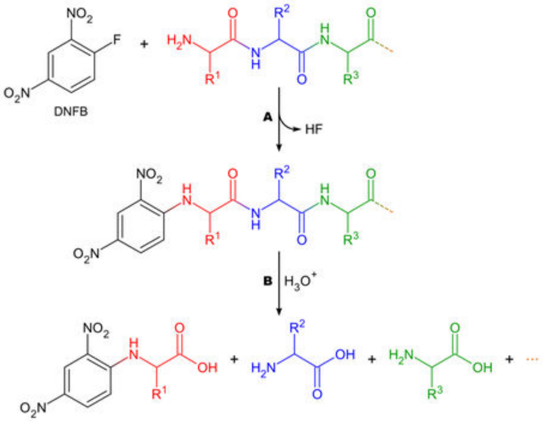
CHAPTER 1 Introduction to Chemistry

Chapter Outline

1.1 WHAT IS CHEMISTRY?
1.2 THE SCIENTIFIC METHOD
1.3 REFERENCES





Diabetes mellitus is a disease characterized by the body's inability to regulate glucose levels. Glucose (a component of table sugar) is needed to provide biochemical energy for all the cells of the body. When this process is disrupted, the body begins to break down fat and protein to provide the needed energy, which can eventually lead to death. Diabetes is mediated by a protein called insulin. A key piece of our understanding of diabetes came when Frederick Sanger, a British biochemist, carried out experiments to determine the structure of the insulin molecule. Sanger (shown in the opening image) used basic chemistry techniques and reactions and took twelve years to complete his research. Today, automated instruments based on his approach can perform the same analysis in a matter of days. Sanger was awarded the Nobel Prize in Chemistry in 1958 for his insulin research. The chemical processes that won Sanger the Nobel Prize is pictured on the right in the opening image. In this chapter, we will look at the history of chemistry, see the many areas of our lives that are touched by chemistry, and develop a basic understanding of what is involved in the process of scientific discovery.

Sanger image: Courtesy of the National Institutes of Health. commons.wikimedia.org/wiki/File:Frederick_Sanger2.jpg. Molecule: User:Sponk/Wikimedia Commons.

1.1 What is Chemistry?

Lesson Objectives

- Define the term “chemistry.”
- Describe the activities of alchemists and how they contributed to the modern science of chemistry.
- List some of the key scientists from the early history of chemistry along with their primary contributions to the field.
- List various modern items that have been developed through the study of chemistry.

Lesson Vocabulary

- **chemistry**: The science of the properties, reaction, composition, and structures of matter.
- **matter**: Anything that has mass and takes up space.
- **alchemist**: A practitioner of the Medieval science of alchemy, which aimed mainly to transform everyday metals into gold.
- **philosopher’s stone**: A substance that could cause the transmutation of lead into gold.

A Brief History of Chemistry

What is Chemistry?

If we look up the word “ **chemistry**” in the dictionary, we’ll find something like this: “The science of the composition, structure, properties, and reactions of **matter**, especially of atomic and molecular systems” (Free Online Dictionary). This definition is accurate, but it does not give us a good picture of the scope of chemistry or any practical aspects of the field.

Chemistry touches every area of our lives. The medicines we take, the food we eat, the clothes we wear –all these materials and more are, in some way or another, a product of chemistry. Later on in this chapter, we will look in detail at some of the ways that chemistry contributes to our lives.

Where Did Chemistry Come From?

Although the systematic study of chemistry is relatively new, chemical techniques have been used for thousands of years. Some civilizations kept good records of these techniques, which give us direct information about what earlier people knew. Fields of study such as archaeology provide additional information. Legends and folklore are also useful tools to learn about the chemical knowledge of previous cultures.

Thousands of years ago, the ancient Egyptians used chemical practices to develop techniques for producing perfumes and dyes. Studies of objects found in Egyptian tombs show that materials for coloring fabrics were known as far back as 2600 B.C.

Another area of chemistry that was highly developed by the early Egyptians was metallurgy. Beginning in about 3400 B.C., records show a highly developed technology for refining copper, gold, iron, and other metals. Although the reasons these techniques worked were not fully understood, the refiners were able to produce high-quality materials that were used in jewelry, decorations, and money.

Glass production also appears to have been first developed by the Egyptians (see **Figure** 1.1). A number of tomb paintings show glass-blowing and the manufacturing of glass products. The glass was often colored, suggesting an understanding of the use of dyes for decoration.

FIGURE 1.1

This ancient Egyptian glass jar is over 3000 years old.

Various types of medicines were also discovered by many ancient people. Records from civilizations around the world show that certain plants were used for healing specific disorders and for dealing with pain. The earliest medical "textbook" consisted of hundreds of clay tablets found in Mesopotamia, dating from about 2600 B.C. These tablets had information about thousands of plants and plant materials that had beneficial effects. An Egyptian papyrus from around 1550 B.C had over 800 prescriptions and 700 natural materials that were used for medical treatment (see **Figure** 1.2). The famous Greek physician Hippocrates (460-377 B.C.) wrote about using lemon juice as a laxative and an extract from the belladonna plant as an anesthetic. Indian writings from around 900 B.C. describe the preparations of over 300 different medicines. Traditional Chinese medicine has records from 350 B.C. that describe over 240 medicinal preparations and 150 drug combinations used to treat various ailments. Oral traditions from both North and South America also describe preparations used for healing. Some South American tribes used the venom from specific frogs (usually very brightly colored ones) for poisons. The chemical properties of these substances was not understood at the time, but chemical techniques were often used to isolate and purify various useful materials.

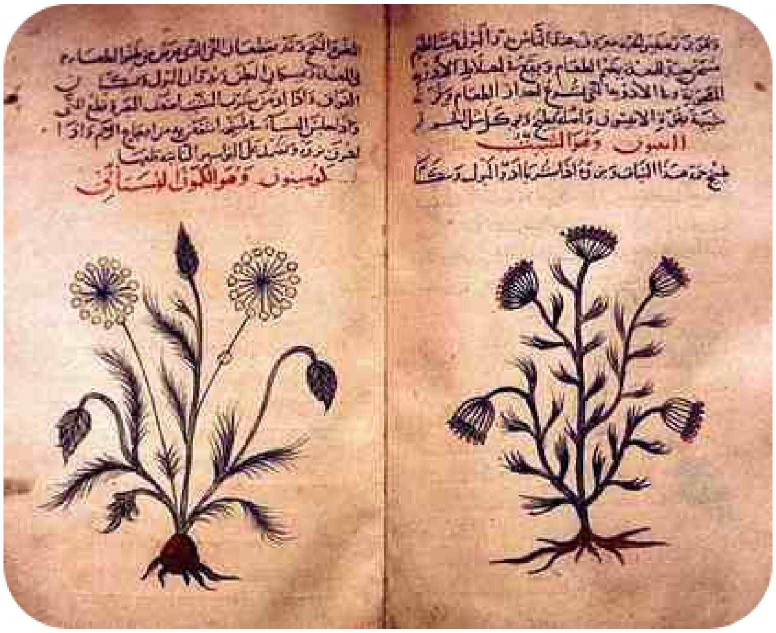


FIGURE 1.2

Pictures of herbal medicines. The Arabic text is from around 1330 A.D.

The Rise and Fall of the Alchemists

One area of technology present in all of the societies we have mentioned was metallurgy. Properly refined metals could be made into useful tools that could last a long time. Weapons could stay sharp longer with improved metals. Additionally, precious metals such as gold and silver could be refined and used in jewelry or as money. Because it was fairly rare, gold was considered to be very valuable and became a common means of paying for goods and services.

We don’t know exactly when humans began mining for gold. Items made from gold have been found in Bulgarian graves that are over 7000 years old. Archaeological studies show clear evidence of gold mining in many parts of the world from over 4000 years ago. During the time of the Roman Empire, the Romans had developed very sophisticated methods for extracting gold from the earth.

However, mining for gold is a slow, dirty, and dangerous process. Additionally, not everyone owns a gold mine –in both the ancient Egyptian society and during the Roman Empire, the gold mines were the property of the state and did not belong to any one individual or group. As a result, there were few ways for most people to legally get any gold for themselves.

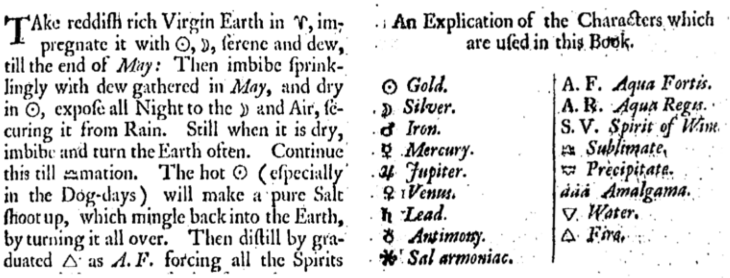
The **alchemists** were a varied group of scholars and charlatans (**Figure** 1.3). Two of the ultimate goals of alchemy were to create the **Philosopher’s Stone** (which is a substance that could cause the transmutation of lead into gold) and the Elixir of Life (which would bestow immortality on the person who possessed it). The origin of the term “alchemy” is uncertain, and the roots of this word are related to a number of Greek, Arabic, and ancient Egyptian words. Three major branches of alchemy are known (Chinese, Indian, and European), and all three have certain factors in common. We will not focus on the philosophical or religious aspects of alchemy, but we will look briefly at the techniques developed by European alchemists that ultimately influenced the development of the science of chemistry.

Many of the specific approaches that alchemists used when they tried changing lead into gold are vague and unclear. Each alchemist had his own methods of recording data, and the processes were kept secret so that others could not

FIGURE 1.3

An alchemist at work on his laboratory.

profit from them. Different scholars developed their own set of symbols as they recorded the information they came up with (see an example in **Figure** 1.4). Also, many alchemists were not very honest; it was not uncommon for an alchemist to take money from a nobleman by claiming to be able to make gold from lead and then to leave town in the middle of the night. Sometimes the nobleman would detect the fraud and have the alchemist hung. By the 1300s, several European rulers had declared alchemy to be illegal and set out strict punishments for those practicing the alchemical arts.



TAke reddiſh rich Virgin Earth in ♈, impregnate it with ☉, ☽, ſerene and dew, till the end of *May:* Then imbibe ſprinklingly with dew gathered in *May*, and dry in ☉, expoſe all Night to the ☽ and Air, ſecuring it from Rain. Still when it is dry, imbibe and turn the Earth often. Continue this till 🝞mation. The hot ☉ (eſpecially in the Dog-days) will make a pure Salt ſhoot up, which mingle back into the Earth, by turning it all over. Then diſtill by graduated △ as *A. F.* forcing all the Spirits

An Explication of the Characters which are uſed in this Book.

☉	*Gold.*	A. F.	*Aqua Fortis.*
☽	*Silver.*	A. ℞.	*Aqua Regis.*
♂	*Iron.*	S. V.	*Spirit of Wine.*
☿	*Mercury.*	🝞	*Sublimate,*
♃	*Jupiter.*	🝟	*Precipitate.*
♀	*Venus.*	ȧȧȧ	*Amalgama.*
♄	*Lead.*	▽	*Water.*
♁	*Antimony.*	△	*Fire.*
✱	*Sal armoniac.*		

FIGURE 1.4

An alchemical procedure and symbols.

However, despite this secrecy several contributions were made to modern-day chemistry. Early acids and bases were discovered, and glassware for running chemical reactions was developed. Alchemy helped improve the study of metallurgy and the extraction of metals from ores. More systematic approaches to research were being developed, although the idea of orderly scientific experimentation was not yet well-established. The groundwork was being laid for the development of chemistry as a foundational science.

The alchemists were never successful in changing lead into gold. Remarkably, modern nuclear physics can accomplish this task. If lead is subjected to nuclear bombardment in a particle accelerator, a small amount of gold can eventually be obtained. However, the cost of this procedure is far more than the value of the gold that can be obtained, so the dream of the alchemists has never (and will never) come true.

Events in the History of Chemistry

The history of chemistry is an interesting and challenging one. As we have already seen, very early chemists often were motivated mainly by the achievement of a specific goal or product. The manufacturing of perfume or soaps did not require a high level of theory, just a good recipe and careful attention to detail. Since there was no standard way of naming materials (and no periodic table that everyone could agree on), it was often difficult to figure out exactly what a particular individual was using. Nevertheless, the science of chemistry gradually developed over the centuries.

Major progress was made in putting chemistry on a solid foundation when Robert Boyle (1637-1691) began his research in chemistry. He developed basic ideas that allowed the behavior of gases to be described mathematically. Boyle also helped formulate the idea that small particles could combine to form molecules, which was expanded by John Dalton into an atomic theory a number of years later.

The field of chemistry began to develop rapidly in the 1700s, mainly through the discovery and isolation of specific materials. Joseph Priestley (1733-1804) isolated and characterized several gases, including oxygen, carbon monoxide, and nitrous oxide. It was later discovered that nitrous oxide ("laughing gas") worked as a general anesthetic, and it was first used for that purpose in 1844 during a tooth extraction. Other gases discovered during that time included chlorine, by C.W. Scheele (1742-1786), and nitrogen, by Antoine Lavoisier (1743-1794). Lavoisier is considered by many scholars to be the "father of chemistry."

Chemistry in the 1800s continued the discovery of new compounds, but a more theoretical foundation also began to develop. John Dalton (1766-1844) put forth his atomic theory in 1807. These ideas allowed scientists to think about chemistry in a much more systematic way. It was also during this time that Avogadro (1776-1856) laid the groundwork for a more quantitative approach to chemistry by calculating the number of particles present in a given amount of a gas. Greater effort was put forth in studying chemical reactions and seeing what new materials could be produced. Following the invention of the battery by Alessandro Volta (1745-1827), the field of electrochemistry was developed through major contributions by Humphry Davy (1778-1829) and Michael Faraday (1791-1867). Other areas of the discipline, including both theoretical ideas and their practical applications, also progressed rapidly.

It would take a very large book to cover every development in the history of chemistry, even if we started only at the beginning of the twentieth century. The history of specific areas will be explored as certain topics are introduced in later chapters. One major area of expansion was in the study of the chemistry of living processes. Research on photosynthesis in plants, the discovery and characterization of enzymes as biochemical catalysts, the elucidation of the structures of biomolecules such as insulin and DNA, and numerous other scientific efforts gave rise to an explosion of information in the field of biochemistry.

The practical aspects of chemistry are numerous as well. The work of Volta, Davy, and Faraday eventually led to the development of batteries that provided a source of electricity to power a number of devices. Charles Goodyear (1800-1860) discovered the process of vulcanization, which produced a stable rubber product that is used in the tires of all modern vehicles. Louis Pasteur (1822-1895) pioneered the use of heat sterilization to eliminate unwanted microorganisms in wine and milk. Alfred Nobel (1833-1896) invented dynamite. After his death, the fortune he made from this product was used to fund the Nobel Prizes in science and the humanities. J.W Hyatt (1837-1920) developed the first plastic and Leo Baekeland (1863-1944) developed the first synthetic resin, which are widely used for inexpensive and sturdy dinnerware.

Examples of Modern Chemistry

From the time we get up in the morning until the time we go to bed at night, chemistry touches our lives in many ways. What we eat, what we wear, how we get around, those cool electronic gadgets we can't live without –chemistry has contributed in some way to the making of each of these things. Let's take a look at several areas where chemistry has an impact on how we live.

Clothing

Many of the fibers that compose the materials for our clothes are naturally occurring. Silk and cotton are examples of natural fibers. Silk is produced by the silkworm, and cotton is grown as a plant. However, several chemical processes are used to treat silk thread so that it is shrink-resistant and will repel water. Chemical dyes are frequently used to color various fabrics. Cleaning requires special soaps or chemicals used to dry-clean materials. Cotton will grow better if the boll weevil (an insect that kills the plant) is eliminated with the use of specific insecticides. Ironing of cotton is made easier by the use of chemicals that produce a permanent press in the material.

Other fabrics are human-made, such as nylon, orlon, polyester, and a number of other polymers. Many of these materials are made from hydrocarbons found in petroleum products. Synthetic polymers are also used in shoes, raingear, and camping items. The synthetic fabrics tend to be lighter than the natural ones and can be treated to make them water-resistant and more durable.

Much protective apparel has its roots in chemical processes. Kevlar^{TM} is a tough polymer that is used for helmets and body armor in combat situations. First used to replace steel in racing tires, Kevlar^{TM} is now found in bicycle tires, sails, and even rope.

FIGURE 1.5

U.S. Marine Corps body armor.

Transportation

Car bodies were at one time made primarily of sheet metal, which could be pounded out fairly easily in case of a collision. Today, most bodies are plastic and need to be replaced when damaged. Plastic parts are easier to manufacture and are lighter in weight than metal ones. Many of the engine components are made of special metals to increase the lifetime of the engine and to make it more efficient.

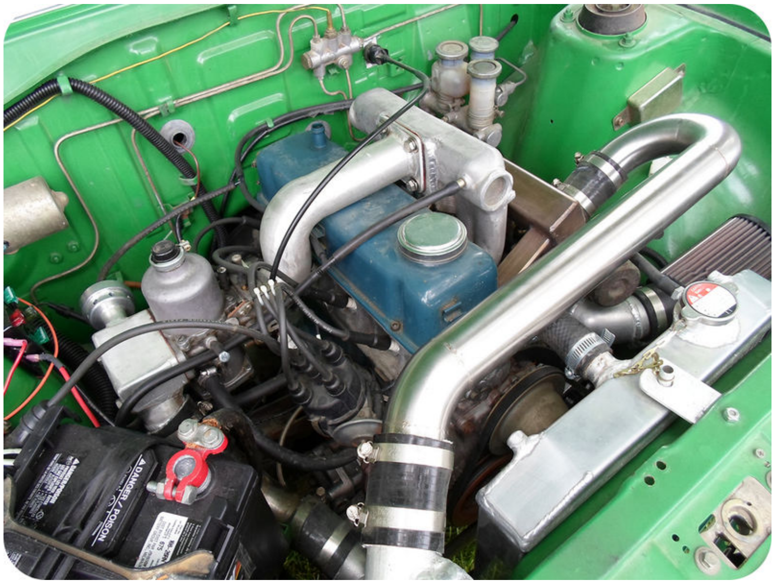


FIGURE 1.6

A modern car engine.

Gasoline and oils are complex chemical mixtures designed to burn in a way that will efficiently produce energy while emitting a minimal amount of air pollution. The refining of gasoline has improved engine performance but is much more complicated than simply using the crude products extracted from oil wells, as was common in the late 1800s. Most gasoline contained lead at one time, because this additive helped the engine run more smoothly. However, this caused lead contamination in the environment, so new "unleaded" formulations were created that could be burned smoothly without the addition of poisonous heavy metals. Oils for lubrication have special additives that reduce engine wear. Some special fuel blends have also been created to generate more power in race car engines.

Farming and Gardening

Three of the most important requirements for crop growth are water, nutrient-rich soil, and protection from predators such as insects. Chemistry has made major contributions in all three of these areas. Water purification uses chemical and physical techniques to remove salt and harmful contaminants that could pollute the soil. Through chemical analysis of soil, farmers can see what nutrients the soil is lacking so these nutrients can be added. In the spring, grocery stores, hardware stores, and gardening centers have high stacks of bags containing fertilizers and weed killers that farmers can then use to enrich the soil and keep unwanted plants from using up the limited water and nutrients in the soil. These same stores also provide a number of chemical sprays or solid treatments to ward off insects that might otherwise snack on the plants.

FIGURE 1.7

A wheat harvest in the Palouse region of Idaho.

Health Care

Major contributions to health care have been made by chemistry. The development of new drugs involves chemical analysis and the synthesis of new compounds. Practically all of the drugs that you might see advertised on television were designed and created by chemists. Clinical laboratory tests for things like high cholesterol or diabetes use a wide variety of analytical chemical techniques and instruments. Chemistry also contributes to the preparation and use of surgical materials such as stitches, artificial skin, and sterile materials.

FIGURE 1.8

A surgical relief mission.

Laboratory tests that at one time were only available in hospitals can now be found in your local drug store because of developments in chemistry. For example, you can test your blood glucose using a simple portable device that runs a chemical test on a blood sample (**Figure** 1.9). This allows a diabetic patient to monitor their blood glucose more easily throughout the day, and regulate how much insulin to administer. Chemistry is also used to produce the insulin drug and disposable syringe that administers the drug.

FIGURE 1.9

A device for testing blood glucose levels at home.

Lesson Summary

- Chemistry has a long and interesting history.
- All societies have used some facets of chemistry in the past, but it was only recently developed into a systematic field of science.
- Although the alchemists never did achieve their goal of making gold from lead, they did give us some useful chemical tools. *Modern chemistry contributes to many areas of our lives, making them easier, safer, and healthier.

Review Questions

1. How can we learn about chemistry knowledge in ancient societies? How do we get chemistry knowledge today?
2. Why was the work of the alchemists important?
3. Read the label on a prepared food product (for example: bread, cereal, dessert). List all the ingredients in the product. Look up each ingredient on the Internet and write down what that material is doing in the food product.
4. Select your favorite hobby or activity. List all the items you use in that activity or hobby. For each item, find out how chemistry has contributed to the creation or better operation of that item.

Further Reading / Supplemental Links

- History of perfumes: http://www.perfumes.com/eng/history.htm
- Traditional herbal medicines: http://monographs.iarc.fr/ENG/Monographs/vol82/mono82-6A.pdf
- The origin and chemistry of petroleum: http://www.dpra.com/index.cfm/m/158
- National Institutes of Health web site dealing with chemistry and health: http://publications.nigms.nih.gov/chemhealth/

Points to Consider

How did people in ancient times know what to use for perfumes, soaps, metal refining, medicines, and other applications of chemistry?

1.2 The Scientific Method

Lesson Objectives

- Describe the approaches used by the ancient Greek philosophers to understand the world around them.
- Define inductive and deductive reasoning.
- Name key individuals and groups who contributed to the science of chemistry.
- Describe the scientific method.
- Describe the rise and fall of the phlogiston theory.

Lesson Vocabulary

- **inductive reasoning**: Involves getting a collection of specific examples and drawing a general conclusion from them.
- **deductive reasoning**: Takes a general principle and then draws a specific conclusion from the general concept.
- **scientific method**: A process consisting of making observations, developing a hypothesis, and testing that hypothesis.
- **phlogiston**: The substance that is lost from a material when it is burned.

Check Your Understanding

Recalling Prior Knowledge

- How did ancient civilizations know what chemical processes to use?

How Do We Know What We Know?

Earth, Air, Fire, and Water

Humans have always wondered about the world around them. One of the questions of interest was (and still is) what is this world made of? Among other definitions, chemistry has often been defined as the study of matter. What matter consists of has been a source of debate over the centuries. One of the key arenas for this debate in the Western world was Greek philosophy.

Philosophy literally means “love of wisdom.” The Greek philosophers held a great deal of influence in society’s general knowledge and belies from about the seventh century to the first century B.C. As the Roman Empire became more powerful, Greek ideas were gradually supplanted by Roman ones. However, many of the ideas carried over into medieval Europe where they were reexamined along with the rise of modern scientific thought.

In ancient Greece, the basic approach to answering questions about the world was through discussion and debate. There was very little gathering of information, and it was believed that the best way to answer fundamental questions was through reasoning and talking. As a result, several ideas about matter were put forth, but these ideas could not really be proven or disproven. For example, Thales of Miletus (~625-545 B.C.) believed that water was the fundamental unit of matter, whereas Anaximenes (~585-525 B.C.) felt that air was the basic unit. Empedocles (~490-430 B.C.) argued for the idea that matter was composed of earth, air, fire, and water. Each of these men had reasons they could offer to support their theories, but there was no way to prove who was right.

The first major philosopher to gather data through observation was Aristotle (384-322 B.C., shown in **Figure** 1.10). He recorded many observations about the weather, the life and behaviors of plants and animals, physical motions, and a number of other topics. Aristotle could potentially be considered the first "real" scientist, because he made systematic observations of nature before trying to understand what he was seeing.

Although Aristotle contributed greatly to Greek knowledge, not all of his observations led to correct theories. Leucippus (~480-420 B.C.) and his student Democritus (~460-370 B.C.) proposed some theories about matter that Aristotle later opposed. Since Aristotle's influence was so great, others chose to reject these theories in favor of Aristotle's ideas. However, it turned out that Aristotle was wrong and Leucippus and Democritus were right, but at the time there was no method for proving or disproving these opposing theories. It took almost 2000 years for people to reconsider this issue since Aristotle was held in such high regard by scholars.

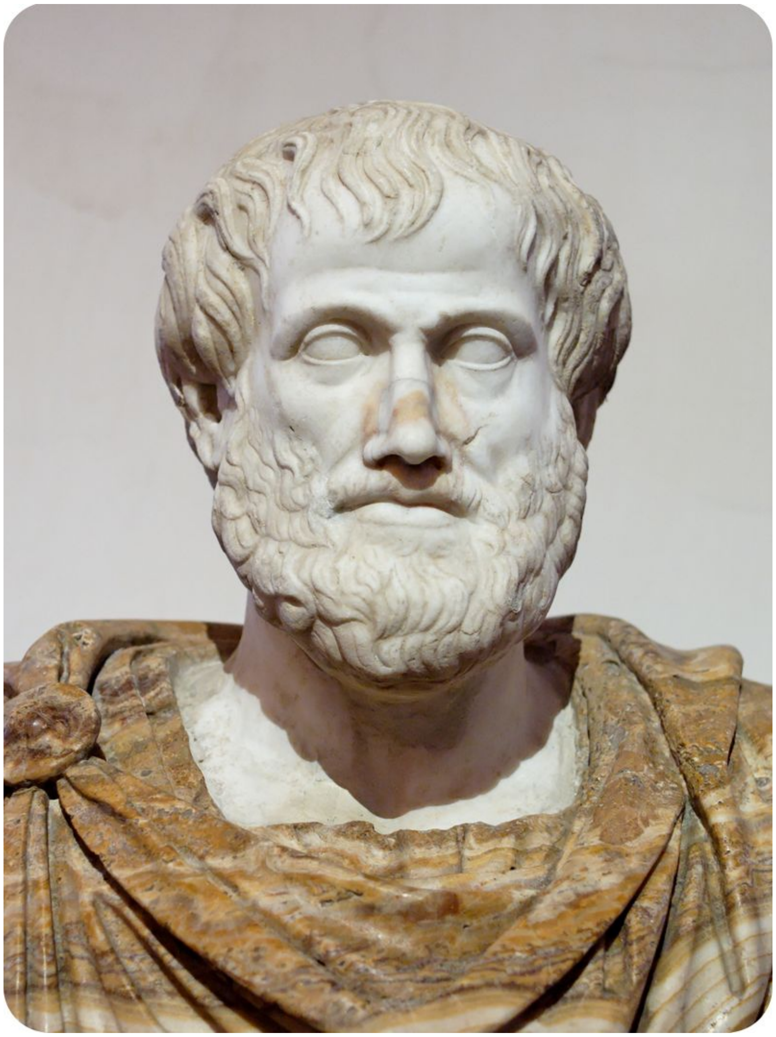


FIGURE 1.10

Aristotle

Inductive and Deductive Reasoning

Two approaches to logical thinking developed over the centuries. These two methods are **inductive reasoning** and **deductive reasoning**. Inductive reasoning involves making specific observations, and then drawing a general conclusion. Deductive reasoning begins with a general principle and a prediction based on this principle; the prediction is then tested, and a specific conclusion can then be drawn.

The first step in the process of inductive reasoning is making specific observations. In the periodic table of elements, which we will discuss later, there is a group of metals with similar properties called the alkali metals. The alkali metals include elements such as sodium and potassium. If I put sodium or potassium in water, I will observe a very violent reaction every time. I draw a general conclusion from these observations: all alkali metals will react violently with water.

In deductive reasoning, I start with a general principle. For example, say I know that acids turn a special material called blue litmus paper red. I have a bottle of vinegar, which I believe is an acid, so I expect the litmus paper to turn red when I immerse it in the vinegar. When I dip the litmus paper in the vinegar, it does turn red, so I conclude that vinegar is in fact an acid. You can see that in order for deductive reasoning to lead to correct conclusions, the general principle you begin with must be true. I can only conclude that vinegar is an acid based on the accuracy of the general principle that acids turn blue litmus paper red.

Inductive and deductive reasoning can be thought of as opposites. For inductive reasoning, we start with specific observations and draw a general conclusion. For deductive reasoning, we start with a general principle and use this principle to draw a specific conclusion.

The Idea of the Experiment

Inductive reasoning is at the heart of what we call the **scientific method**. In European culture, this approach was developed mainly by Francis Bacon (1561-1626), a British scholar. He advocated the use of inductive reasoning in every area of life, not just science. The scientific method as developed by Bacon and others involved several steps:

1. Ask a question –identify the problem to be considered.
2. Make observations –gather data that pertains to the question.
3. Propose an explanation (a hypothesis) for the observations.
4. Design and carry out ways to test the hypothesis.

Note that this should not be considered a "cookbook" for scientific research. Scientists do not sit down with their daily "to do" list and write down these steps. The steps may not necessarily be followed in order, and testing a given explanation often leads to new questions and observations that can result in changes to the original hypothesis. However, this method does provide a general outline of how scientific research is usually done.

During the early days of the scientific enterprise (up to the nineteenth century), scientists generally worked as individuals. They may have had an assistant to help with preparing materials, but their work was usually solitary. Their results might be disseminated in a letter to friends or at a scientific society meeting. Today the practice of science is very different. Research is carried out by teams of people, sometimes at a number of different locations. The details of methods and the results of the experiments are published in scientific journals and books, as well as being presented at local, national, or international meetings. Electronic publication on the Internet speeds up the process of sharing information with others.

Before conclusions can be considered reliable, experiments and results must be replicated in other labs. In order for other scientists to know that the information is correct, the experiments need to be done in other labs to obtain the same results. Researchers in other labs may get ideas for new experiments that could confirm the original hypothesis. On the other hand, they may see flaws in the original thinking and experiments that would suggest the hypothesis was false. The modern scientific approach of carefully recording experimental procedures and data allows results to be tested and replicated to that everyone can have confidence in the final results.

A good experiment must be carefully designed to test the hypothesis. Let's think back to our example of inductive reasoning in observing reactions with alkali metals and water. We believe that all alkali metals produce violent reactions with water. To test this hypothesis, we must design an experiment in which we can observe the reactions of each alkali metal with water. We will test each alkali metal: lithium, sodium, potassium, rubidium, cesium, and francium. In order for this experiment to produce consistent results, we should use the same amount of water and same size sample of these metals each time a test is formed. Based on our hypothesis, we expect a violent reaction to occur when any one of these metals is added to water. If a sample of lithium is added to our water and we observe a small explosion, our hypothesis is strengthened. If lithium is added to our water and nothing happens, our hypothesis must not be true. We can either modify our hypothesis to include this new data, or replace our hypothesis with a new one.

When a hypothesis is confirmed repeatedly, it eventually becomes a theory. A theory is a general principle that is offered to explain a natural phenomenon. A theory offers a description of *why* something happens. Although theories, like hypotheses, can be disproved, it is more likely for a theory to be modified. However, while a hypotheses is a suggested explanation of a phenomena, a theory is a proved explanation based off of many hypotheses and much experimentation. Over time, theories evolve with new research and data, but are rarely discarded completely. A law, on the other hand, is a statement that is always true, but does not include an explanation as to why. The law of gravity says a rock will fall when dropped, but it does not explain why (gravitational theory is very complex and incomplete at present). The kinetic-molecular theory of gases, on the other hand, tells us what happens when a gas is heated in a closed container (the pressure increases), but also explains why (the motions of the gas molecules are increased due to the change in temperature). Theories do not get "promoted" to laws, because laws do not answer the "why" question.

Phlogiston - The Rise and Fall of a Theory

Early chemists spent a lot of time heating things and setting them on fire (on purpose, unlike some modern-day chemistry students). They observed that flammable materials tended to weigh less after being burned. As more materials were studied, this observation was found to be very consistent. A seemingly reasonable explanation for this phenomenon was that some substance was lost from the material when it was burned. This substance was named **phlogiston** from the Greek word φλογιστ´ν (transliterated as phlogistón), which means "burning up." The phlogiston theory was first put forth in 1667 by the German physician and alchemist Johann Joachim Becher (1635–1682, shown in **Figure** 1.11).

FIGURE 1.11

Johann Becher

Becher had taken the four ancient Greek elements (earth, air, fire, and water) and discarded fire and air. He expanded the "earth" category to three groups, one of which was involved in burning. In 1703, George Stahl, a German professor of medicine and chemistry, renamed this particular fraction of Becher's earth as phlogiston.

What was the evidence that led to the development of this theory? One obvious experiment involved the burning of wood. The ashes remaining after the fire weighed considerably less than that original wood sample. Therefore, it seemed that phlogiston had been released during the burning process, leaving the "dephlogisticated" ashes behind.

If wood or a candle was burned in a closed container, the fire would soon be extinguished. This was taken by supporters of the theory as evidence that air could only absorb so much phlogiston. Later, carbon dioxide gas was discovered and studied. An experiment was performed in 1772 that exhausted all the air in a container. Further burning of a candle and of phosphorus were then carried out in the container. After removing the carbon dioxide with an absorbent, a gas was found that did not support life or combustion. This gas (which we now know as nitrogen and which comprises about 78% of the atmosphere) was believed to be phlogiston.

So far, so good. We have observations –things lose weight when they burn. We have an explanation –the original material loses phlogiston when it burns. What we don't know is what phlogiston is or how much of it is in a given material. But are there other experiments that lead us in a different direction?

Other scientists started to ask questions and run experiments. They noticed some results that seemed to contradict what would be expected if the phlogiston theory was correct. If magnesium is heated, the product (a solid) weighs more than the original magnesium metal. The explanation offered was that phlogiston had negative weight in this case. Can the same material have both a positive weight and a negative weight? When mercuric oxide was heated in the absence of any charcoal, it returned to its pure metal form. The phlogiston theory would require that charcoal (thought to be essentially pure phlogiston) be present to provide the phlogiston for restoring the metal.

The French scientist Antoine Lavoisier (**Figure** below) carried out studies on oxygen (which had originally been discovered by Joseph Priestley, an ardent supporter of the phlogiston theory). Lavoisier found that when mercury was heated, it would become mercuric oxide and gain weight. When the mercuric oxide was heated, it returned to mercury and released a gas he identified as oxygen. He also carried out a number of experiments that conclusively demonstrated the essential role of oxygen in combustion processes.

FIGURE 1.12

Antoine Lavoisier and his wife Marie-Anne Pierrette Paulze, who was also a chemist and made contributions to the work of her husband.

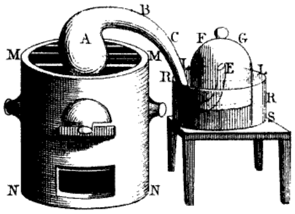


FIGURE 1.13

The device used by Lavoisier to study the decomposition of mercuric oxide.

Eventually the phlogiston theory was replaced by the oxygen-based combustion ideas developed by Lavoisier and others. Today the theory is studied as an example of how to approach a scientific question and how one theory can be supplanted by another theory that more closely fits the data. It should also be noted that the phlogiston idea took time to develop, it took time to become accepted, and it took time for researchers to discard it in favor of a better theory.

Lesson Summary

- The early Greek philosophers spent a great deal of time talking about nature, but they did little or no actual exploration or investigation.
- Inductive reasoning means developing a general conclusion from a collection of observations.
- Deductive reasoning means making a specific statement based on a general principle.
- Scientific method is a process consisting of making observations, developing a hypothesis, and testing that hypothesis.
- Phlogiston theory is the disproven idea that materials lost phlogiston when they burned.

Lesson Review Questions

1. What was a major shortcoming of the approach taken by Greek philosophers to understanding the material world?
2. How did Aristotle improve this approach?
3. Define "inductive reasoning" and give an example.
4. Define "deductive reasoning" and give an example.
5. What is the difference between a hypothesis and a theory?
6. What is the difference between a theory and a law?
7. What was the major evidence that supported the phlogiston theory?
8. What was the major evidence that contradicted the phlogiston theory?

Further Reading / Supplemental Links

- Overview of the scientific method: http://www.sciencebuddies.org/science-fair-projects/project_scientific_method.shtml
- Research using the scientific method: http://www.teachersdomain.org/asset/drey07_int_scprocess/
- Lavoisier video: http://www.schooltube.com/video/5a2cb561ceabe931f2b5/Antoine-Lavoisier-the-man
- Information about Lavoisier and phlogiston theory: http://cti.itc.virginia.edu/~meg3c/classes/tcc313/200Rprojs/lavoisier2/home.html

Points to Consider

Chemistry is the study of matter and the changes that matter can undergo.

- What is matter?
- Where do you encounter matter in your everyday life?
- What are the states of matter?
- Can matter be changed?

1.3 References

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CHAPTER 2 Matter and Change

Chapter Outline

2.1 PROPERTIES OF MATTER
2.2 CLASSIFICATION OF MATTER
2.3 CHANGES IN MATTER
2.4 REFERENCES

Matter is anything that has mass and takes up space. Matter is everywhere. The air we breathe, the water we drink, the food we eat, and the ground we walk on are all comprised of matter. Matter can take on a variety of different forms which all have a variety of different properties. In this chapter, we will introduce the characteristics of matter and study how these characteristics vary in different types of matter.

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2.1 Properties of Matter

Lesson Objectives

- Classify properties of materials as extensive, intensive, chemical, or physical. Give examples of each.
- Describe the concepts of intensive and extensive properties and be able to describe these properties in a given material.
- Describe the concepts of physical properties and chemical properties and be able to describe these properties for a given material.
- Explain the concept of density as it relates to other physical properties of matter.

Lesson Vocabulary

- **chemical properties**: Properties that describe matter's reactions with other substances.
- **physical properties**: Properties of matter that can be observed without changing the matter's composition.
- **intensive properties**: Physical properties that are independent on the amount of a substance present.
- **extensive properties**: Physical properties that depend on the amount of a substance present.

Check Your Understanding

- What are some ways that you can distinguish different substances from each other?
    - For example, what is different between sand and sugar?

Introduction

All substances have special properties by which they can be identified. For instance, substances have unique colors, densities, and boiling points. They also behave in unique ways with other substances. For example, they may react with air, water, or acids. In chemistry, we study these properties and use them to identify and categorize matter.

Chemical Properties

All types of matter exhibit **chemical properties**. Chemical properties are the properties that describe matter's reactions with other substances. We can determine these chemical properties by seeing what happens to a substance when it is placed in the presence of the following:

- air

- water
- an acid
- a base
- other chemicals

Chemical properties indicate how the composition of a substance will change when exposed to various other substances. You can observe many chemical properties in the objects around you. For example, the metal frame of a bicycle will become rusty over time. The process of the frame becoming rusty can be described by a chemical property of iron, one of the metals in the frame. The iron will react with the oxygen in the air to form iron oxide, or rust.

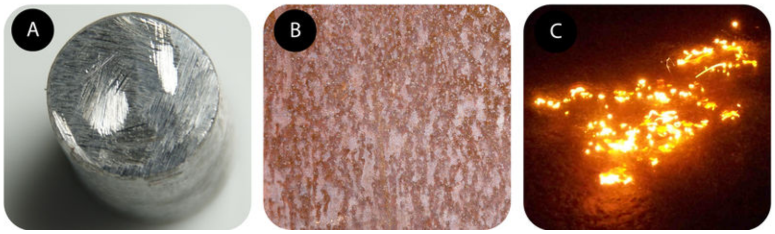


FIGURE 2.1

(A) Elemental iron. (B) Oxidized iron plate. (C) Iron "burning."

In the **Figure** 2.1 we can observe the difference in color between pure iron, which is a lustrous dark gray color, and rusted iron, which is cinnamon colored. We can also observe the reaction that takes place when iron is heated by a flame, in which the hot air to reacts more rapidly with the pure iron. The changes that iron undergoes when exposed to air show us some of iron's chemical properties and help us to classify iron as specific type of matter.

Example 2.1

Which of the following would be examples of a chemical property?

A. Most metals will react with acids.
B. Water can be a solid, liquid, or a gas.
C. Water mixes well with ethanol.

Answer: A is an example of chemical properties. Statement B does not reflect chemical properties; these are physical characteristics of water. The process described in answer C would not be a chemical property because no reaction takes place. There are no changes in the composition of either the water or the ethanol as a result of the mixing, and both components can be separated from one another using physical processes.

Physical Properties

Matter also exhibits **physical properties**. Physical properties are used to observe and describe matter. Physical properties can be observed or measured without changing the composition of matter. These are properties such as mass, weight, volume, and density. Density calculations will be discussed later on in chapter three, but for now just remember that density is a physical property.

Intensive Properties

Physical properties that do not depend on the amount of substance present are called **intensive properties**. Intensive properties do not change with changes of size, shape, or scale. Examples of intensive properties are as follows in the **Table** 2.1.

TABLE 2.1:

Intensive Properties	Example
color	Aluminum metal is gray colored.
taste	Lemon juice (citric acid) is sour.
melting point	Aluminum has melting point of 660°C.
boiling point	Water has a boiling point of 100°C.
density	Water has a density of 1 g/mL.
luster	Metals are lustrous (shiny).
hardness	Diamond is the hardest substance known.

Extensive Properties

Physical properties that do depend on the amount of substance present are called **extensive properties**. Examples of extensive properties include:

- Mass
- Volume
- Length

Example 2.2

Which of the following is an intensive property of a box of crackers?

A. Calories per serving.
B. Total grams.
C. Total number of crackers.
D. Total calories.

Answer: A. Calories per serving. Total grams, total crackers, and total number of calories are extensive properties. A larger amount of crackers would have more grams, crackers, and total calories but the same number of calories per serving.

Example 2.3

Which of the following is an extensive property?

A. The color of charcoal is black.
B. Gold is shiny.
C. The volume of orange juice is 25 mL.

Answer: C. The volume of orange juice is 25 mL. Charcoal's black color and gold's luster are intensive properties, and are not dependent on how much *charcoal or gold is present. However if you had more or less orange juice, its volume would not stay the same. So, this is an extensive property.*

Lesson Summary

- Matter is anything that has mass and takes up space.
- The properties of matter can be classified as either chemical or physical.
- Chemical properties describe the reactions that can occur when matter is treated with other substances, such as how a substance reacts with air or with an acid.

- Physical properties, such as mass, volume, density, and color, can be observed without changing the identity of the matter.
- We can further categorize the physical properties of matter as either intensive or extensive.
- Intensive properties do not depend on the amount of the substance present. Some examples of intensive properties are color, taste, and melting point.
- Extensive properties vary according to the amount of matter present. Examples of extensive properties include mass, volume, and length.

Review Questions

1. Compare and contrast physical properties and chemical properties.
2. Which of these is a chemical property?
    (a) Oxygen is a gas at 25°C.
    (b) Helium is very nonreactive.
    (c) Ice melts at 0°C.
    (d) Sodium is a soft, shiny metal.
3. Indicate whether each of the following is a chemical property or a physical property. If it is a chemical property, indicate whether it is and intensive or extensive property.
    (a) Water boils at 100°C.
    (b) Diamonds are the hardest known substance.
    (c) Salt is capable of dissolving in water.
    (d) Vinegar reacts with baking soda.
    (e) Most metals are lustrous.
    (f) Most metals react with acids.
    (g) A given sample of lead weighs 4.5 g.
    (h) The length of a piece of aluminum foil is 12.2 cm.
    (i) Gold conducts electricity.

Further Reading / Supplemental Links

- Examples of laboratory techniques used for separating mixtures: http://sciencepark.etacude.com/projects/

Points to Consider

- How could you categorize types of matter based on differing chemical and physical properties?

2.2 Classification of Matter

Lesson Objectives

- Distinguish between gases, liquids, and solids. Explain how these states differ at the molecular level.
- Classify samples of matter as pure substances, homogeneous mixtures, heterogeneous mixtures, compounds, and elements.
- Use sketches to show how elements, compounds, and mixtures differ at the molecular level.
- Describe six different techniques for separating mixtures.
- Relate the names of elements to their international element symbols.
- Name the major groups and regions on the periodic table and identify elements belonging to these groups.
- Distinguish between metals, nonmetals, and metalloids using the periodic table.

Lesson Vocabulary

- **pure substances**: Have a constant composition and can only be changed by chemical reactions.
- **elements**: Substances that cannot be decomposed into simpler substances by chemical or physical means.
- **compounds**: Substances that can be broken down into their individual elements, but only through chemical processes.
- **mixtures**: A combination of two or more pure substances.
- **homogeneous mixtures**: A mixture with uniform composition throughout.
- **heterogeneous mixtures**: A mixture with visibly distinguishable components, exist primarily in the solid and liquid states.

Check Your Understanding

- Give some examples of chemical properties and physical properties of matter.
- What would be some chemical and physical properties of the following substances:
  - a glass of water
  - aluminum foil
  - argon

Introduction

As we studied in our last lesson, matter can be described by its physical and chemical properties. We have seen examples of how matter exhibits specific physical and chemical properties, which can be used to distinguish one type of matter from another. In this lesson, we are going to use these properties to categorize the various forms of matter.

States of Matter

Matter typically exists in one of three states: solid, liquid, or gas. The state of a given substance is a physical property. Some substances exist as gases at room temperature (such as oxygen and carbon dioxide), while others (like water and mercury metal) exist as liquids. Most metals exist as solids at room temperature. All substances can exist in any of these three states.

Water is a very common substance that we frequently encounter in all three states of matter, as seen in **Figure** 2.2. When water is in the solid state, we call it ice, while water in the gaseous state is referred to as steam or water vapor. The physical state of matter is a physical property because the identity of a **pure substance** does not change when it is melted, frozen, or boiled.

FIGURE 2.2

Water is the same substance in any of its three states. (A) A frozen waterfall in Hungary. (B) The Nile River in Egypt. (C) A steam powered train in Wales.

Solid

A solid is a form of matter that has a definite shape and volume. The shape of a solid does not change if it is transferred from one container to another. The particles of a solid are packed tightly together in fixed positions, usually in an orderly arrangement. Solids are almost completely incompressible, meaning that solids cannot be squeezed into a smaller volume. When a solid is heated or cooled, it expands or contracts only slightly.

Liquid

A liquid is a form of matter that has a definite volume, but an indefinite shape. As water is poured from one container into another, it adopts the shape of its new container. However, the volume of the water does not change, because the water molecules are still relatively close to one another in the liquid state. Unlike a solid, the arrangement of particles in a liquid is not rigid and orderly. Liquids are also incompressible.

Gas

A gas is a form of matter that has neither a definite shape nor a definite volume. A gas takes up the shape and volume of its container. This is because the particles of a gas are very far apart from one another compared to the particles that make up solids and liquids. Gases are easily compressed because of the large spaces in between gas particles. Gas particles are often invisible, but they can be detected in various ways, such as the light emitted when an electric current is passed through a sample of a gas (**Figure** 2.3).

Molecular View of Solids, Liquids, and Gases

We are quite familiar with the properties of solids, liquids, and gases from our everyday experience. These properties are fundamentally based on differences in the arrangement of atoms or molecules at the microscopic level. **Figure**

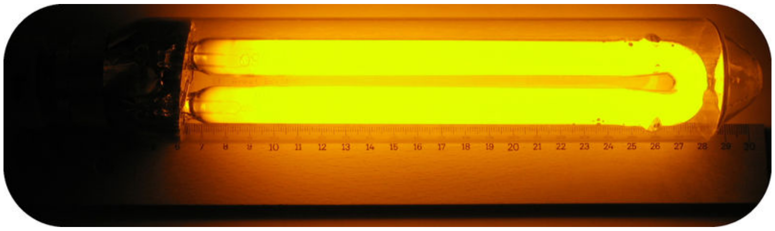


FIGURE 2.3

Sodium vapor lamps glow with a distinctive yellow color.

2.4 shows the differences between the ways in which particles appear in each of these three states. Remember, any substance can be present as a gas, liquid, or solid when placed under specific conditions.

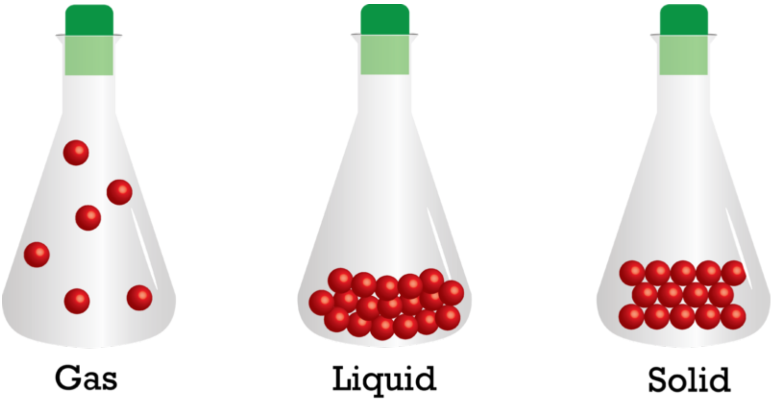


FIGURE 2.4

The particles of a gas are very far apart compared to the particles of a liquid or a solid.

As **Figure** 2.4 shows, the distance between particles is much smaller for the solid and liquid states than for the gas state. In the solid state, particles are fixed in place, while particles are more free to move in the liquid and gas states. The particles in the solid and liquid states "stick together," but in the gas state, they move freely about the container. In general, it requires energy to separate individual particles. If we want to make a solid adopt a liquid form, we can add energy in the form of heat, increasing the temperature of the substance. Conversely, if we want to convert a substance from a gas to a liquid or from a liquid to a solid, we remove energy from the system and decrease the temperature. Pressure also plays an important role in changes of state, which will be discussed later on. We will study these difference in greater detail in the chapter *States of Matter*.

Pure Substances

When studying the different states that matter exhibits, we have been looking at **pure substances**. Pure substances have a constant composition and can only be changed through chemical reactions. Constant composition indicates that a sample of a pure substance always contains the same elements in the same proportions. There are two main types of pure substances:

- **elements**: Substances that cannot be decomposed into simpler substances by chemical or physical means.
- **compounds**: Substances that can be broken down into elements through chemical means.

Figure 2.5 shows pure substances in the form of elements and compounds.

FIGURE 2.5

Pure substances: (*left*) the element sulfur and (*right*) the compound water.

The image on the left shows elemental sulfur in the solid state. The image on the right shows water in its liquid form. Sulfur is a pure element, and water is a compound comprised of the elements hydrogen and oxygen. Both of these substances have a constant composition, but water can be broken down into its elements, whereas sulfur cannot be decomposed into a simpler substance. Water can be broken down into its elements by passing electricity through a salt solution.

Periodic Table of Elements

Chemists have classified and organized all of the known elements into what is called the periodic table. All known substances are made of some combination of these elements. The periodic table is a tool that we use to help identify and describe the composition of a given substance. All pure substances which cannot be broken down further, which we have called elements, are displayed in the periodic table. **Figure** 2.6 shows our modern periodic table. We will study the periodic table in more detail in the chapter *The Periodic Table*.

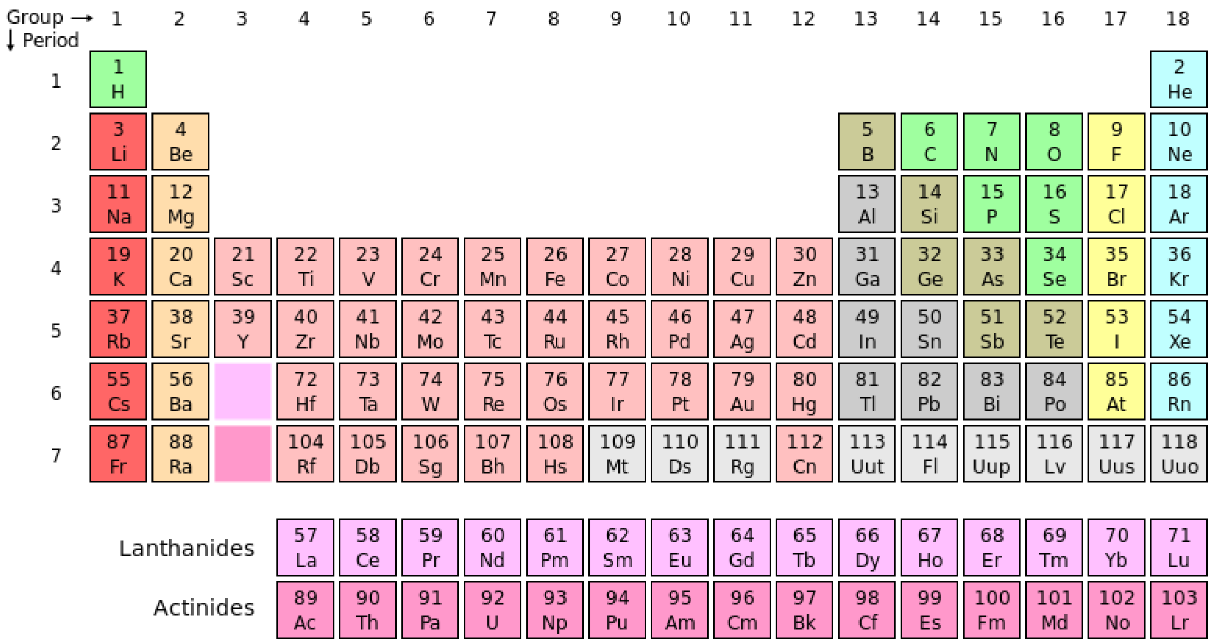
Mixtures

When two or more pure substances are combined together, a **mixture** is formed. Unlike pure substances, mixtures have a variable composition. Variable composition indicates that the relative proportions of the mixtures components may vary, and they can be separated by physical methods. There are two main types of mixtures.

Homogeneous Mixtures

A **homogeneous mixture** is one in which the composition is uniform throughout the mixture. A glass of salt water is a homogeneous mixture because the dissolved salt is evenly distributed throughout the entire sample. It is often easy to confuse a homogeneous mixture with a pure substance because they are both uniform, and it can be difficult to tell which type you have by the naked eye. The difference is that the composition of the pure substance is always the same, while the composition of a homogeneous mixture can vary. For example, you may dissolve a small amount or a large amount of salt into a given sample of water. Although the ratio of salt to water will differ, the mixtures will both be homogeneous. However, pure water will always have the same ratio of elements that make it a pure substance (two hydrogen atoms per oxygen atom).

Wine, air, and gunpowder are other examples of common homogeneous mixtures (**Figure** 2.7). Their exact compositions can vary, making them mixtures rather than pure substances. Wine is a liquid mixture of water,



Group → ↓ Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo
Lanthanides				57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinides				89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

FIGURE 2.6

The modern periodic table.

ethanol, and a variety of other dissolved substances. Air is a mixture of nitrogen gas (78%), oxygen gas (21%), and small amounts of various other gases. Gunpowder is a solid mixture comprised of potassium nitrate (75%), charcoal (15%) and sulfur (10%).

FIGURE 2.7

Examples of homogenous mixtures: wine and gunpowder.

In this figure, we see that the components of these mixtures cannot be distinguished from one another. However, the substances comprising these mixtures can be separated through physical means.

Heterogeneous Mixtures

Heterogeneous mixtures have visibly distinguishable parts. These mixtures will typically exist in the solid or liquid states, but not the gas state. Gas state heterogeneous mixtures are not possible because gas particles freely mix and disperse. Heterogeneous mixtures are quite common. For example, oil-and-vinegar salad dressing is a heterogeneous mixture that is in the liquid state. Its composition varies and typically includes olive oil mixed with red vinegar. An example of a solid heterogeneous mixture is soil. Soil is primarily comprised of organic and inorganic material, including substances like decaying plants and animals, minerals, water, and air. The composition of soil varies greatly from one location to another. **Figure** 2.8 shows these mixtures.

FIGURE 2.8

Examples of heterogeneous mixtures: (*left*) oil and vinegar and (*right*) soil.

The substances that comprise heterogeneous mixtures can also be separated by physical means. We will discuss separation techniques in the following lesson.

Lesson Summary

- Matter exhibits specific physical and chemical properties.
- Matter can exist in one of three states: solid, liquid, or gas.
- In the solid state, particles are fixed in place relative to one another. In the liquid and gas states, individual particles are free to move.
- Under the right pressure conditions, lowering the temperature of a substance in the gas state causes the substance to liquefy. The opposite effect occurs if temperature is increased.
- Under the right pressure conditions, lowering the temperature of a substance in the liquid state causes the substance to solidify. The opposite effect occurs if the temperature is increased.
- Pure substances have a constant composition and can only be changed by chemical reactions. They can be classified as either elements or compounds.
- Elements are substances that cannot be decomposed into simpler substances by chemical or physical means. Compounds, however, can be broken down further through chemical, but not physical, means.
- The periodic table is a tool that we use to help identify and describe the composition of a given substance. The table is an arrangement of elements based on their physical and chemical properties.
- Homogeneous or heterogeneous mixtures are formed when two or more pure substances are combined. A homogeneous mixture has a uniform distribution throughout the sample, whereas a heterogeneous mixture has visibly distinguishable components.

Review Questions

1. Compare and contrast the three states of matter. Try to describe similarities and differences apparent at a microscopic level as well as at the observable level between these states of matter.
2. Which of the following would be an example of a pure substance?
   a. plastic
   b. milk
   c. 100% ethanol
   d. cake flour
3. Which of the following would be an example of an element?
   a. water
   b. orange juice
   c. steel
   d. iron
4. Which of the following would be an example of a compound?
   a. water
   b. sulfur
   c. aluminum
   d. brass
5. Compare and contrast a pure substance with a mixture and give an example.
6. Which of the following statements is true?
   a. The periodic table is a list of various compounds found throughout the world.
   b. The periodic table is randomly organized.
   c. The periodic table has been the same for 50 years.
   d. The periodic table is an organized assembly of the various elements that have been discovered.
7. Classify the following as a homogeneous mixture, a heterogeneous mixture, or neither.
   a. powdered sugar
   b. mayonnaise
   c. scrambled egg
   d. air
   e. soda pop
   f. concrete
   g. apple juice
   h. glass
   i. steel
   j. copper

Further Reading / Supplemental Links

- Examples of laboratory techniques used for separating mixtures can be found at Science Park: http://scienceepark.etacude.com/projects/

Points to Consider

- As we saw, compounds can be broken down into their elemental components. How might you go about breaking down a compound into its elements?
- The components that comprise homogeneous and heterogeneous mixtures can be separated out by physical means. How might you go about separating out components of a soil mixture?

2.3 Changes in Matter

Lesson Objectives

- Describe methods for separating mixtures, such as chromatography, distillation, fractional distillation, evaporation, and filtration.
- Given a specific mixture, propose methods by which the mixture's components could be isolated.
- Identify the chemical properties of a substance.
- Describe chemical changes and differentiate them from physical changes.
- Use various visual clues to identify whether a chemical reaction is taking place.

Lesson Vocabulary

- **chemical change**: A change during which the chemical identity of a substance is altered. Chemical changes are often accompanied by a change in color, temperature, or odor, or the production of a gas or precipitate.
- **physical change**: A change in which the physical form and properties of a substance change.
- **chromatography**: The separation of a mixture by passing it through a medium in which the components move at different rates.
- **distillation**: A purification process in which the components of a liquid mixture are vaporized and then condensed and isolated.
- **evaporation**: A technique used to separate out homogeneous mixtures in which one or more solids are dissolved in a liquid.
- **filtration**: A method used to separate mixtures in which some of the particles are large enough in size to be captured with a porous material while others are not.
- **chemical property**: The ability of a substance to undergo a specific chemical change.

Check Your Understanding

- Compare and contrast chemical properties and physical properties.
- Give examples of physical properties and chemical properties.
- Compare and contrast the following pairs of terms: element and compound; pure substance and mixture.

Introduction

In the previous lesson, we discussed pure substances and mixtures. We indicated that the components of a mixture could be separated by physical means, but the components of a pure substance could not. Pure substances can only be broken down further through chemical means. In this lesson, we list several methods for separating mixtures. We will also be looking at **chemical changes** which alter the chemical identity of a substance, and how to recognize when a chemical change is taking place.

Physical Change

Any time the physical properties of a substance are changed, we can say the substance has undergone a **physical change**. All substances undergo physical changes where there is a change in the form of the substance but not in its chemical composition. For instance, the grinding of granular sugar into powdered sugar is a physical change. Similarly, dissolving sugar in water is a physical change. We can also use physical changes to separate mixtures into their components. There are a variety of methods used, and the best procedure depends largely on the nature of the mixture. Depending on the states of matter involved, the relative sizes of the mixtures components, and whether the mixture is homogeneous or heterogeneous will determine the necessary separation technique.

Methods for Separating Mixtures

Chromatography

Chromatography is the separation of a mixture by passing it through a medium in which the components move at different rates. Mixtures that are solutions (such as salt water), suspensions (such as sand mixed with water), or even vapors can be separated in this way. Paper chromatography is a type of chromatography that can be used for separating and identifying mixtures in which one or more components are colored, especially pigments. The following video shows paper chromatography being used to separate out the dyes present in a variety of water-soluble inks: http://www.youtube.com/watch?v=ac9vALSoxbY (0:43).

MEDIA

Click image to the left for more content.

In this video, we see several different dyes that have been placed on paper through which water was absorbed. Dyes, such as the ink in colored markers, are usually a mixture of several different colored compounds. The dyes in water-soluble inks dissolve easily in water, while permanent inks dissolve more readily in organic solvents such as ethanol.

Distillation

Distillation is an effective method to separate mixtures comprised of two or more pure liquids. Distillation is a purification process in which the components of a liquid mixture are vaporized (transformed from liquid to gas) and then condensed (transformed from gas back to liquid) and isolated. In a simple distillation, a mixture is gradually heated. The solution with the lowest boiling point will change into a gas first. This gas, or vapor, then passes through a cooled tube (a condenser) where it condenses back into its liquid state. This condensed liquid is called the distillate. **Figure** 2.9 illustrates this.

When a mixture contains several components with similar boiling points, the one-step distillation may not give a pure substance in the receiving vessel. Therefore, more elaborate methods are used to completely separate a mixtures components. Distillation is an especially effective physical technique in separating out a homogeneous mixture comprised of two or more pure liquids, such as alcohol and water.

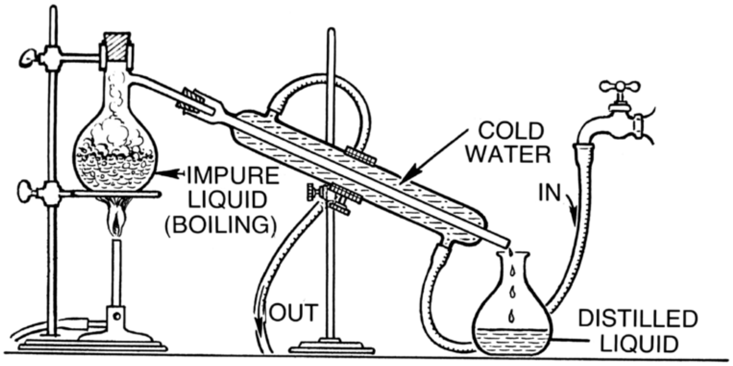


FIGURE 2.9

In this figure, we see several important pieces of equipment. There is a heat source and a flask containing the liquid to be distilled. At the center of the set-up is the condenser. The distillate is collected in a flask. There are other more complicated assemblies for distillation that can also be used, especially to separate mixtures which are comprised of pure liquids with boiling points that are close to one another.

Evaporation

Evaporation is a technique used to separate out homogeneous mixtures in which one or more solids are dissolved in a liquid. Typically, the mixture is heated until all of the liquid has vaporized, leaving behind the dissolved solids (**Figure** 2.10). The vapor can also be captured and recondensed into a liquid if desired.

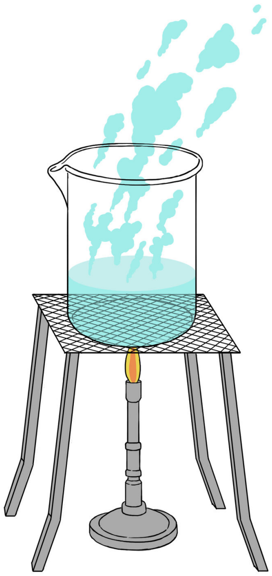


FIGURE 2.10

Evaporation

This method can only be used to separate volatile liquid components (those which will evaporate at low temperatures) from nonvolatile solid components (those which will not evaporate at low temperatures). If there is more than one liquid or solid component, that portion of the mixture cannot be isolated purely.

Filtration

Filtration can be used to separate mixtures in which the some of the particles are large enough in size to be captured with a porous material while others are not. Particle sizes can vary considerably. For instance, stream water is a mixture that contains naturally occurring biological organisms like bacteria, viruses, and protozoans. Some water filters can filter out bacteria, the length of which is on the order of 1 micrometer. Other mixtures, like wet soil, contain relatively large particles that can be filtered out using something like a coffee filter.

Chemical Change

Much of the field of chemistry is devoted to the study of chemical changes. A **chemical change**, also referred to as a chemical reaction, is one in which the chemical identity of a substance is altered. We witness chemical changes every day. For example, the burning of wood or the rusting of iron are chemical changes. The burning of wood is a process in which cellulose molecules break down into water and carbon dioxide. The rusting of iron is a process in which elemental iron combines with oxygen (from air or water) to produce iron oxide (**Figure** 2.11).

FIGURE 2.11

Rust (iron oxide) forms on an unprotected iron surface.

As the rust forms on the surface of the iron, it flakes off to expose more iron, which will continue to rust. Rust is clearly a substance that is different from iron. Rusting is an example of a chemical change. Some chemical changes are not as obvious but are still hugely important. For example, photosynthesis and cellular respiration are chemical changes that we could not live without. Chemical changes involve the combination, decomposition, or rearrangement of elements and compounds to form new substances.

A **chemical property** describes the ability of a substance to undergo a specific chemical change. A chemical property of iron is that it is capable of combining with oxygen to form iron oxide, the chemical name of rust. A more general term for rusting and other similar processes is corrosion. Other terms that are commonly used in descriptions of chemical changes are burn, rot, explode, decompose, and ferment. Chemical properties are very useful as a way of identifying substances. However, unlike physical properties, chemical properties can only be observed as the substance is in the process of being changed into a different substance.

Recognizing Chemical Changes

How can you tell if a chemical change is taking place? Certain visual clues indicate that a chemical change is likely (but not necessarily) occurring, including the following examples:

1. A change of color occurs.

2. A gas is produced.
3. A solid product called a precipitate is produced.
4. A change of energy is apparent, due to a change in temperature or the appearance of light such as a flame.

Mercury(II) oxide is a red solid. When it is heated to a temperature above 500°C, it easily decomposes into mercury and oxygen gas. The red color of the reactant, mercury oxide, is gradually replaced by the silver color of the product, mercury. The color change is one sign that this reaction is occurring. Watch this decomposition take place at http://www.youtube.com/watch?v=_Y1alDuXm6A (1:12).

MEDIA

Click image to the left for more content.

When zinc reacts with hydrochloric acid, the reaction bubbles vigorously as hydrogen gas is produced (**Figure** 2.12). The production of a gas is also an indication that a chemical reaction may be occurring.

FIGURE 2.12

Zinc reacts with hydrochloric acid to produce bubbles of hydrogen gas.

When a colorless solution of lead(II) nitrate is added to a colorless solution of potassium iodide, a yellow solid called a precipitate is instantly produced (**Figure** 2.13). A precipitate is a solid product that forms from a reaction and settles out of a liquid mixture. The formation of a precipitate may also indicate the occurrence of a chemical reaction.

All chemical changes involve a transfer of energy. When zinc reacts with hydrochloric acid, the test tube becomes very warm as energy is released during the reaction. Some other reactions absorb energy. While energy changes are a potential sign of a chemical reaction, care must be taken to ensure that a chemical reaction is indeed taking place. Physical changes may also involve a transfer of energy. A solid absorbs energy when it melts, and the condensation

FIGURE 2.13

A yellow precipitate of solid lead(II) iodide forms immediately when solutions of lead(II) nitrate and potassium iodide are mixed.

of a gas releases energy. The only way to be certain that a chemical reaction has occurred is to test the composition of the substances after the change has taken place to see if they are different from the starting substances.

Lesson Summary

- Matter can undergo chemical and physical changes.
- Mixtures can be separated through physical changes, including techniques such as chromatography, distillation, evaporation, and filtration. Physical changes do not alter the nature of the substance, they simply alter the form.
- Pure substances, such as compounds, can be separated through chemical changes. Chemical changes change the chemical composition of a substance and can only occur through a chemical reaction.
- Four clues to a possible chemical reaction include a color change, the production of a gas, the formation of a precipitate, and an observable transfer of energy.

Review Questions

1. Can elements be broken down further into other pure substances?
2. For each of the following mixtures, describe how you might separate out the components using one of the techniques discussed in this chapter.
   a. separating dyes in inks
   b. separating sand from water
   c. separating ethanol from water
   d. separating water from ink
   e. separating salt from water
3. A candle is a mixture of substances that, when burned, breaks down primarily into carbon dioxide and water. How might you test for the presence of water that is produced when a candle is burned?

4. Carbonated beverages contain carbon dioxide gas that is dissolved in solution. Do you think a carbonated beverage is a mixture or a pure substance? Explain.
5. Classify each of the following as a chemical change or a physical change.
    a. Sugar dissolves in water.
    b. A peach rots.
    c. Icicles melt in the warm sunlight.
    d. A baking cake rises in the oven.
    e. A leaf changes its color in the fall.
    f. Food coloring is added to a glass of water.
6. The **Figure** 2.14 shows two different mixtures. The mixture on the left is comprised of muddy water, while the mixture on the right is a mixture of sugar and water. Describe how you might go about separating out the components of each of these mixtures.

FIGURE 2.14

(*left*) Muddy water. (*right*) Sugar water.

Further Reading / Supplemental Links

- School Science Lessons: http://www.uq.edu.au/_School_Science_Lessons/topic10.html
- Examples of laboratory techniques used for separating mixtures at Science Park: http://sciencepark.etacude.com/projects/
- Ophardt, Charles E. 2011. Virtual Chembook. Elmhurst College 20032011. Available from: http://www.elmhurst.edu/~chm/vchembook/index.html

Points to Consider

- We have thus far assumed that elements cannot be broken down further into constituent parts. Is this completely true?
- What do you suppose elements are comprised of and how might you be able to distinguish or measure the components of an element?

2.4 References

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12. User:Chemicalinterest/Wikimedia Commons. http://commons.wikimedia.org/wiki/File:Zn_reaction_with_HCl.JPG . Public Domain
13. Paige Powers (Flickr:paigggeyy). http://www.flickr.com/photos/paigggeyy/5533819494/ . CC BY 2.0
14. Muddy water: Image copyright Alena Brozova, 2014; Sugar water: Image copyright m.bonotto, 2014. http://www.shutterstock.com . Used under licenses from Shutterstock.com

CHAPTER 3 Measurement

Chapter Outline

3.1 UNITS OF MEASUREMENT

3.2 UNIT CONVERSIONS, ERROR, AND UNCERTAINTY

3.3 REFERENCES

When we think of measurement, a couple of things may come to mind. We may think of numbers, or we may think about instruments or equipment. The scale shown above, for instance, is an example of a common instrument that is used in measurement. In this case, the scale is measuring the weight of citrus fruit. Adjacent to the fruit is a 1 kilogram weight. If we were getting fruit at the market, we would likely purchase fruit in weight equivalents, like a kilogram or a pound, or some fraction of these equivalents. Measurement, in this example, allows us to measure quantities of fruit in a reliable fashion. Can you think of other food items you might measure? You might measure the temperature of a casserole, or the volume of milk used in a recipe, or the weight of dough in a pizza. Measurements depend on estimates, like estimating the weight of fruit. These estimates depend on reference points or equivalents, like one kilogram or a fraction of a kilogram. We also use measurement frequently in our study of the chemical world. Much of our modern understanding of chemistry is based on our ability to measure various physical quantities of chemical species.

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3.1 Units of Measurement

Lesson Objectives

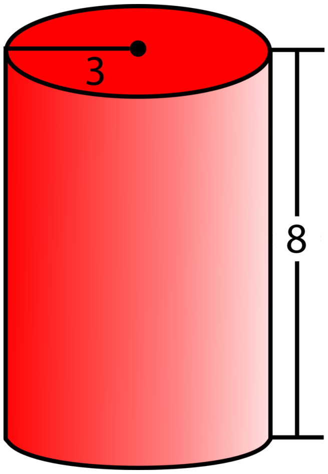
- Distinguish between a quantity, a unit, and a measurement standard.
- Distinguish between base units and derived units.
- Perform calculations using the SI system of measurement, with the use of appropriate prefixes.
- Name the SI units for length, mass, time, volume, and density.
- Describe the concepts of magnitude and scale and how they relate to measurement.
- Use scientific notation to report very small and very large numbers.
- Be able to perform calculations with numbers that are reported in scientific notation.

Lesson Vocabulary

- **Systeme International (SI)**: A common metric system of units of measurement used by scientists.
- **base unit**: A measurement that has its own independent scale and cannot be expressed in terms of other base units.
- **derived unit**: A measurement that is a combination of base units.
- **conversion factor**: A factor used in solving problems in which a certain measurement must be expressed with different units.
- **dimensional analysis**: A technique that uses the units (dimensions) of the measurement in order to express quantities in the appropriate units.
- **scientific notation**: A way to express very large and very small numbers as the product of two numbers: a coefficient and the number 10 raised to a power.

Check your Understanding

1. What will it cost to carpet a room if the room is 10 feet wide and 12 feet long? The carpet costs $12.51 per square yard.
   (a) $166.80
   (b) $175.90
   (c) $184.30
   (d) $189.90
   (e) $19.20
2. What is the volume in cubic centimeters of the following cylinder, given that the lengths are expressed in centimeters?

3. 

   (a) 210.91 cm^3
   (b) 226.20 cm^3
   (c) 75.36 cm^3
   (d) 904.32 cm^3
   (e) 28.26 cm^3

4. Kathy has three pieces of material. The first piece is 1 yd. 2 ft. 6 in. long, the second piece is 2 yd. 1 ft. 5 in. long, and the third piece is 4 yd. 2 ft. 8 in. long. How much material does Kathy have?
   (a) 7 yd. 1 ft. 8 in.
   (b) 8 yd. 4 ft. 4 in.
   (c) 8 yd. 11 in.
   (d) 9 yd. 7 in.
   (e) 10 yd.

Introduction

We make measurements all the time in our daily lives without even realizing it. When we walk, we visually measure the proximity of objects in our environment. When we pick up an item, we measure its weight and adjust our muscular response according to our initial estimates. Measurements are observations of a quantitative nature that are taken by some form of equipment. Some equipment, like our five senses, can give us very approximate measurements, while other technology, like a scale, provides more exact measurements. Many types of instruments are used to measure and study our chemical world. Some of the common quantities we measure in chemistry are distance (length), volume, mass, time, velocity, temperature, density, pressure, amount, concentration, energy, and electric charge. In this chapter, we will investigate how various methods of measurement are used to study the chemical nature of matter.

Measurement and Numbers

Measurement is a fundamental aspect of science and chemistry. Our understanding of the chemical world would not be possible if we did not compare, contrast, categorize, and analyze our observations to obtain the information we have about chemical substances. Let's consider water as an example. Many of the qualitative (non-numerical) properties of water, including its taste, smell, texture, and color, can be observed using our senses. We can also measure quantitative (numerical) properties of water by using equipment. For example, we can use a thermometer to measure water's boiling point in degrees Celsius or a measuring cup to measure the volume of a given liquid.

There can be different units that are used to measure the same physical quantity. For example, temperature can be expressed in degrees Fahrenheit (°F), degrees Celsius (°C), or degrees Kelvin (K). No one set of units is more correct than the other. However, as we begin measuring, calculating, and sharing measurements, we will want a standard set of values that we and others can use. An international governing body has developed a metric system of units of measurement for scientists called the **Système International (SI)**. Some of these units are listed in **Table** 3.1.

TABLE 3.1: **SI Base Units**

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

Base Units vs. Derived Units

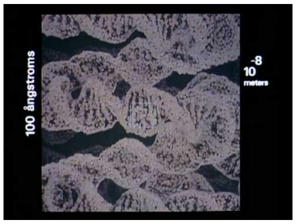
With the **base units** listed above, we can describe many physical details of a given chemical substance. Base units are measurements that have their own independent scale and cannot be expressed in terms of other base units. All other measurement quantities, such as volume, force, and energy, can be derived from these seven base units. For instance, volume is calculated by multiplying together three different lengths (height, width, and depth). We call these combinations of base units **derived units**. Some examples of derived units are listed in **Table** 3.2.

TABLE 3.2: **SI Derived Units**

Physical Quantity	Name of SI Unit	Abbreviation
area	square meter	m^2
volume	cubic meter	m^3
speed, velocity	meter per second	m/s
acceleration	meter per second squared	m/s^2
force	Newton (mass × acceleration)	N ($kg\ m/s^2$)
mass density	kilogram per cubic meter	kg/m^3
energy	joule (force × distance)	J ($kg\ m^2/s^2$)

Magnitude and Scale

When we think about the physical quantities that are measured in chemistry, we must also consider the concepts of magnitude and scale. The following video introduces these concepts: http://www.youtube.com/watch?v=0fKBhvDjuy0 (9:01).



MEDIA

Click image to the left for more content.

As the video suggests, chemistry is a discipline in which we study things that are very, very small. We measure things like the size of an atom, which is approximately 1/10000000000 of a meter. Because individual atoms are so small, the substances that we can actually see and study, even something as small as a drop of rain, are comprised of an incredibly large number of atoms. There are literally thousands of billions of billions of particles in a drop of water. In both of these examples, we expressed size in terms of fractions or multiples of the number 10. When describing very small or very large physical quantities, we use prefixes to write the unit as a power of 10. **Table** 3.3 displays most of these prefixes.

TABLE 3.3: **Commonly Used SI Prefixes**

Prefix	Meaning	Abbreviation	Numeric value	Exponential Notation
exa-	billion billion	E	1000000000000000000	10^{18}
peta-	thousand trillion	P	1000000000000000	10^{15}
tera-	trillion	T	1000000000000	10^{12}
giga-	billion	G	1000000000	10^{9}
mega-	million	M	1000000	10^{6}
kilo-	thousand	k	1000	10^{3}
hecto-	hundred	h	100	10^{2}
deka-	ten	da	10	10
n/a	one	n/a	1	10^{0}
deci-	one tenth	d	0.1	10^{-1}
centi-	hundredth	c	0.01	10^{-2}
milli-	thousandth	m	0.001	10^{-3}
micro-	millionth	μ	0.000001	10^{-6}
nano-	billionth	n	0.000000001	10^{-9}
pico-	trillionth	p	0.000000000001	10^{-12}
femto-		f	0.000000000000001	10^{-15}
atto-		a	0.000000000000000001	10^{-18}

The Relative Size of Things

We can express the relative size of things with which we are familiar. For instance, the **Figure** 3.1 shows the height of a human as measured in meters, or 10^0 scale. We see a dust mite, measured in micrometers –10^{-6} scale; and a virus, measured in nanometers –10^{-9} scale. These are examples of length related to relative size and scale.

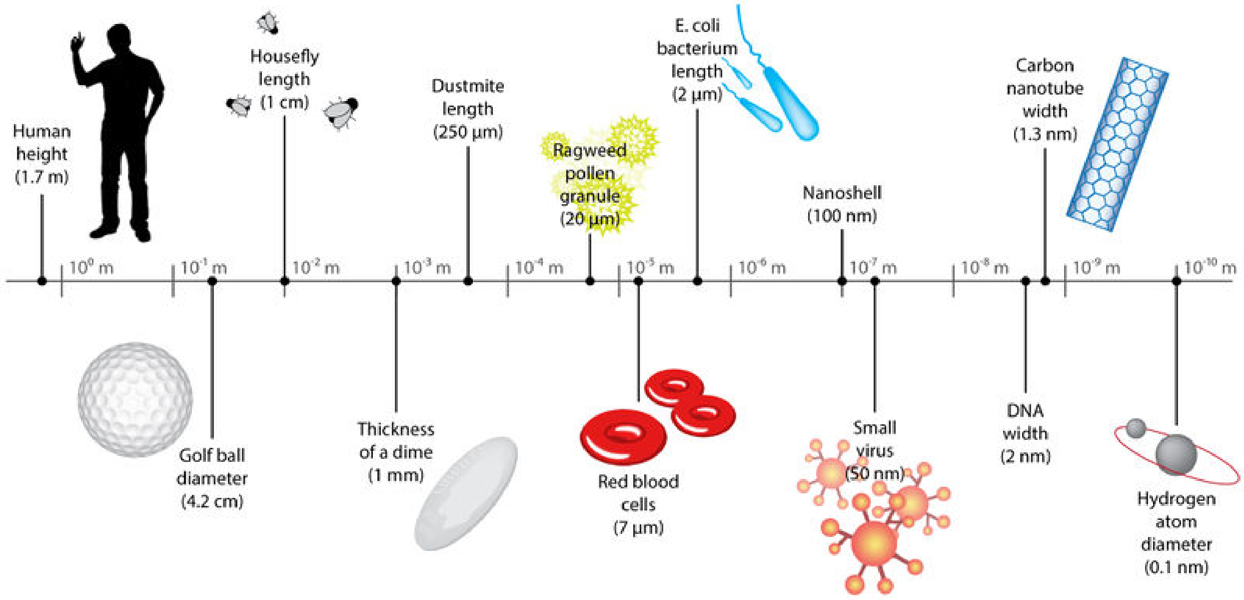


FIGURE 3.1

Relative size and scale of things.

Dimensional Analysis

Conversion factors are used in solving problems in which a certain measurement must be expressed in different units. When a given measurement is multiplied by an appropriate conversion factor, the numerical value changes, but the actual size of the quantity measured remains the same. **Dimensional analysis** is a technique that uses the units (dimensions) of the measurement in order to correctly convert between units to solve problems. Dimensional analysis is best illustrated with an example.

Example 3.3

How many seconds are in a day?

Step 1: List the known conversion factors.

- 1 day = 24 hours
- 1 hour = 60 minutes
- 1 minute = 60 seconds

Step 2: Use the conversion factors as fractions to convert the given units to the desired units.

The known quantities above represent the conversion factors that we will use. The first conversion factor will have day in the denominator so that the "day" unit will cancel. The second conversion factor will then have hours in the denominator, while the third conversion factor will have minutes in the denominator. As a result, the unit of the last numerator will be seconds and that will be the units for the answer.

$$1\,\cancel{\text{d}}\times\frac{24\,\cancel{\text{h}}}{1\,\cancel{\text{d}}}\times\frac{60\,\cancel{\text{min}}}{1\,\cancel{\text{h}}}\times\frac{60\text{ s}}{1\,\cancel{\text{min}}}=86,400\text{ s}$$

In this technique, we are essentially "multiplying by 1" several times. For example, because 1 day is equal to 24 hours, a fraction in which one of these values is in the numerator and the other is in the denominator will be equal to 1. Because multiplying by 1 does not change the value of a number, the final value is equivalent to the original one.

Dimensional Analysis and the Metric System

The metric system's many prefixes allow quantities to be expressed in many different units. Dimensional analysis is useful to convert from one metric system unit to another.

Example 3.4

A particular experiment requires 120 mL of a solution. The teacher knows that he will need to make enough solution for 40 experiments to be performed throughout the day. How many liters of solution should he prepare?

Step 1: Perform the calculation.

$$120 \text{ mL} \times 40 = 4800 \text{ mL}$$

Step 2: Use a metric conversion factor (1 L = 1000 mL) to convert the given units to the desired units.

$$4800 \cancel{\text{mL}} \times \frac{1 \text{ L}}{1000 \cancel{\text{mL}}} = 4.8 \text{ L}$$

Note that the conversion factor is arranged so that the mL unit is in the denominator. It therefore cancels out, leaving L as the remaining unit in the answer.

Some metric conversion problems are most easily solved by breaking them down into more than one step. When both the given unit and the desired unit have prefixes, one can first convert to the simple (unprefixed) unit, followed by a conversion to the desired unit. An example will illustrate this method.

Example 3.5

Convert 4.3 cm to μm.

Step 1: List the known conversion factors.

- 1 m = 100 cm
- 1 m = 10^6 μm

Step 2: Use the conversion factors as fractions to convert the given units to the desired units.

$$4.3 \cancel{\text{cm}} \times \frac{1 \cancel{\text{m}}}{100 \cancel{\text{cm}}} \times \frac{10^6 \mu\text{m}}{1 \cancel{\text{m}}} = 43,000 \mu\text{m}$$

Each conversion factor is written so that unit of the denominator cancels with the unit of the numerator of the previous factor.

Scientific Notation

Scientific notation is a way to express numbers as the product of two numbers: a coefficient and the number 10 raised to a power. A coefficient is a numerical value that comes before the multiplying number, in this case the number 10 raised to a power. As an example, the distance from Earth to the Sun is about 150,000,000,000 meters –a very large distance indeed. In scientific notation, the distance is written as 1.5×10^{11} m. The coefficient is 1.5 and must be a number greater than or equal to 1 and less than 10. The power of 10, or exponent, is 11. See **Figure** 3.2 for two more examples of scientific notation. Scientific notation is sometimes referred to as exponential notation.

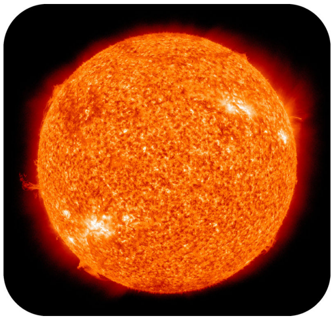


FIGURE 3.2

The Sun is very large and very distant, so solar data is better expressed in scientific notation. The mass of the Sun is 2.0×10^{30} kg and its diameter is 1.4×10^{9} m.

Very small numbers can also be expressed using scientific notation. The mass of an electron in decimal notation is 0.000000000000000000000000000911 grams. In scientific notation, the mass is expressed as 9.11×10^{-28} g. Notice that the value of the exponent is chosen so that the coefficient is between 1 and 10.

Example 3.4

A common mosquito weights approximately 0.0000025 kg. Write the mosquito's weight in scientific notation.

In scientific notation we will write this quantity as a coefficient multiplied by 10 raised to some power.

Step 1: Our coefficient must be a number between 1 and 10. From 0.0000025 kg, we determine the coefficient to be 2.5.

Step 2: The quantity 0.0000025 kg is less than 1, so 10 must be raised to a negative exponent. The decimal place must be moved to the right by 6 places to write the coefficient 2.5, so we will write 10^{-6} as our power of 10

Step 3: Coefficient + Power of 10. This gives us 2.5×10^{-6} kg. Remember, our units in this case have not changed, we are just changing the way we are writing the numerical value.

Adding and Subtracting

There are times when we will want to add or subtract numbers that are expressed in scientific notation. We will approach such calculations in one of two ways.

Same Base Units

Example 3.5

$1.235 \times 10^3 \text{ meters} + 3.45 \times 10^2 \text{ meters}$

Step 1: Convert numbers to regular notation.

$1235 \text{ meters} + 345 \text{ meters}$

Step 2: Add.

$$\begin{array}{r} 1235 \text{ meters} \\ \underline{+\ 345 \text{ meters}} \\ 1580 \text{ meters} \end{array}$$

Step 3: Convert back to scientific notation (depending on the result, this is not always necessary).

1.580×10^3 m

We would follow the same steps for subtraction, as well as for numbers with negative exponents.

Different Base Units

Example 3.6

1.5×10^2 liters $-$ 3.45×10^2 deciliters

Step 1: Convert numbers to regular notation.

150 liters $-$ 345 deciliters

Step 2: Decide on which unit you want the final answer to be expressed as and convert the numbers to this unit.

$$345\ \cancel{\text{dL}} \times \left(\frac{1\ \text{L}}{10\ \cancel{\text{dL}}}\right) = 34.5\ \text{L}$$

Step 3: Subtract.

$150\ \text{L} - 34.5\ \text{L} = 115.5\ \text{L}$

Step 4: Convert to scientific notation.

$1.155 \times 10^2\ \text{L}$

Multiplying and Dividing

Same Base Units

Example 3.7

$(4.65 \times 10^3$ meters$) \times (3.56 \times 10^2$ meters$)$

Step 1: Group the coefficients and the exponential terms together.

$(4.65 \times 3.56) \times (10^3 \times 10^2)$ meters $\times$ meters

Step 2: Multiply coefficients and add the exponents.

$(16.55) \times (10^5)$ meters^2

Step 3: Change to scientific notation. Remember that the coefficient must be a number between 1 and 10.

$1.655 \times 10^6\ \text{m}^2$

Note that when two values are multiplied together, the units are multiplied as well. This is different than the case for addition and subtraction, where the units for the answer are the same as the units for each of the starting values.

Different Base Units

The procedure here is the same, except that a conversion is made so that both values are expressed in the same units.

Example 3.8

$(4.65 \times 10^{-4}$ liters$) \times (3.56 \times 10^2$ milliliters$)$

Step 1: Convert to a common unit.

In this case, we chose the common unit to be milliliters.

$$4.65 \times 10^{-4}\ \cancel{\text{L}} \times \left(\frac{1000\ \text{mL}}{1\ \cancel{\text{L}}}\right) = 4.65 \times 10^{-1}\ \text{mL}$$

Step 2: Group the coefficients and the exponential terms together.

$(4.65 \times 3.56) \times (10^{-1} \times 10^2)\ \text{mL}^2$

Step 3: Multiply coefficients and add the exponents.

$(16.55) \times (10^1) = 165.5\ \text{mL}^2$

Step 4: Change to scientific notation.

1.655×10^2 mL^2

Lesson Summary

- Measurement is the process of making an observation in terms of a numerical scale and recording the value.
- In chemistry, we measure things that range from extremely small to extremely large. Common quantities measured include distance, mass, time, temperature, volume, density, pressure, amount, concentration, energy, velocity, molarity, viscosity, and electric charge.
- Because chemistry deals with very large and very small physical quantities, we utilize powers of 10 to express base units and derived units.
- Base units have independent scales and cannot be described by a combination of any other base units. Examples of base units used in chemistry are length, mass, temperature, and time.
- Derived units can be expressed as some combination of base units. Examples of derived units are area, volume, and speed.
- The Systeme International (SI) is a standard metric system of units that is used by scientists.
- Dimensional analysis is a method of problem solving in which conversion factors are arranged so that a value can be converted from one set of units to another.

Review Questions

1. Convert the following numbers to scientific notation.
   a. 13,000,000
   b. 4020.0
   c. 0.00040
   d. 0.0004002
2. Convert the following using conversion factors given in the table of Commonly Used SI Prefixes.
   a. 126 kg to grams
   b. 826 mL to L
   c. 2.45×10^{-12} g to nanograms
   d. 1.24×10^{-12} meters to picometers
3. Perform the following calculations, and write your final answer in scientific notation.
   a. 1.06×10^3 kilograms + 8.6×10^{13} nanograms
   b. 100.06 mL + 35 L
   c. 3.56×10^5 cm + 1.23×10^2 m
4. Which SI unit and prefixes would be used to report the following
   a. A person's weight
   b. The length of a ladybug
   c. The volume of a large lake
   d. The weight of a human hair
   e. The width of a human hair
5. Calculate the number of seconds in the month of December.
6. How many donuts can you buy with $23.00 if they cost $3.00/dozen?
7. A light year is the distance light travels in one year. Sirius (the dog star), the brightest in the sky, is approximately 8.6 light years from earth. How far (in km) from earth is it if light travels 3.0×10^8 m/s?

Further Reading / Supplemental Links

- Robinson, A. (2007). The Story of Measurement. New York: Thames and Hudson.
- Mass of snowflake approximation: http://hypertextbook.com/facts/2001/JudyMoy.shtml

Points to Consider

- In this lesson we discussed base units and derived units. We saw that there are SI base and derived units. Can you think of base units or derived units you are familiar with that are not SI units?
- What do you suppose might be the difference between a measurement and a number? How might they be the same or different?

3.2 Unit Conversions, Error, and Uncertainty

Lesson Objectives

- Differentiate between accuracy and precision as they relate to a given measurement.
- Describe the reliability of a measurement and how it can be expressed in terms of uncertainty.
- Distinguish between mass and weight and describe how mass and weight are determined.
- Understand the concept of volume and how it can be determined for various substances, including regularly shaped and irregularly shaped solids.
- Define density and perform density calculations.
- Describe how many significant figures there are in a given measurement, and be able to perform measurement calculations involving numbers with significant figures.

Lesson Vocabulary

- **meniscus**: The curved upper surface of a liquid in a tube.
- **estimate**: A process of referencing a physical quantity in terms of a calibration or reference point.
- **uncertainty**: All measurements have an uncertainty equal to one half of the smallest difference between reference marks.
- **accuracy**: Describes how close an estimate is to a known standard.
- **precision**: Describes how close estimates are to one another.
- **calibration**: A method of setting or correcting a measuring device by matching it to known measurement standards.
- **percent uncertainty**: The ratio of the uncertainty to the measured value, multiplied by one hundred.
- **percent error**: An expression of the accuracy of a measurement, standardized to how large the measurement is.
- **significant figures**: Consist of all the certain digits in that measurement plus one uncertain or estimated digit.
- **density**: An expression of the mass of substance in terms of the volume occupied by the substance.
- **mass**: The quantity of inertia possessed by an object.
- **weight**: The gravitational force acting on a mass, as measured on a scale.
- **Fahrenheit scale**: The most commonly used scale in the United States, it defines the normal freezing point and boiling point of water as 32°F and 212°F, respectively.
- **Celsius scale**: The most commonly used scale around the world, it defines the normal freezing point and boiling point of water as 0°C and 100°C, respectively.
- **Kelvin scale**: Referred to as the absolute temperature scale, it defines absolute zero as the lowest theoretically possible temperature.

Check Your Understanding

1. What will it cost to carpet a room if the room is 10 feet wide and 20 feet long, and the price of carpet is \$2.36 per ft^2?

2. Which of the following is the larger amount: 2.35×10^2 L or 3.46×10^5 mL?
3. List two SI units that would be appropriate for measuring each of the following quantities: volume, weight, and length.

Introduction

In the last lesson, we studied the concept of measurement and how numbers are used to express various physical quantities. We studied scale and magnitude and investigated how to use scientific notation and SI units to report numbers in an efficient and consistent manner. However, we have not yet studied how measurement takes place. There are many different measurements we make in our investigations of the chemical world. Measurements such as distance, volume, and mass are important values that are frequently used to describe the characteristics and behavior of chemical species. To make measurements, we use instruments labeled with a known scale. However, it is impossible for measurements to be exact. In this lesson, we are going to study how measurements are made as well as the error and uncertainty involved in measurements.

Uncertainty

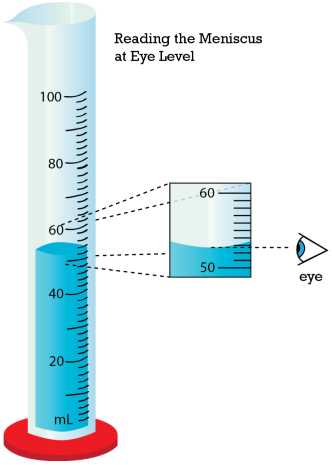


FIGURE 3.3

Figure 3.3 shows a graduated cylinder, which is an instrument that is used to measure volume. The graduated cylinder gets its name because of the gradation or scaled lines drawn on its side. These serve as reference points that correspond to known volumes. When we make a measurement using a graduated cylinder, we look at the **meniscus**, or curved surface, of the liquid and **estimate** where the bottom of the meniscus is relative to the gradations. All measurement devices have reference marks of some kind. Can you think of another example of a measurement device with regular reference marks?

Example 3.9

Make an estimate of the volume that is shown in **Figure** 3.3.

Answer:

We see the bottom of the meniscus is at approximately 52.9 mL. We report this in mL because our cylinder is a 100 mL graduated cylinder, with mL reference marks. There are 9 equally spaced marks between the 50 mL and 60 mL *lines, so each one must represent 1 mL. As we will see next, the space between these marks represents an area of uncertainty with regard to the estimate.*

When the volume in our previous example was reported to be 52.9 mL, the **uncertainty** associated with this estimate also needed to be reported. For example, we know for certain that the true value for the volume must be between 52 mL and 53 mL. However, there is uncertainty regarding how close the value is to 52 or 53. We estimated the volume to be 52.9, but some students may have reported 52.8 or 53.0. These would be accurate estimates because they fall within the acceptable uncertainty of the device. All measurements have an uncertainty equal to one half of the smallest difference between reference marks. For our graduated cylinder, there is 1 mL between consecutive marks, so the uncertainty is one half of that value, 0.5 mL. To be rigorous about our certainty regarding this measured value, the estimate of 52.9 mL should be reported as 52.9 ± 0.5 mL.

Accuracy

In measuring quantities we always aim for high **accuracy**. Estimates that fall within the range of uncertainty for a given instrument are said to be accurate. In our previous example, all of the values between and including 52.4 mL and 53.4 mL would be considered accurate. Estimates that fall outside this range are inaccurate. Accuracy describes how close an estimate is to a known standard.

Precision

Precision describes how close estimates are to one another. Estimates that are relatively close to one another are precise. Let's assume that ten different students made an estimate of the volume shown in **Figure** 3.3, and the values were: 52.9, 52.8, 52.9, 52.9, 53.3, 52.0, 52.8, 52.9, 53.0, 52.8. We can determine how precise these data are by analyzing how close they are to an average. The average could be the mean, median or mode. The most common understanding of the average is the mean. This value is calculated by adding up all the numbers and then dividing by the total number of values. Other terms that can refer to the average are the median and the mode. The median is the middle value in a numerically ordered list of numbers. The mode is the value that occurs most often in a set of numbers. If no number is repeated, there is no mode for the list. Here are the calculated averages:

$$\text{Mean} = \frac{52.9+52.8+52.9+52.9+53.3+52.0+52.8+52.9+53.0+52.8}{10} = 52.8$$

$$\text{Median} = 52.0, 52.8, 52.8, 52.8, [52.9], 52.9, 52.9, 52.9, 53.0, 53.3 = 52.9$$

$$\text{Mode} = 52.0, 52.8, 52.8, 52.8, [52.9, 52.9, 52.9, 52.9], 53.0, 53.3 = 52.9$$

Based on this analysis, we see the value 52.8 was the mean, and 52.9 was the median and mode. Therefore, values that are relatively close to these averages would be considered precise. We can also calculate the standard deviation for these data, which is a more refined way of determining the precision of estimates. However, we will not concern ourselves with standard deviation at this point.

Accuracy vs. Precision

As we just saw, accuracy describes how close a given set of data is to the "real" value, while precision describes how close the data points are to one another. These concepts are illustrated in **Figure** 3.4.

Target A represents the best possible "data". All of the data point points are clustered in the center, close to the "actual" value and close to one another. This data is both accurate and precise. In target B, the set of data has good accuracy overall if the points are averaged together. However, the three points are not very close to each other making the imprecise. Target C, on the other hand, shows precise but inaccurate data. The three data points are close together, making them precise, but are far from the center of the target, giving low accuracy. Target D represents the worst possible "data". The data points are far from the center of the target lacking any accuracy, as well as being far apart from each other, lacking precision.

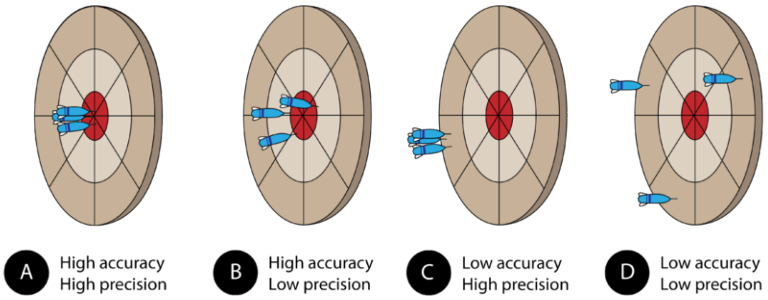


FIGURE 3.4
Here we see three darts thrown at four different targets. Accurate shots would be those that were close to the bull's-eye (the inner circle). Precision would be the shots that were close to one another.

Calibration

When using measuring devices, we often use a technique called **calibration** to increase the accuracy of our measurements. Calibration is a method of setting or correcting a measuring device by matching it to known measurement standards. To better understand calibration, we will look at the example of calibrating a thermometer. All thermometers are slightly different in their temperature readings. One way to calibrate a thermometer is by using the freezing point and boiling point of water (**Figure** 3.5). If we know that water freezes at 0°C and boils at 100°C, we can calibrate our thermometer by measuring the temperature of ice water and of boiling water. We place the thermometer in ice water and wait for the thermometer liquid to reach a stable height, then place a mark at this height which represents 0°C. Then we place the thermometer in boiling water, and after waiting for the thermometer liquid to reach a stable height, we place a mark at this height which represents 100°C. We can then place 100 equally spaced divisions between our 0 and 100°C marks to each represent 1°C. Our thermometer has now been calibrated using the known values for the freezing point and boiling point of water, and can be used to measure temperatures of objects between 0 and 100°C.

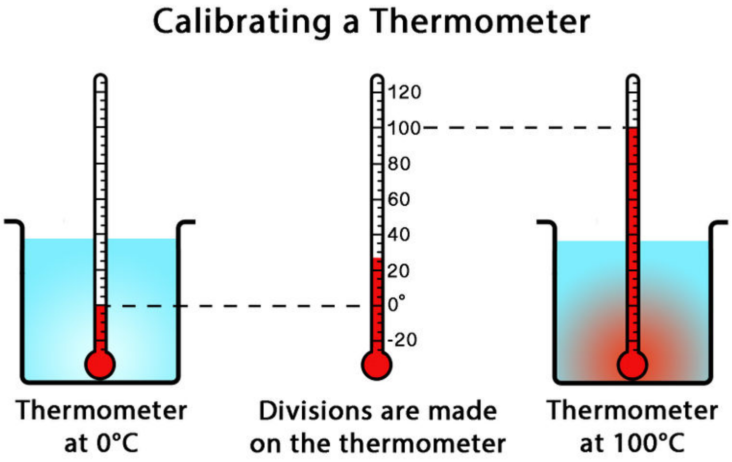


FIGURE 3.5
A thermometer can be calibrated by measuring the freezing point (0 ℃) and the boiling point (100 ℃) of water. One hundred equally spaced divisions can then be made between 0 and 100 ℃.

Calibration is used to standardize a variety of measuring devices, including meter sticks, graduated cylinders, scales, and thermometers. It is a good idea to calibrate any measuring equipment you use in an experiment to make sure the data you are collecting is measured as accurately as possible.

Percent Uncertainty

To express the uncertainty in a measurement, we can calculate **percent uncertainty**. Percent uncertainty is the ratio of the uncertainty to the measured value, multiplied by one-hundred. For instance, the percent uncertainty associated with the measurement of (52.9 ± 0.5 mL), would be

$$\% \text{ uncertainty} = \frac{0.5}{52.9} \times 100 = 0.95\% \approx 1\%$$

Example 3.10

Using our estimate of 52.9 mL, what would be the range of possible values for the true volume?

Answer

Upper estimate = 52.9 + 0.5 = 53.4 mL

Lower estimate = 52.9 - 0.5 = 52.4 mL

Assuming that our equipment is accurate, we can be confident that the true volume of the sample is somewhere in between these two values.'

Percent Error

On the other hand, **percent error** is an expression of the accuracy of a measurement. There are various possible sources of error that arise in measurement. For example, there can be error associated with the observation, like misreading a graduated cylinder. There is error associated with the method or the procedure, like not drying a wet solid before weighing. Error can also arise from the object being measured. For example, a pure solid may have a residue fixed to it that affects its mass. There can also be errors that arise from the measurement instrument, like not zeroing a balance, or improper calibration. Percent error is calculated as follows:

$$\% \text{ error} = \frac{|\text{Measured} - \text{Accepted}|}{\text{Accepted}} \times 100$$

Example 3.11

Make an estimate of volume for the image shown in **Figure** 3.6, and answer the questions below.

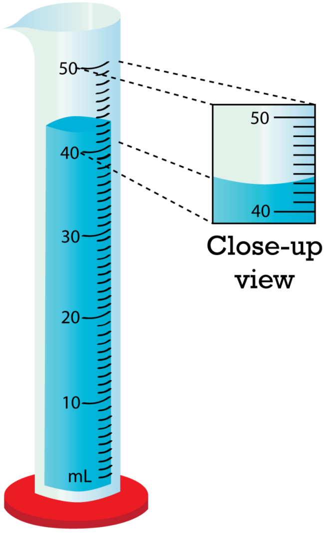


FIGURE 3.6

Which of the following estimates would be accurate? Report your answer in terms of uncertainty.

Which of the following sets of estimates would be *most* precise?

If a student reported an volume of 45.0 mL, calculate the percent error in his or her measurement if the actual volume is exactly 43.0 mL.

Significant Figures

The **significant figures** in a measurement consist of all the certain digits in that measurement plus one uncertain or estimated digit. In the graduated cylinder example from the previous section, the measured value was reported to be 52.9 mL, which includes 3 significant figures. In a correctly reported measurement, the final digit is significant but not certain. Insignificant digits are not reported. It would not be inncorrect to report the volume as 52.923 mL, because even the tenths place (the 9) is uncertain, so no reasonable estimate could be made for any of the following digits.

When you look at a reported measurement, it is necessary to be able to count the number of significant figures. **Table** 3.4 details the rules for determining the number of significant figures in a reported measurement. For the examples in the table, assume that the quantities are correctly reported values of a measured quantity.

TABLE 3.4: **Significant Figure Rules**

Rule	Examples
1. All nonzero digits in a measurement are significant	A. 237 has three significant figures. B. 1.897 has four significant figures.
2. Zeros that appear between other nonzero digits are always significant.	A. 39,004 has five significant figures. B. 5.02 has three significant figures.
3. Zeros that appear in front of all of the nonzero digits are called left-end zeros. Left-end zeros are never significant.	A. 0.008 has one significant figure. B. 0.000416 has three significant figures.
4. Zeros that appear after all nonzero digits are called right-end zeros. Right-end zeros in a number that lacks a decimal point are not significant.	A. 140 has two significant figures. B. 75,210 has four significant figures.
5. Right-end zeros in a number with a decimal point are significant. This is true whether the zeros occur before or after the decimal point.	A. 620.0 has four significant figures. B. 19,000. has five significant figures

It needs to be emphasized that just because a certain digit is not significant does not mean that it is not important or that it can be left out. Though the zero in a measurement of 140 may not be significant, the value cannot simply be reported as 14. An insignificant zero functions as a placeholder for the decimal point. When numbers are written in scientific notation, this becomes more apparent. The measurement 140 can be written as 1.4×10^2, with two significant figures in the coefficient. A number with left-end zeros, such as 0.000416, can be written as 4.16×10^{-4}, which has 3 significant figures. In some cases, scientific notation is the only way to correctly indicate the correct number of significant figures. In order to report a value of 15,000,000 with four significant figures, it would need to be written as 1.500×10^7. The right-end zeros after the 5 are significant. The original number of 15,000,000 only has two significant figures.

Exact Quantities

When numbers are known exactly, the significant figure rules do not apply. This occurs when objects are counted rather than measured. In your science classroom, there may be a total of 24 students. The actual value cannot be

23.8 students, as there is no such thing as 8 tenths of a student. So the 24 is an exact quantity. Exact quantities are considered to have an infinite number of significant figures; the importance of this concept will be seen later when we begin looking at how significant figures are dealt with during calculations. Numbers in many conversion factors, especially for simple unit conversions, are also exact quantities and have infinite significant figures. There are exactly 100 centimeters in 1 meter and exactly 60 seconds in 1 minute. Those values are definitions and are not the result of a measurement.

Adding and Subtracting Significant Figures

The sum or difference is determined by the smallest number of significant figures to the right of the decimal point in any of the original numbers.

Example 3.13

$89.332 + 1.1 = 90.432 \quad \text{round to } 90.4$

Example 3.14

$2.097 - 0.12 = 1.977 \quad \text{round to } 1.98$

Multiplying and Dividing Significant Figures

The number of significant figures in the final product or quotient is equal to the number of significant figures in the starting value that has the fewest significant figures.

Example 3.15

$2.8 \times 4.5039 = 12.61092 \quad \text{round to } 13$

Example 3.16

$6.85 \div 112.04 = 0.0611388789 \quad \text{round to } 0.0611$

Example 3.17

For this example, the value 8 is known to be exact (so it has an infinite number of significant figures).

$0.2786 \times 8 = 2.229$

Calculating Density

Imagine holding a tennis ball in one hand and an orange in the other. Why does the orange feel heavier than the tennis ball, even though the two objects are about the same size? This can be explained with the concept of **density**. Density is an expression of the mass of a substance in terms of the volume occupied by the substance. The equation for density is:

$$\text{Density} = \frac{\text{mass}}{\text{volume}}$$

$$D = \frac{m}{V}$$

So, even though a tennis ball and an orange may be about the same volume, the orange contains more mass within that volume than does the tennis ball. Therefore, the orange has a higher density. This is because the orange contains mostly water and the tennis ball contains mostly air; as you might imagine, water is much heavier than air.

Density is typically reported in terms of gram per milliliter (g/mL) or the equivalent value, grams per cubic centimeter (g/cm^3). Oftentimes, scientists compare the density of an object to the density of water which is 1 g/mL at room temperature (25°C). The densities of some common materials are listed in the **Table** 3.5.

TABLE 3.5:

Material	Density (g/mL)
hydrogen	0.00009
oxygen	0.0014
water	1.0
aluminum	2.7
iron	7.9
gold	19.3

Mass vs. Weight

The terms mass and weight, while often used interchangeably, are technically different terms. **Mass** is the quantity of inertia possessed by an object. **Weight** refers to the gravitational force acting on a mass, as measured on a scale. On the surface of the earth, the numerical values of mass and the corresponding force of gravity (weight) are approximately equivalent. For now, we will use the terms mass and weight interchangeably although mass is the more appropriate scientific term.

Determining the Volume of Regularly Shaped Objects

In order to calculate density, we must know the volume the object occupies. We can calculate the volumes of some regularly shaped objects using the following expressions in **Table** 3.6.

TABLE 3.6: **Formulas for Calculating Volumes of Regularly Shaped Objects**

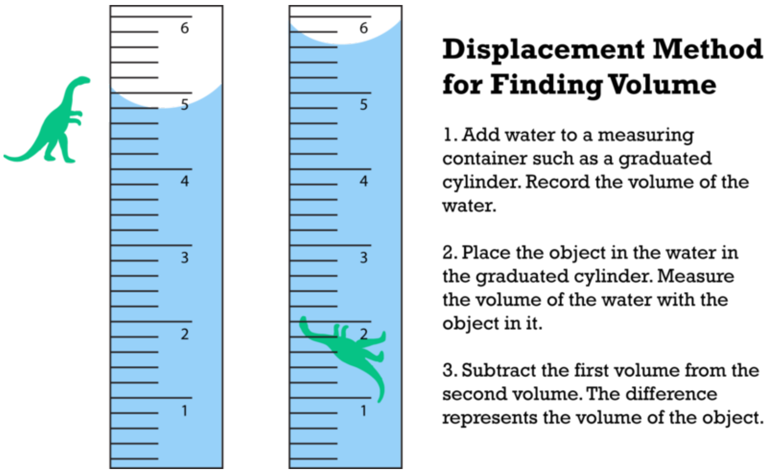
Volume of a cube	$l \times w \times h$
Volume of a sphere	$\frac{4}{3}\pi r^3$
Volume of a cylinder	$\pi r^2 h$
Volume of a cone	$\frac{1}{3}\pi r^2 h$

Determining the Volume of Irregularly Shaped Objects

If a solid is irregularly shaped, we can determine its volume by measuring the volume of water displaced by the solid. For example, say you want to measure the volume of the toy dinosaur in **Figure** 3.7. After placing the dinosaur in the water, the volume measured in the container increases by an amount that is equal to the total volume of the dinosaur. Note that this method only works for solids that do not dissolve in water. If you tried to measure the volume occupied by a pile of salt, the salt would dissolve in the water and this method would not work very well.

Temperature Scales

There are three temperature scales that are commonly used in measurement. Their units are °F (degrees Fahrenheit), °C (degrees Celsius), and K (Kelvin). The **Fahrenheit scale**, which is the most commonly used scale in the United States, defines the normal freezing point and boiling point of water as 32°F and 212°F, respectively. The **Celsius scale** defines the normal freezing point and boiling point of water as 0°C and 100°C, respectively. The Celsius



Displacement Method for Finding Volume

1. Add water to a measuring container such as a graduated cylinder. Record the volume of the water.

2. Place the object in the water in the graduated cylinder. Measure the volume of the water with the object in it.

3. Subtract the first volume from the second volume. The difference represents the volume of the object.

FIGURE 3.7

Displacement of water by irregular solid.

scale is commonly used in most countries across the globe. The **Kelvin scale**, which is also referred to as the absolute temperature scale, defines absolute zero as the lowest theoretically possible temperature, which means that temperatures expressed in Kelvin cannot be negative numbers. We will further study the origins of this temperature scale in the chapter *States of Matter*.

Converting Temperature Scales

Regardless of the temperature scale used, it is important to be able to convert from one scale to another. Here are the conversions we use.

°F to °C

$T_{^\circ C} = (T_{^\circ F} - 32) \times \frac{5}{9}$

°C to °F

$T_{^\circ F} = \frac{9}{5} \times (T_{^\circ C}) + 32$

°C to K

$T_K = T_{^\circ C} + 273.15$

K to °C

$T_{^\circ C} = T_K - 273.15$

Example 3.19

The melting point of mercury is -38.84°C. Convert this value to degrees Fahrenheit and degrees Kelvin.

Answer

$$\begin{aligned}
T_{^\circ F} &= \frac{9}{5} \times (-38.84^\circ\mathrm{C}) + 32 \\
T_{^\circ F} &= -37.12^\circ\mathrm{F} \\
T_K &= -38.84^\circ\mathrm{C} + 273.15 \\
T_K &= 234.75\ \mathrm{K}
\end{aligned}$$

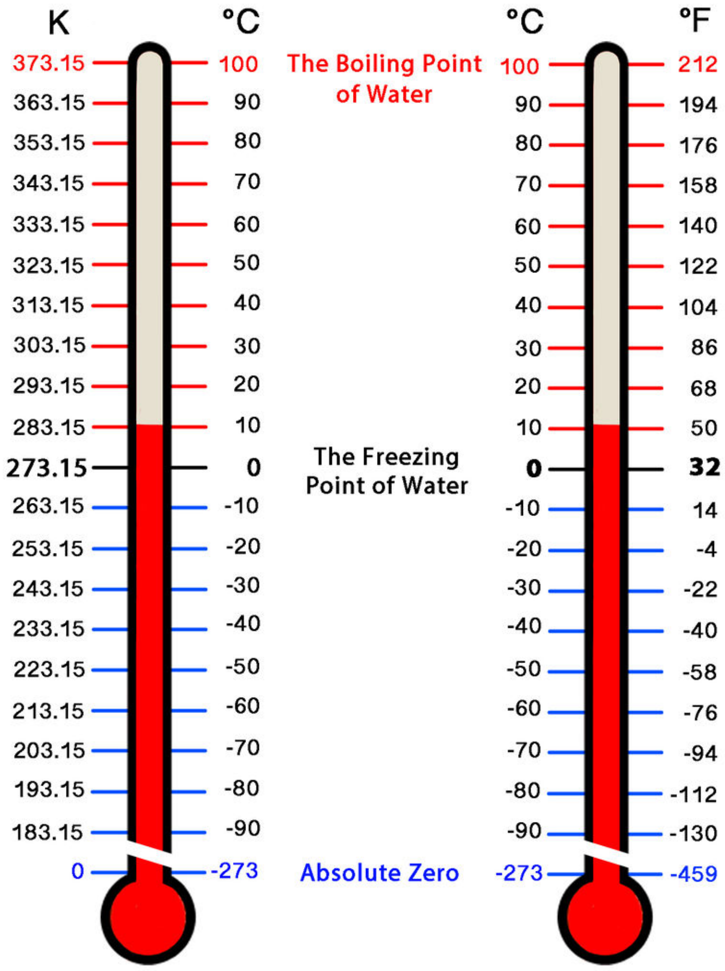


FIGURE 3.8

Lesson Summary

- Accuracy describes how close an estimate is to a known standard.
- Precision describes how close estimates are to one another.
- The accuracy of an estimate cannot be improved through calculation.
- Calibration is a technique used to standardize a measuring instrument and increase the accuracy of measurements.
- Estimation, as used in measurement, is the process of referencing a physical quantity in terms of a calibration or reference point. All measurement devices have reference marks of some kind.
- All measurements have an associated uncertainty. It is expressed as one-half of the smallest difference between calibration marks. It can also be expressed as a percent.
- Percent error is an expression of the accuracy of a measurement, standardized to how large the measurement is.
- Sources of error can originate from observation errors, methods or procedural errors, as well as errors associated with object that are measured. They can also originate from the measurement instrument itself.
- Significant figures are figures associated with uncertainty of a measurement.
- Density is an expression of the mass of substance in terms of the volume occupied by the substance.

- Density is typically reported in terms of grams/mL (g/mL) or grams per cubic centimeter (g/cm^3).
- If a solid is irregularly shaped, we can determine its volume by measuring the volume of water that the solid displaces.
- There are three temperature scales that are commonly used. Their units are °F (degrees Fahrenheit), °C (degrees Celsius), and K (Kelvin).

Review Questions

Make an estimate of the length that is shown in **Figure** 3.9 and use this information to answer the following questions.

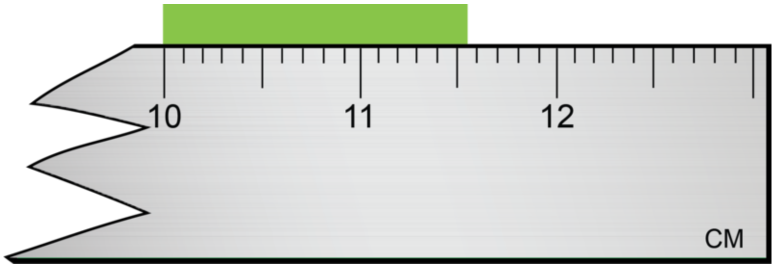


FIGURE 3.9

1. If the length in **Figure** 3.9 were estimated to be 11.65 cm ± 0.05, what would be the range of values that fall within the acceptable uncertainty for this instrument?
2. Which of the following length estimates would be accurate for **Figure** 3.9?
   (a) 11.59
   (b) 11.71
   (c) 11.64
   (d) 12
3. Which of the following length estimates would be precise for the **Figure** 3.9?
   (a) 11.64, 11.65, 11.65
   (b) 11.60. 11.56, 11.45
   (c) 10.9, 12.2, 12
   (d) 11, 11.23, 11.234
4. A student measures the density of gold and finds it to be 18.3 g/mL. The accepted value from the Handbook of Chemistry and Physics is 19.3 g/mL (Lide 1992-1993). What is the percent error of the student's results?
5. How would you report 40.889 m^3 to three significant figures using scientific notation?
6. Complete the **Table** below.

TABLE 3.7:

	°F	°C	K
A	57		
B		37	
C	-40		

7.
8. What is the average mass of three objects whose individual masses are 10.3 g, 9.334 g, and 9.25 g?

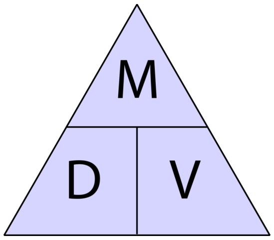
9. Complete the following calculation and report the answer with the correct number of significant figures: (1.68)(7.874)(1.0000/55.85).
10. Solve the following equation for n and report the answer with the correct number of significant figures: (11.2/760.0)(123.4) = n(0.0821)(298.3)

Further Reading / Supplemental Links

- Robinson, A. (2007). The Story of Measurement. New York: Thames and Hudson.
- Mass of snowflake approximation: http://hypertextbook.com/facts/2001/JudyMoy.shtml
- Uncertainty of Volumetric Glassware: http://www.wellesley.edu/Chemistry/Chem105manual/Appendices/uncertainty_volumetric.html
- Online Temperature Converter: http://www.onlineconversion.com/temperature.htm
- Lide, D. R. (Ed.). (1992-1993). CRC Handbook of Chemistry and Physics (73rd ed.). Boca Raton, Florida: CRC Press, Inc.

Points to Consider

- Compare and contrast the differences between a number and a measurement? What would be an example of a number and an example of a measurement?
- One way to remember the formula for density, as well as how to rearrange variables within the density equation is with the following formula triangle



- In this lesson we have seen that all measurements have an associated uncertainty. Yet, this does not imply there are flaws in the process of measurement. How might you explain to someone the concept of uncertainty, and how reconciling uncertainty in measurement actually makes the estimate more trustworthy, not less?

3.3 References

1. Zachary Wilson and Laura Guerin. CK-12 Foundation . CC BY-NC 3.0
2. Courtesy of NASA/SDO. http://commons.wikimedia.org/wiki/File:The_Sun_by_the_Atmospheric_Imaging_-Assembly_of_NASA%27s_Solar_Dynamics_Observatory_-_20100819.jpg . Public Domain
3. Christopher Auyeung. CK12 Foundation . CC BY-NC 3.0
4. Christopher Auyeung. CK12 Foundation . CC BY-NC 3.0
5. Laura Guerin. CK-12 Foundation . CC BY-NC 3.0
6. Christopher Auyeung. CK12 Foundation . CC BY-NC 3.0
7. Christopher Auyeung. CK-12 Foundation . CC BY-NC 3.0
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CHAPTER 4 Atomic Structure

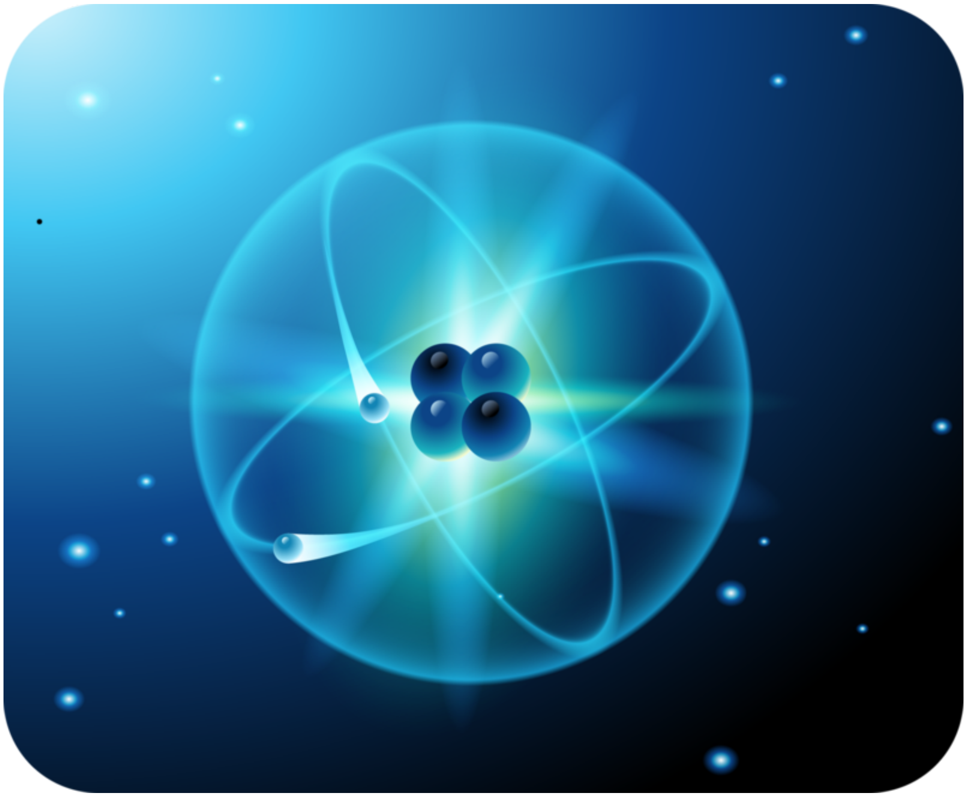
Chapter Outline

4.1 EVOLUTION OF THE ATOMIC MODEL

4.2 STRUCTURE OF THE ATOM

4.3 ISOTOPES AND ATOMIC MASS

4.4 REFERENCES



The concept of the atom was first proposed roughly two thousand years ago by the Greek philosopher Democritus. He argued that matter was finite and comprised of particles that are indivisible. Like all the philosophers of his time, Democritus based his argument on reason, not experimental data. In more recent years, the composition of matter has been studied further, and only within the last century was it determined that the atom is indeed divisible. Today, scientists believe that even some subatomic particles can theoretically be divided even further. The figure above illustrates our modern model of the atom. At the center is a nucleus containing protons and neutrons. Around the nucleus are much lighter particles called electrons. The atom is largely comprised of empty space. Can you think of how we might go about studying the behavior of matter at the atomic and subatomic level? How do you suppose we might study aspects of matter that cannot be directly observed? These are the questions that philosophers and scientists have pondered for millennia. We will address some of these questions as we attempt to further understand the particles that make up matter.

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4.1 Evolution of the Atomic Model

Lesson Objectives

- Describe the development of the concept of the atom from Democritus to the modern day.
- Compare and contrast the continuous and discontinuous theories of matter.
- State the law of conservation of mass, the law of definite proportions, and the law of multiple proportions.
- Summarize the five essential points of Dalton's atomic theory.
- Describe the relationship between Dalton's atomic theory and the law of conservation of mass, the law of definite proportions, and the law of multiple proportions.

Lesson Vocabulary

- **continuous theory of matter**: The concept that matter is continuous, infinite, and comes in every form all around us, and could be divided and subdivided into smaller and smaller pieces without limit.
- **discontinuous theory of matter**: The concept that matter is actually finite and not limitless.
- **atom**: Fundamental, indivisible particles that make up matter.
- **law of definite proportions**: States that chemical compounds always contain the same proportion of elements by mass, regardless of amount.
- **law of conservation of mass**: States that the mass of a reactant must equal the mass of the product for any chemical process.
- **law of multiple proportions**: States that if two elements form more than one compound between them, then the ratios of the masses of the second element that combine with a fixed mass of the first element will be ratios of small whole numbers.

Check Your Understanding

- What are the general properties of matter? For example, what are the properties of water that distinguish it from other substances?
- We widely accept that all matter is comprised of similar kinds of particles that are too small to detect with the unaided eye. We know that when a candle burns it gives off carbon dioxide and water vapor, but we cannot actually "see" these gases. How can we study something that we cannot directly see? Can you give an example?

Introduction

For centuries, humans have been fascinated with the behavior of matter. They have recognized that certain things, like candles, burn while other things, such as metals, do not readily burn. Humans have noticed that certain substances react with one another. For instance, iron will rust over time in the presence of air or water. Similarly, they have recognized that some matter is not visible, such as the air that we breathe, but it is still there. Early philosophers believed that matter was comprised of four fundamental substances: earth, air, fire, and water. These became known as elements. Later, philosophers postulated that all matter was comprised of a fundamental particle, the atom, which was indivisible. We now know that the atom is comprised of even smaller subatomic particles that display unique behaviors. In this chapter, we will look at how our understanding of the atom has evolved over time.

Discontinuous Theory of Matter

FIGURE 4.1

Aristotle and Plato.

Our understanding of matter today is much different than it was long ago. In 440 BC, Aristotle and Plato (**Figure** 4.1) proposed that matter was continuous, infinite, present in every form, and always all around us. It was thought that matter could be divided and subdivided into smaller and smaller pieces without limit. This concept was called the **continuous theory of matter**. One debate of the time revolved around how far a grain of sand could be divided. Most philosophers of the time believed that the sand could be sub-divided indefinitely. These were logical interpretations of their observations about the natural world.

In 400 BC, Democritus (**Figure** 4.2) proposed an alternate view, referred to as the **discontinuous theory of matter**. He expanded upon the work of Leucippus, a mentor of his, who believed matter was actually finite and not limitless. Democritus held that a grain of sand could only be divided a finite number of times. However, this idea was not well-received at the time. Aristotle, who was considered a greater "authority," taught against it and influenced other philosophers to reject the ideas of Democritus. It would be thousands of years before his ideas were revisited and found to be consistent with more recently available scientific evidence.

Democritus proposed that all matter is composed of fundamental, indivisible particles that he called **atoms**. The essential ideas behind his theory are the following:

1. Everything is composed of “atoms,” which are physically indivisible.
2. Atoms are indestructible and constantly in motion.
3. There is empty space between atoms.

Proust’s Law of Definite Proportions

The French scientist Joseph Louis Proust (1754-1826) studied chemical compounds and their mass proportions. Through his experiments, Proust found chemical compounds always contain the same proportion of elements by

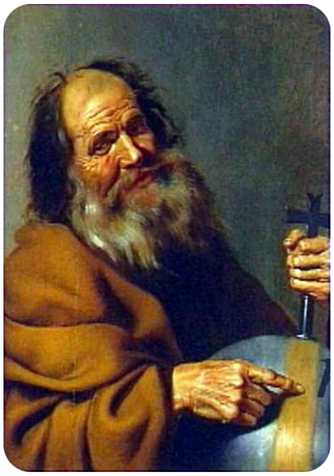


FIGURE 4.2

Democritus

mass, no matter the amount. Based off of this idea, Proust developed the **law of definite proportions** which was published in 1799. To illustrate this, suppose compound AB is made of element A and element B. Regardless of how much AB is present, the ratio between the mass of A and the mass of B will be the same for any sample. In other words, elements combine in fixed ratios based on their mass. Water, H_2O, is always 1/9 by mass hydrogen and 8/9 by mass oxygen, regardless of whether we are looking at one drop or an entire lake.

Lavoisier's Law of Conservation of Mass

At the same time, another French scientist named Antoine Lavoisier was studying mass relations in chemical reactions. He noticed that for an isolated system, the mass of the reactants must equal the mass of the products for any chemical process. This discovery was later called the **law of conservation of mass**. This law greatly influenced chemistry because it quantified gaseous chemical species, which were often viewed as "missing matter" that was not involved in chemical processes.

FIGURE 4.3

John Dalton

While it must be assumed that many more scientists, philosophers and others studied the composition of matter after Democritus, a major leap forward in our understanding of the composition of matter took place in the 1800s with the work of John Dalton (**Figure** 4.3). John Dalton, a school teacher from England, studied the weights of various elements and compounds. He noticed that matter always combined in fixed ratios based on weight (and volume, in the case of gases). Chemical compounds always contain the same proportion of elements by mass, regardless of amount, which provided further support for Proust's law of definite proportions. Dalton also observed that there was more than one mass ratio in which two elements could combine.

TABLE 4.1: Combining Ratios in Elements in Compounds

CO and CO_2	NO_3 and N_2O_3 NO_3 and N_2O_2
$FeCl_2$ and $FeCl_3$	N_2O_3 and N_2O_4

Notice in **Table** 4.1 that the elements combine in different but predictable ratios with other elements. Carbon can combine in a 1:1 ratio with oxygen to form carbon monoxide –a poisonous gas. Change the ratio to 1:2 carbon to oxygen, and you get carbon dioxide, which is a gas that we exhale. His work led to the development of the **law of multiple proportions**. This law states that if two elements form more than one compound between them, then the ratios of the masses of the second element that combine with a fixed mass of the first element will be ratios of small whole numbers.

Dalton's Atomic Theory (1804)

From his experiments and observations, as well as the work of contemporary scientists, Dalton proposed a new theory of the atom. This later became known as Dalton's atomic theory. The general tenets of this theory were as follows:

1. All matter is composed of extremely small particles called atoms.
2. Atoms of a given element are identical in size, mass, and other properties. Atoms of different elements differ in size, mass, and other properties.
3. Atoms cannot be subdivided, created, or destroyed.
4. Atoms of different elements can combine in simple whole number ratios to form chemical compounds.
5. In chemical reactions, atoms are combined, separated, or rearranged.

Dalton's atomic theory has been largely accepted by the scientific community, although a couple of modifications have been made since its conception. We know now that (1) an atom can be further sub-divided, and (2) not all atoms of an element have identical masses.

Lesson Summary

- Early Greek philosophers thought that matter could be divided and subdivided into smaller and smaller pieces without limit.
- In 400 BC, Democritus proposed that there was a point at which matter could no longer be divided any further. He suggested that all matter was composed of tiny indivisible particles, which he called atoms.
- Joseph Proust found that compounds always contain the same proportion of elements by mass, regardless of amount. This was later called the law of definite proportions.
- Antoine Lavoisier proposed the law of conservation of mass, which states that in a chemical reaction mass is not created nor destroyed.
- John Dalton discovered that certain combinations of elements could combine in multiple ratios. This was called the law of multiple proportions.
- In 1804, John Dalton proposed a modern atomic theory. This theory is still largely accepted by the scientific community, with a couple modifications.

Review Questions

1. Compare and contrast the continuous theory of matter with the discontinuous theory of matter.
2. Which of the following did Proust discover?
   a. Elements combine in unpredictable ratios with other elements.
   b. The mass of an element is always changing even when combined with another element.
   c. Chemical compounds always contain the same proportion of elements by mass, regardless of amount.
   d. Elements combine only in fixed ratios based on volume, but not mass.
3. Which of the following did Lavoisier discover?
   a. When matter reacts, there is a small portion that is lost and unaccounted for.
   b. For an isolated system, the mass of the reactants must equal the mass of the products.
   c. When matter reacts, there can be mass that comes from nowhere and is unaccounted for.
   d. Mass cannot be accurately accounted for in chemical processes.
4. What did John Dalton discover about chemical compounds? How did his theory differ from Proust's?
5. Summarize Dalton's atomic theory.
6. What were two points made by Dalton's atomic theory that are no longer considered correct?

Further Reading / Supplemental Links

- Kotz, John, and Heith Purcell. 1991. Chemistry Chemical Reactivity. Orlando, FL: Holt, Rinehart and Winston.
- Partington, J. R. 1989. A Short History of Chemistry. 3 ed. New York: Macmillan. Reissued by Dover Publications.

Points to Consider

- In this lesson, we discussed the early evolution of theories about the atom. More recent evidence has shown that the atom is comprised of subatomic particles that exhibit unique properties and affect the overall behavior of an atom. In our next lesson, we will look at subatomic particles, including how they were discovered and how they behave.

4.2 Structure of the Atom

Lesson Objectives

- Describe the properties of cathode rays that led to the discovery of the electron.
- Describe the experiment carried out by Rutherford and his co-workers that led to the discovery of the nucleus.
- List the properties of protons, neutrons, and electrons.
- Describe the properties of X-rays and how they were discovered.
- Describe the currently accepted model of the atom.

Lesson Vocabulary

- **electron**: A negatively charged particle that has a very small mass compared to the mass of other subatomic particles and surrounds the atom.
- **plum pudding model**: An experiment, led by J.J. Thomson, which proposed that the atom was comprised of negatively charged particles in a disperse field of positively charged particles.
- **radioactivity**: When certain substances emit charged particles.
- **gold foil experiment**: An experiment, led by Ernest Rutherford, which proposed that atoms consist of a small positively charged nucleus surrounded by negatively charged electrons.
- **proton**: A positively charged particle that has a relatively large mass compared to electrons. Protons can be found in the nucleus of the atom.
- **neutron**: An uncharged particle with a mass nearly equal to that of the proton. Neutrons can be found in the nucleus of the atom.

Check Your Understanding

- Describe Dalton's atomic theory.
- List two changes that were made to Dalton's theory based on more recent evidence.

Introduction

After the development of Dalton's atomic theory, several important discoveries were made that led to a new understanding of the atom. A number of experiments revealed that the atom is comprised of subatomic particles called electrons, neutrons, and protons. Most of the atom's mass is concentrated in a central nucleus, which contains protons and neutrons. The nucleus is surrounded by much less massive electrons, which account for most of the volume occupied by the atom. The electron was the first subatomic particle to be discovered, followed by discoveries of the nucleus, the proton, and the neutron. In this lesson, we are going to study these important discoveries and how they led to our current understanding of the atom.

Discovery of Cathode Rays

In 1877, William Crookes (1832-1919) was studying how electrical current behaves in a vacuum tube. In one experiment, he passed an electric current through an evacuated phosphorous-coated glass cylinder with an object in the center, as shown in **Figure** 4.4.

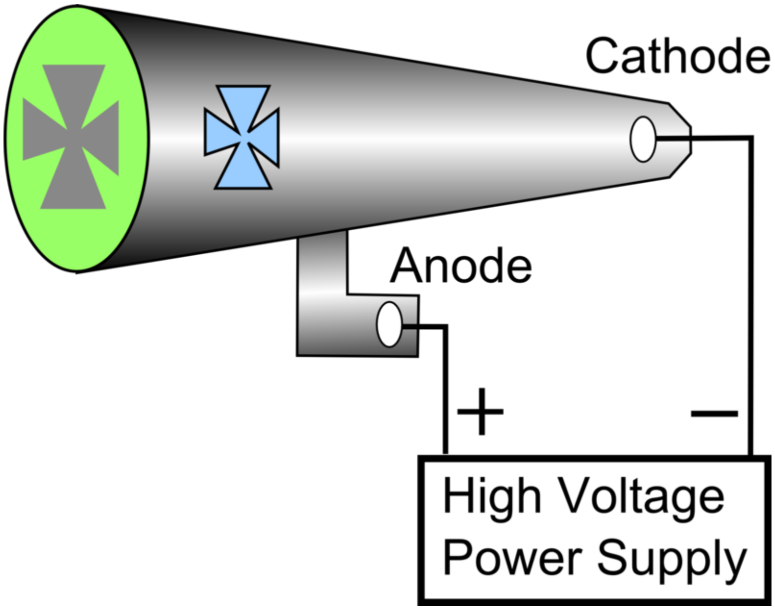
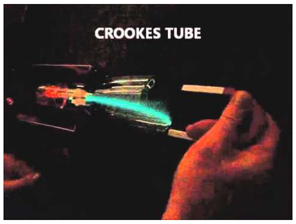


FIGURE 4.4
Diagram of Crookes tube.

Upon passing a current through the tube, Crookes noticed that a "shadow" was cast by the object in the tube. The phosphorus on the terminal end of the tube became brightly fluorescent, except for the region directly behind the central object. He interpreted this to mean that the electrical current was blocked by the object. He reasoned that the electrical current, which he later called cathode rays, was composed of streams of particles. Crookes's work was later expanded upon by several other scientists. One scientist in particular, J. J. Thomson, was able to show that cathode rays could be deflected by a magnetic field, as shown in the following video: http://www.youtube.com/watch?v=M1REuKMeI34 (0:58).



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Thomson's interpretation of this effect was that cathode rays must consist of charged particles that have mass. Thomson presented his work in 1897, where he referred to these negatively charged particles as corpuscles. Later on, this name was changed and negatively charged particles became known as **electrons**. Thomson revised the model of the atom into what became known as the **plum pudding model**. He hypothesized that the atom was comprised of negatively charged particles in a field of positive charge (positively charged particles had not yet been discovered). This proposed arrangement was compared to the arrangement of plums in plum pudding, as illustrated in **Figure** 4.5.

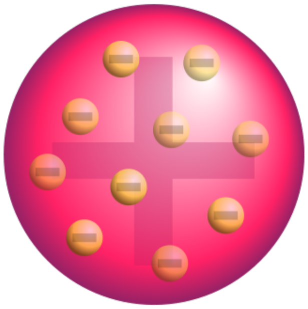


FIGURE 4.5

Plum pudding model of the atom.

The Charge of the Electron

In 1909, Robert Millikan and Harvey Fletcher devised what is known as the oil drop experiment to determine the charge of a single electron. The oil drop experiment consisted of an apparatus in which small, charged oil drops were passed through an electric field. The electric field was created by two oppositely charged parallel metal plates. The rate at which the oil drops fell through the field was used to determine the magnitude of the charge of an electron.

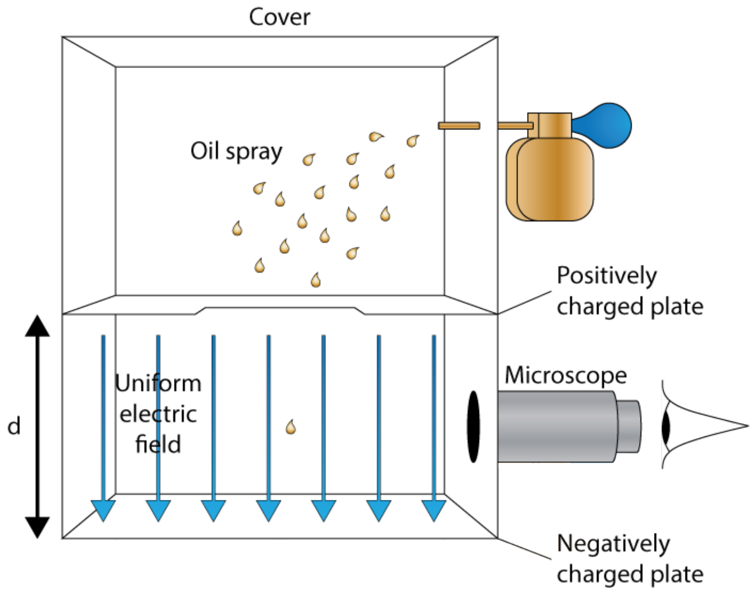
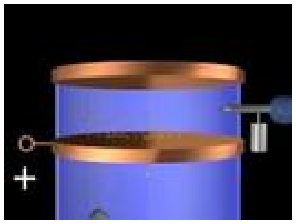


FIGURE 4.6

Millikan's oil drop experiment.

The following video illustrates this experiment and explains how the charge of an electron was determined: http://www.youtube.com/watch?v=XMfYHag7Liw (1:14).



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Using this information, Millikan calculated the charge of an electron to be 1.5924×10^{-19} coulombs. A coulomb (C) is the SI unit for electric charge, where 1 coulomb = 1 ampere × 1 second. (Remember, an ampere is an SI base unit for electric current.) Today, the accepted value for the charge of an electron is $1.602176487 \times 10^{-19}$ C. Despite the relatively simple apparatus with which it was determined, Millikan's value was within 1% of the currently accepted value. Combining this value with information from J. J. Thomson's experiments, Millikan was also able to calculate the mass of an electron. The currently accepted value is $9.10938215 \times 10^{-31}$ kg.

Discovery of the X-ray

Right around the time that Thomson was formulating his model of the atom, a scientist named Wilhelm Conrad Roentgen was studying the behavior of electricity in discharge tubes. These were partially evacuated gas-filled tubes which would conduct an electric current, similar to the Crookes tube used in the cathode ray experiments. He devised an experiment in which he covered a discharge tube with black cardboard, and several feet away, he placed a sheet of paper that had been chemically treated with a compound called barium-platinum cyanide. When he applied voltage to the discharge tube, he noticed the screen several feet away became fluorescent, emitting light. This was peculiar, because the tube had been completely covered by material that would block the escape of any cathode rays. Roentgen continued to explore this phenomenon. He moved the screen further away, he turned the screen around, and he placed objects between the screen and the discharge tube. In all cases, the screen still fluoresced when the discharge tube was turned on. Then Roentgen had his wife place her hand atop a photographic plate, and the rays were shone towards the plate. After developing the plate, he observed an image of his wife's hand that "showed the shadows thrown by the bones of her hand and that of a ring she was wearing" (Wilhelm Conrad Roentgen - Biography). **Figure** 4.7 is an image of what he saw.

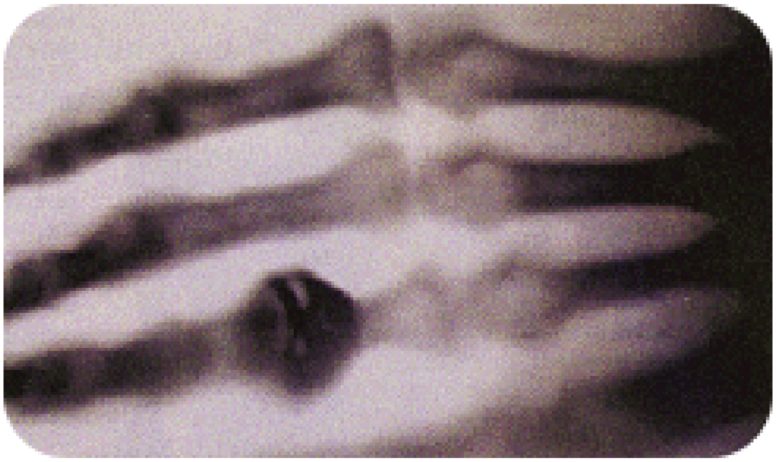


FIGURE 4.7

The skeleton of Roentgen's wife's hand, as captured on the photographic plate. What do you think the dark spot in the picture might be caused by?

This was the first "roentgenogram" ever taken. He interpreted this to mean that another ray, other than the cathode rays, was being produced that could penetrate and travel through objects at a distance. He called these X-rays, and he received the Nobel Prize in Physics in 1901 for his brilliant work. Modern day X-rays that one might receive for a medical exam operate on the same principles that Roentgen discovered. Several major discoveries followed shortly after Roentgen's discovery of X-rays. Just two months later, in 1896, **radioactivity** was discovered by a Frenchman named Henri Becquerel. Becquerel discovered that certain substances, like uranium salts, emit charged particles. Following this work, Marie and Pierre Curie began to study the behavior of various radioactive substances in 1897. In fact, Madame Curie coined the word "radioactivity." Their work resulted in the discovery of mass changes in radioactive elements, which later became known as radioactive decay. They also identified two new radioactive elements, which later became known as polonium and radium. The Curies were awarded the Nobel Prize in Physics in 1903 for their work. Marie Curie later won a Nobel Prize in Chemistry (1911) for her contributions to our understanding of radioactivity. We will study radioactivity further in the chapter *Nuclear Chemistry*.

Discovery of the Nucleus

FIGURE 4.8

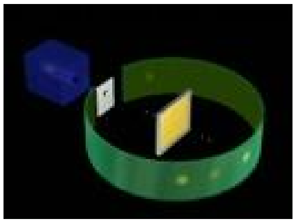
Ernest Rutherford (1871-1937).

By 1900, it was known that the electron carried a negative charge. It was also known that the electron makes up an extremely small fraction of the mass of an atom. Ernest Rutherford set out to determine how the remainder of the mass and charge was distributed in the atom. Rutherford was a physicist from New Zealand who was working under the direction of J. J. Thomson. He conducted several experiments on the radioactive properties of uranium. He discovered that uranium released two different types of particles, which he referred to as alpha (α) particles, which were positively charged, and beta (β) particles, which were negatively charged. It was later shown that beta particles were simply free electrons.

Gold Foil Experiment

One of Rutherford's famous experiments was called the **gold foil experiment** (illustrated in the **Figure** 4.9). In this experiment, Rutherford used a radioactive source to direct alpha particles toward a very thin sheet of gold foil. Surrounding the foil was a screen that fluoresced when struck by the alpha particles.

Here is a short video of his experiment: http://www.youtube.com/watch?v=5pZj0u_XMbc (0:47).



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As shown in the video, most alpha particles easily passed through the gold foil and struck the fluorescent screen behind the foil. However, there were some instances in which the alpha particles were deflected very strongly, often back toward the emission source. If the plum pudding model were correct, all of the alpha particles would be expected to pass through the gold foil with little or no deflection. The strong deflection experienced by a small

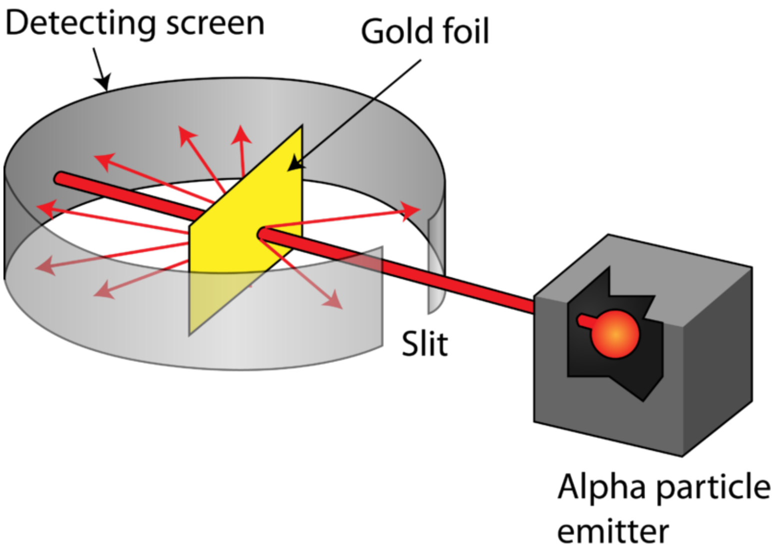


FIGURE 4.9
Rutherford's gold foil experiment.

portion of the alpha particles could be better explained by an atom that contained a very small, dense **nucleus**. Because some of the alpha particles emitted from the source were repelled by the nucleus, Rutherford concluded that the nucleus must be made up of these positively charged alpha particles, which he named **protons**. He proposed that atoms consist of a small, positively charged nucleus surrounded by negatively charged electrons, as shown in the **Figure** 4.10.

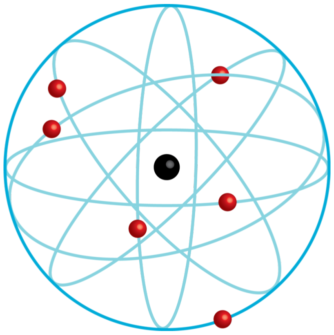


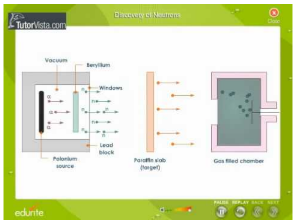
FIGURE 4.10
Rutherford's atomic model.

Bohr's Atomic Model

In 1913, shortly after Rutherford's work on the nucleus, Neils Bohr proposed what became known as a planetary model of the atom. Bohr's model was based upon the work done by Max Planck and Albert Einstein, who at the time were studying quantum theory which looks at the energy associated with matter. The planetary model was useful for relating atomic structure to the wavelengths of light that an element emits when heated. Bohr's model, as well as the work of Planck and Einstein, will be discussed in the chapter *Electrons in Atoms*.

Discovery of the Neutron (1932)

In 1932, James Chadwick discovered the neutron. Chadwick was an English physicist who was mentored by Rutherford. His experiment consisted of bombarding beryllium atoms with alpha particles through a paraffin wax target and studying the effects. From his analysis, he concluded that the nucleus also contains a particle which has equal mass to the proton, but unlike the proton, is electrically neutral - hence the name **neutron**. Here is a short video clip describing Chadwick's experiment: http://www.youtube.com/watch?v=HnmEI94URK8 (2:14).



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Chadwick's work resulted in a new understanding of the nucleus of the atom; it is comprised of both protons and neutrons. Because the masses of subatomic particles are so small, a new unit, called an atomic mass unit (amu), was defined. Protons and neutrons each have a mass of approximately one amu. The **Table** 4.2 describes the characteristics of the three subatomic particles we have discussed.

TABLE 4.2: Characteristics of Subatomic Particles

Particle	Charge (C)	Mass (kg)	Mass (amu)	Location
proton	$+1.6022 \times 10^{-19}$	1.67262×10^{-27}	1.0073 (~1)	nucleus
electron (e^-)	-1.6022×10^{-19}	9.10938×10^{-31}	5.4858×10^{-4} (~0)	outside nucleus
neutron	0	1.67493×10^{-27}	1.0087 (~1)	nucleus

Lesson Summary

- Experiments conducted during the early twentieth century revealed that the atom is comprised of subatomic particles called electrons, neutrons, and protons.
- In 1877, William Crookes discovered cathode rays, which later became known as electrons. Crookes discovered these rays using an apparatus he developed called the Crookes tube or cathode-ray tube.
- Electrons, which were initially called cathode rays, are negatively charged and have a very small mass compared to the masses of other subatomic particles.
- In 1895, Wilhelm Conrad Roentgen discovered X-rays.
- In 1897, J. J. Thomson showed that cathode rays are deflected in a magnetic field and proposed that cathode rays are streams of negatively charged particles. Thomson proposed the plum-pudding model of the atom. This model described the atom as a disperse field of positive charge containing small negatively charged particles.
- In 1909, the magnitude of the charge carried by an electron was determined by Robert Millikan in an experiment known as the oil drop experiment. Information from this experiment was later used to also calculate the mass of an electron.
- In 1919, Rutherford discovered the presence of a positively charged nucleus with his famous gold foil experiment.
- Rutherford proposed a new atomic model that described the atom as comprised of a positively charged nucleus surrounded by negatively charged electrons. In this model, most of the atom was thought to be empty space.*Protons are positively charged and have a relatively large mass compared to electrons. Protons can be found in the nucleus of the atom.
- In 1932, Chadwick discovered the neutron, a particle with a mass similar to that of the proton but without any electrical charge.
- Neutrons are particles with a mass similar to that of the proton, but they have no electrical charge. Neutrons also reside in the nucleus.

Review Questions

1. What id Crookes discover in his cathode ray tube experiments?
2. Describe the atom using Thomson's plum pudding model. Draw a picture of this model.
3. How did Millikan set up his oil drop experiment?
4. Describe how Roentgen took his first x-ray.
5. How did Rutherford's gold foil experiment contradict the plum pudding model of the atom?
6. What is the modern view of the nucleus and its composition?
7. Sketch a modern view of the atom indicating the locations of protons, neutrons, and electrons.
8. List the properties of electrons, neutrons, and protons.

Further Reading / Supplemental Links

- The History of the Discovery of Radiation and Radioactivity: http://mightylib.mit.edu/Course%20Materials/22.01/Fall%202001/discovery%20of%20radiation.pdf
- Biography of Wilhelm Conrad Rontgen: http://www.nobelprize.org/nobel_prizes/physics/laureates/1901/rontgen-bio.html
- Radioactivity: http://hyperphysics.phy-astr.gsu.edu/hbase/nuclear/radact.html
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- Kotz, John, and Heith Purcell. 1991. Chemistry Chemical Reactivity. Orlando, FL: Holt, Rinehart and Winston.
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Points to Consider

- In this lesson we learned that neutrons and protons in the nucleus have similar mass. How might we measure the amount of mass contained in different elements?

4.3 Isotopes and Atomic Mass

Lesson Objectives

- Explain the workings of a mass spectrometer and describe how this device is used to determine average atomic mass.
- Define atomic number and mass number.
- Define isotope.

Lesson Vocabulary

- **atomic number**: The number of protons in the nucleus of each atom of an element.
- **mass number**: The total number of protons and neutrons in an atom.
- **A-Z notation**: The shorthand notation of the composition of any atom using the atomic number (Z) and the mass number (A).
- **isotopes**: Atoms that have the same atomic number but different mass numbers due to a difference in the number of neutrons.
- **mass spectrometer**: An instrument that determines the masses of atoms, molecules, and molecular fragments.
- **percent abundance**: The percentage of atoms of a particular isotope in a naturally occurring sample of the pure element.
- **atomic mass**: The weighted average of the atomic masses of the naturally occurring isotopes of an element.

Check Your Understanding

- Describe the composition of an atom.
- What are the three subatomic particles and what are their properties?

Introduction

Atoms are the fundamental building blocks of all matter and are composed of protons, neutrons, and electrons. Because atoms are electrically neutral, the number of positively charged protons must be equal to the number of negatively charged electrons. One of Dalton's points in his atomic theory was that all atoms of a given element are identical in mass. In this section, we will see how this is not strictly true, due to variability in the number of neutrons that an atom may contain.

Atomic Number

The **atomic number** of an element is the number of protons in the nucleus of each atom of that element. An atom can be classified as a particular element based solely on its atomic number. For example, any atom with an atomic number of 8 (its nucleus contains 8 protons) is an oxygen atom, and any atom with a different number of protons would be a different element. The periodic table (**Figure** 4.11) displays all of the known elements and is arranged in order of increasing atomic number. In this table, an element's atomic number is indicated above the elemental symbol. Hydrogen, at the upper left of the table, has an atomic number of 1. Every hydrogen atom has one proton in its nucleus. Next on the table is helium, whose atoms have two protons in the nucleus. Lithium atoms have three protons, beryllium atoms have four, and so on. Since atoms are neutral, the number of electrons in an atom is equal to the number of protons. Therefore, hydrogen atoms all have one electron occupying the space outside of the nucleus.

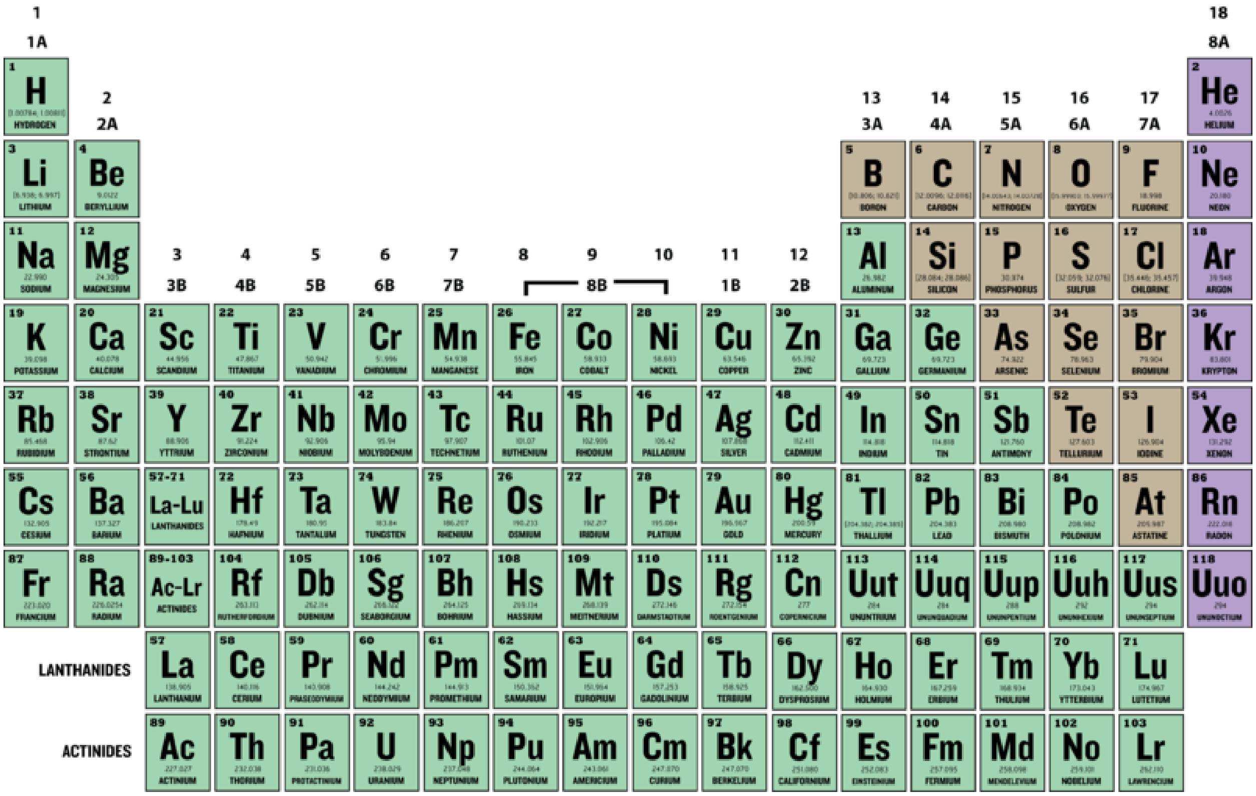

FIGURE 4.11

The periodic table of the elements.

Mass Number

Rutherford's experiment showed that the vast majority of the mass of an atom is concentrated in its nucleus, which is composed of protons and neutrons. The mass of an electron is very small compared to the mass of a neutron or proton, so the electrons in an element do not contribute much to the total mass. The **mass number** is defined as the total number of protons and neutrons in an atom. Remember that both protons and neutrons have a mass of approximately 1 amu. Knowing the mass number and the atomic number of an atom therefore allows you to determine the number of neutrons present in that atom by subtraction:

Number of neutrons = mass number - atomic number

The composition of any atom can be illustrated with a shorthand notation, sometimes called **A-Z notation**, using the atomic number (Z) and the mass number (A). The general form for this notation is as follows:

$^{A}_{Z}\mathrm{X}$

For example, a chromium atom that has 24 protons and 28 electrons could be written as:

$^{52}_{24}\mathrm{Cr}$

Another way to refer to a specific atom is to write the mass number of the atom after the name, separated by a hyphen. The above atom would be written as chromium-52.

Isotopes

As stated earlier, not all atoms of a given element are identical. Specifically, the number of neutrons in the nucleus can vary for many elements. As an example, naturally occurring carbon exists in three forms, which are illustrated in **Figure** 4.12.

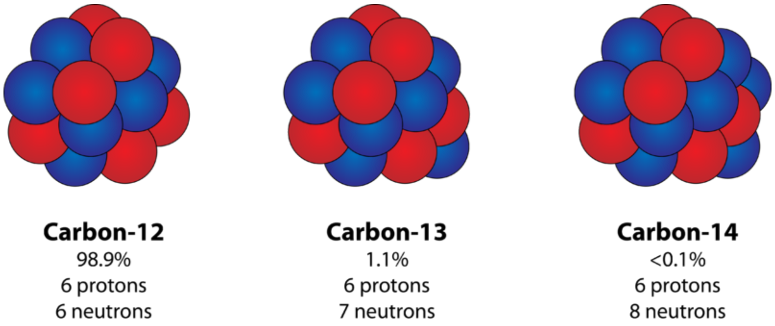

FIGURE 4.12

Nuclei of the three isotopes of carbon: Almost 99% of naturally occurring carbon is carbon-12, whose nucleus consists of six protons and six neutrons. Carbon-13 and carbon-14, with seven or eight neutrons, respectively, have a much lower natural abundance.

Each carbon atom has the same number of protons (6), which is equal to its atomic number. Each carbon atom also contains six electrons, allowing the atom to remain electrically neutral. However the number of neutrons varies from six to eight. **Isotopes** are atoms that have the same atomic number but different mass numbers due to a change in the number of neutrons. The three isotopes of carbon can be referred to as carbon-12 ($^{12}_{6}\mathrm{C}$), carbon-13 ($^{13}_{6}\mathrm{C}$), and carbon-14 ($^{14}_{6}\mathrm{C}$). Naturally occurring samples of most elements are mixtures of isotopes. Carbon has only three natural isotopes, but some heavier elements have many more. Tin has ten stable isotopes, which is the most of any element. While the presence of isotopes affects the mass of an atom, it does not affect its chemical reactivity. Chemical behavior is governed by the number of electrons and the number of protons. Carbon-13 behaves chemically in exactly the same way as the more plentiful carbon-12.

Example 4.1

Silver has two known isotopes, one with 60 neutrons and the other with 62 neutrons. What are the mass numbers and symbols of these isotopes?

Atomic Mass and the Mass Spectrometer

Beginning in the early part of the twentieth century, scientists were approaching a new understanding of the composition of the atom. Several major discoveries demonstrated that the atom contained a nucleus, where protons and neutrons are situated. It was discovered that electrons surrounded the nucleus and it was later determined that electrons primarily determine the chemical properties of elements. Several devices were created during this time which demystified the inner workings of the atom and the composition of elements. One such device was the **mass spectrometer**, which was developed in 1918 by Arthur Jeffrey Dempster. The mass spectrometer is an instrument for determining the masses of atoms, molecules, and molecular fragments. The **Figure** 4.13 illustrates a modern mass spectrometer.

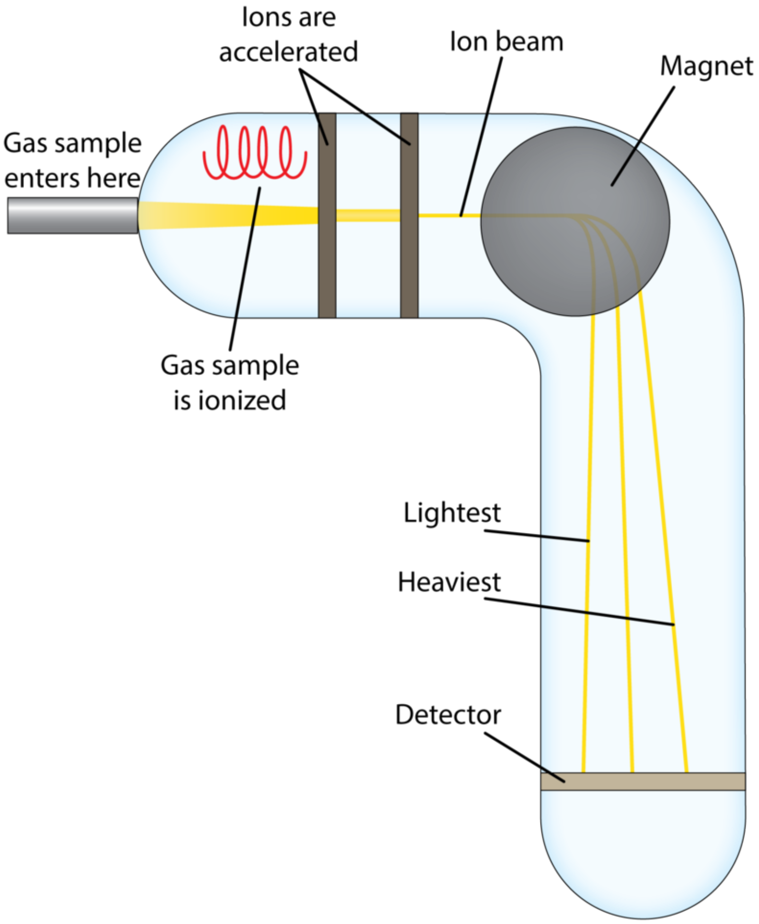

FIGURE 4.13

An electron is removed from an atom to yield a positive ion (such as H^+, O^+, or N^+). The ions are then accelerated and deflected by a magnetic field. The degree of deflection directly relates to the mass of the ion: the lighter the ion, the greater the deflection and the heavier the ion, the lesser the deflection. The beam of ions is then detected and the relative abundance of each isotope of an element can then be determined.

If we were to place a sample of carbon into a mass spectrometer and analyze its mass, we would find that some of the carbon atoms have a relative mass of 12, while other atoms have a relative mass of 13, and still others have a relative mass of 14. The mass spectrometer measures the **percent abundance** of these carbon isotopes. Percent abundance is the percentage of atoms in a naturally occurring sample of the pure element that are a particular isotope. We can represent the percent abundance of carbon with what is known as a mass spectrogram, shown in the **Figure** 4.14.

The spectrogram reveals the percent abundances of the variants of carbon atoms consists of 98.9% ^{12}C, 1.1% ^{13}C, and «0.1% ^{14}C. Because we generally deal with very large amounts of atoms, it is more practically useful to know the average mass of each atom in a large sample as determined by the percent abundance of each isotope. The **atomic mass** of an element is the weighted average of the atomic masses of the naturally occurring isotopes of that

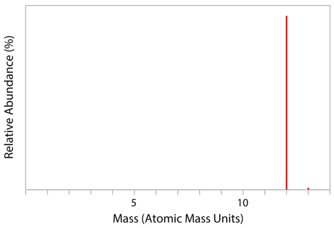

FIGURE 4.14

Mass spectrogram for carbon.

element.

Example 4.2

Using the percent abundances for each carbon isotope as given above, calculate the weighted average for the atomic mass of carbon.

Answer:

We calculate average atomic mass by taking the percent abundance of each isotope and multiplying this by the atomic mass of the isotope.

^{12}C

$0.989 \times 12 = 11.868$

^{13}C

$0.011 \times 13 = 0.143$

Then, add these values together to get the relative atomic mass:

$11.868 + 0.143 = 12.011$

Therefore, the average atomic mass of carbon is calculated to be 12.011. This is the same number that is listed on the periodic table.

Lesson Summary

- The atomic number (Z) of an element is equal to the number of protons in its nucleus.
- The mass number (A) of an element is equal to the sum of the protons and the neutrons in its nucleus.
- Isotopes are atoms of the same element that have a different mass number (A) but the same atomic number (Z).
- Isotopes have the same number of protons and electrons, but a different number of neutrons.
- The mass spectrometer measures the percent abundance of different isotopes in a given sample.
- The average atomic mass of an element can be calculated from the atomic mass and percent abundance of each naturally occurring isotope.

Review Questions

1. Describe in general terms how a mass spectrometer functions.
2. Complete **Table** 4.3:

TABLE 4.3: practice

	^{1}H	^{2}H	^{3}H	^{23}Na	^{35}Cl	^{14}C	^{12}C
protons							
electrons							
neutrons							

3. What is the mass number of a tin atom that has 69 neutrons? Write its full symbol.
4. How many neutrons are there in an atom of platinum with a mass number of 195?
5. What is the mass number of a copper atom with 34 neutrons?
6. How many protons, neutrons, and electrons are there in a $^{59}_{28}$Ni atom?
7. Silicon has three isotopes with 14, 15, and 16 neutrons, respectively. What are the mass numbers and symbols of these three isotopes?
8. A natural sample of boron consists of two isotopes. One has an exact mass of 10.0129 amu and its percent abundance is 19.91. The other isotope, of mass 11.0093 amu, has a percent abundance of 80.09. Calculate the average atomic mass.

Further Reading / Supplemental Links

- The History of the Discovery of Radiation and Radioactivity: http://mightylib.mit.edu/Course%20Materials/22.01/Fall%202001/discovery%20of%20radiation.pdf
- Two amazing X-ray stories: http://www.faltublog.com/2011/09/23/the-worlds-2-most-shocking-x-ray-stories/
- Biography of Wilhelm Conrad Roentgen: http://www.nobelprize.org/nobel_prizes/physics/laureates/1901/rontgen-bio.html
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Points to Consider

- In this chapter, we discussed the structure of the atom and saw that it contains a nucleus that consists of protons and neutrons. The nucleus is surrounded by negatively charged particles called electrons. How do you think electrons might be arranged around the nucleus?

4.4 References

1. Raphael. http://commons.wikimedia.org/wiki/File:Sanzio_01_Plato_Aristotle.jpg . Public Domain
2. Hendrick Bloemaert. http://commons.wikimedia.org/wiki/File:Hendrick_Bloemaert_Democritus.jpg . Public Domain
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CHAPTER 5 Electrons in Atoms

Chapter Outline

5.1 PROPERTIES OF LIGHT

5.2 THE BOHR AND QUANTUM MECHANICAL MODELS OF THE ATOM

5.3 ELECTRON ARRANGEMENT IN ATOMS

5.4 REFERENCES

Light has always intrigued humans. Whether it was the light from the sun or the light from a fire, we have used light and made light when none was naturally available. The interaction of light with different materials has long been studied. Research by scientists in the late nineteenth century led to an intriguing discovery. Light, under the right conditions, creates a small voltage (ejects electrons) when shined on certain metals. Einstein eventually explained this photoelectric effect, adding to our essential understanding of the nature of light. This discovery formed the foundation for a technology which later became known as photovoltaic cells. Photovoltaic cells are the materials found in the solar panels shown in the figure above. The solar panels shown here can generate enough electricity throughout the day to power 5 average American homes (assuming an average monthly energy use of about ~1000 kWh). Photovoltaic cells have become quite affordable and are now a reasonable alternative for electricity generation.

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5.1 Properties of Light

Lesson Objectives

- Describe the mathematical relationship between the speed, wavelength, and frequency of electromagnetic radiation.
- Describe the experiments that led to the discovery of the photoelectric effect and how the results were used to further inform our understanding of electrons and light.

Lesson Vocabulary

- **light**: A form of energy that behaves both as a particle and a wave.
- **frequency**: Inversely proportional to wavelength. Photons with high frequency light have more energy than photons with low frequency light (Zukav 1979).
- **wavelength**: The distance between two crests of a wave of light. The color of light is related to its wavelength. This is inversely proportional to frequency.
- **photoelectric effect**: Occurs when same types of electromagnetic radiation are shined on certain kinds of matter.
- **photon**: A description of light as particles.

Check Your Understanding

- What are the general properties of light?
- Are there substances whose color varies with changes in the environment or natural surroundings?

The Nature of Electromagnetic Radiation

Many kinds of waves exist, such as sound waves and water waves. Visible **light** is also a wave. It is a specific type of a more general phenomenon called an electromagnetic wave. All waves can be described in terms of the basic physical properties **frequency** and **wavelength**. These two properties are related to the speed of a wave by the following equation:

$$\text{speed} = \lambda\nu$$

where λ is the wavelength (usually expressed in meters) and ν is the frequency (expressed in Hertz, where 1 Hz = 1 s^{-1}). All electromagnetic waves travel at a speed of 2.998×10^8 meters/second (about 186,000 miles per hour), which is known as the speed of light. We commonly abbreviate the speed of light as c when used in equations. In the case of electromagnetic radiation, this equation becomes the following:

$c = \lambda\nu$

If c is expressed in meters per second, the wavelength must be expressed in meters.

Example 5.1

The brilliant red colors seen in fireworks are due to the emission of light from strontium salts such as $Sr(NO_3)_2$ and $SrCO_3$. Calculate the frequency in Hz of red light with a wavelength of 6.50×10^2 nm.

Answer:

$\lambda\nu = c$
$\nu = c/\lambda = (2.998 \times 10^8 \text{ m/sec})/(6.5 \times 10^{-7} \text{ m}) = 4.61 \times 10^{14} \text{ sec}^{-1} = 4.61 \times 10^{14}$ Hz

Electromagnetism

Much of our understanding of the light and the way it behaves is based on the work of Michael Faraday, James Maxwell, and Heinrich Hertz. In 1845, the English chemist and physicist Michael Faraday (1791–1867) discovered that light exhibited magnetic properties. His early experiments measured what happened to light when passed through magnetic fields. Following Faraday's work, the Scottish physicist and mathematician James Maxwell (1831–1879) studied electromagnetic radiation and light. Maxwell calculated the speed of light, which was later confirmed by other scientists to be the very value Maxwell proposed. From his work, Maxwell inferred that light was probably a transverse electromagnetic wave (**Figure** 5.1). He published this conclusion in 1873.

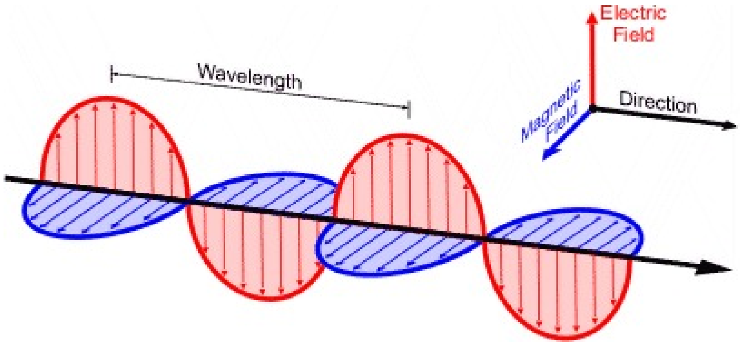


FIGURE 5.1

The image shows light as a transverse wave. It consists of oscillating magnetic and electric fields that are perpendicular to each other and to the direction in which the light is traveling.

The Electromagnetic Spectrum

In 1888, shortly after Maxwell published his findings, German physicist Heinrich Hertz (1857–1894) confirmed Maxwell's inference, showing that light was indeed an electromagnetic wave. Hertz extended Maxwell's work and produced electromagnetic radiation with wavelengths that were not in the visible part of the spectrum. In fact, visible light makes up only a very small part of the entire electromagnetic spectrum (**Figure** 5.2).

Example 5.2

Which type of light has a longer wavelength: red or blue?

Answer:

*As is shown in **Figure** 5.2, red light has longer wavelength than blue light. It is to the left of blue light in the diagram.*

Example 5.3

Based on what is displayed in the figure above, what is the relationship between wavelength and frequency?

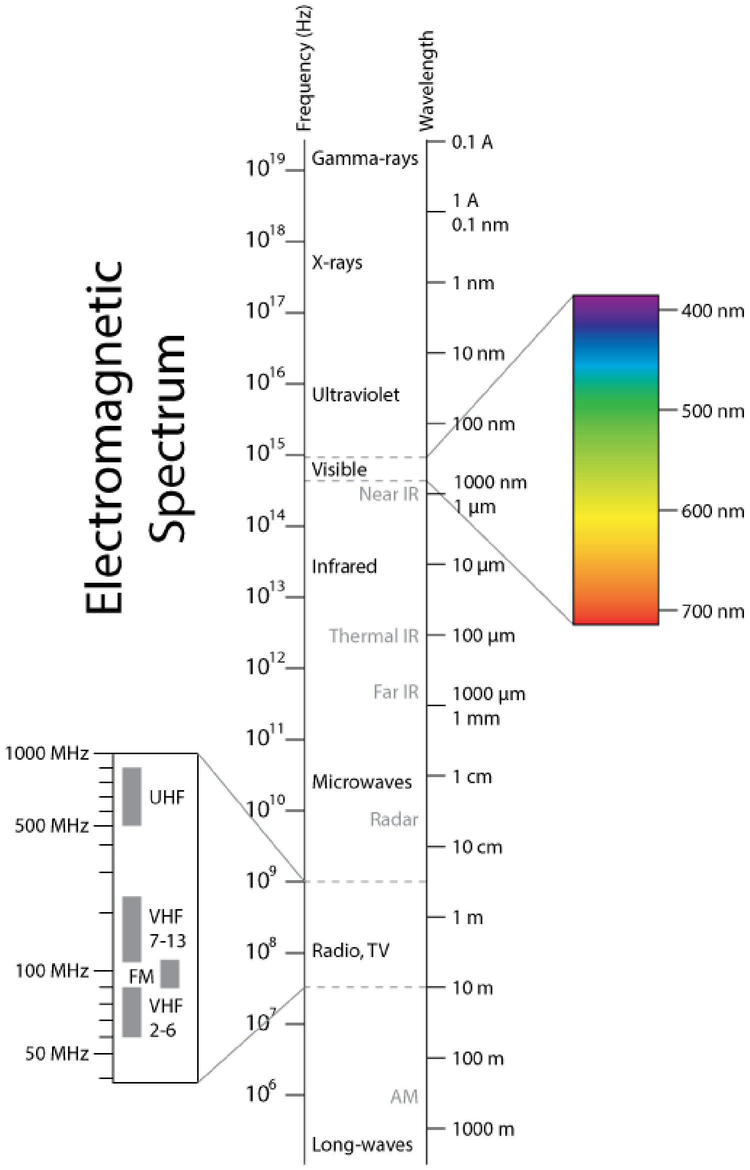


FIGURE 5.2

In this figure we see the electromagnetic spectrum. Each form represented on the spectrum has a unique range of wavelengths and frequencies. For example, all visible light has wavelengths that range between ~400 nm to 700 nm.

Answer:

Wavelength is inversely proportional to frequency. As wavelength increases, frequency decreases. As wavelength decreases, frequency increases.

Photoelectric Effect

Under the right conditions, light can be used to eject electrons from a solid material. This phenomenon, known as the **photoelectric effect**, occurs when some types of electromagnetic radiation are shined on certain kinds of matter. **Figure** 5.3 shows light rays of a specific wavelength striking a metal object and causing electrons, or photoelectrons, to be ejected from the surface.

The photoelectric effect was explored by many scientists in the 1800s. It involves the same fundamental principle by

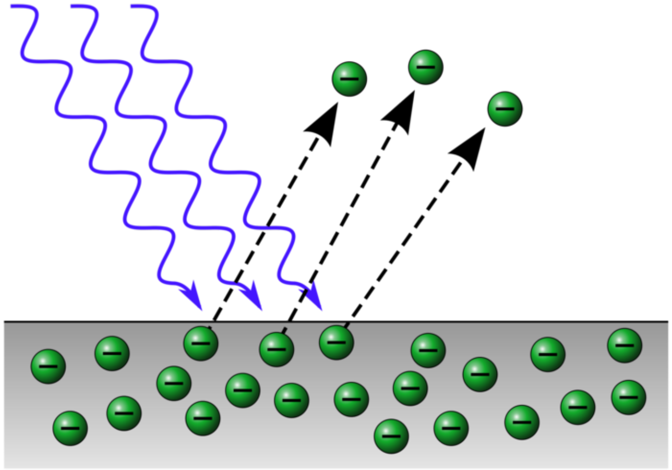


FIGURE 5.3

Photoelectric effect.

which modern-day solar cells operate. Whether electrons will be released depends on two factors: the wavelength of the light source and the material onto which the light is being shined. Here is a video of a simple photoelectric experiment: http://www.youtube.com/watch?v=WO38qVDGgqw (0:26).

MEDIA

Click image to the left for more content.

Light Exhibits Particle Behavior

Further study of the photoelectric effect revealed some perplexing behavior that could not be explained by the classical view of light as just a wave phenomenon. For example, the intensity of the light did not effect the amount of energy possessed by the ejected photoelectrons. Photoelectrons emitted with the use of a very bright light had the same energy as those emitted with the use of a dim light of the same frequency. However, a relationship was observed between the number of photoelectrons ejected and the intensity of the light source. It was found that the brighter the light sources, the more photoelectrons were ejected. Another puzzling aspect of the photoelectric effect was that a minimum frequency of light was required in order to eject any electrons at all, regardless of how intense the light source was.

Albert Einstein (1879–1955) studied this effect further, and in 1905, he postulated that light can also be thought of in terms of particles, now called **photons**. Photons of high frequency light have more energy than the photons of low frequency light (Zukav 1979), which explained why a minimum frequency was required for electrons to be ejected by a given light source. **Figure** 5.4 illustrates this effect.

Materials that eject electrons when illuminated with light, such as potassium, are called photoemissive. Not all materials are photoemissive, nor are all light sources capable of initiating electron emission from a given substance. For example, in **Figure** 5.4, we see that 700 nm light will not initiate electron ejection, while 550 nm light will.

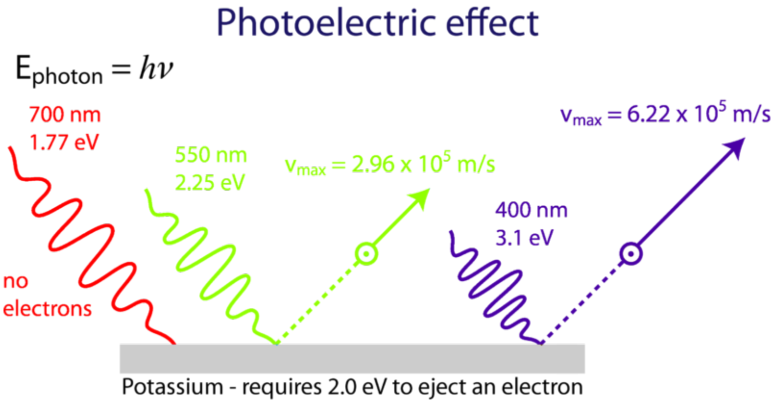


FIGURE 5.4
Wavelength of Light and Photoelectric Effect

Lesson Summary

- Light behaves both as a particle and as a wave.
- Michael Faraday discovered that light exhibited magnetic properties.
- James Maxwell demonstrated that the speed of light is constant and that light exists as a transverse wave.
- Hertz showed that light was an electromagnetic wave and only one type of electromagnetic radiation in a much larger electromagnetic spectrum.
- The color of light is related to its wavelength, which is the distance between two crests of a wave of light.
- The photoelectric effect occurs when sufficiently energetic electromagnetic radiation is shined on certain kinds of matter, causing electrons to be ejected.
- The photoelectric effect provides an example of light acting as a particle instead of a wave.

Review Questions

FIGURE 5.5
Left: Radio antenna. Right: Longwave (CB radio) antenna

1. What type of electromagnetic radiation (what wavelength) do you suppose the antenna on each of these vehicles shown in the **Figure** 5.5 is designed to receive?
2. Black lights are used for a variety of applications, including sterilization of materials. Why do you suppose the light is called "black light"? Are there other forms of black light?
3. The laser in an audio compact disc player uses light with a frequency of 3.844×10^{14} Hz. Calculate the wavelength of this light in nm.

4. An FM radio station broadcasts at 99.5 MHz. Calculate the wavelength in meters of the corresponding radio waves.
5. Microwave radiation has a wavelength on the order of 1.0 cm. Calculate the frequency in s^{-1} of a single photon of this radiation.
6. As the frequency of electromagnetic radiation doubles, the wavelength ___ ?
7. As the wavelength of electromagnetic radiation is quadrupled, the frequency ___ ?
8. The yellow light given off by a sodium vapor lamp has a wavelength of 589.0 nm. What is the frequency of this radiation in Hz?

Further Reading / Supplemental Links

- Young's Double Slit Experiment: http://www.studyphysics.ca/newnotes/20/unit04_light/chp1719_light/lesson58.htm
- National Geographic's Patterns in Nature: http://photography.nationalgeographic.com/photography/patterns-in-nature/
- Following the Path of Discovery: http://www.juliantrubin.com/bigten/hertzexperiment.html
- International Lighting Vocabulary: http://www.cie.co.at/publ/abst/17-4-89.html

5.2 The Bohr and Quantum Mechanical Models of the Atom

Lesson Objectives

- Describe Planck's work with hydrogen emission spectra, and explain how this work further informed our understanding of the atom.
- Describe the discoveries of de Broglie, Schrodinger, and Heisenberg, and explain how their work led to a revised understanding of the atom, electrons, and light.
- Describe the Bohr model and the quantum model of the atom.

Lesson Vocabulary

- **emission spectra**: When most substances are heated to high enough temperatures that they give off light of various wavelengths.
- **Heisenberg's uncertainty principle**: States that the more precisely the position of a particle is determined, the less precisely the momentum is known in this instant, and vice versa.

Check Your Understanding

- What are some sources for light of different wavelengths?
- What is the relationship between the color of visible light and its wavelength?

Introduction

Toward the end of the 1800s, we understood light as being composed of electromagnetic radiation waves that travel at a constant speed (c) and can be described by their wavelength (λ) or frequency (ν). However, beginning in the 1900s, new findings emerged about the workings of the atom and the composition of matter. It began with confirmation that light sometimes behaved as a particle, as seen in experiments on the photoelectric effect. Light particles, or photons, were found to have a defined and measurable amount of energy. Other findings emerged at this time, showing that not only could waves (like light) behave as a particle, but particles (such as electrons) could sometimes behave like waves. This concept of wave-particle duality ultimately led to a revolution in our understanding of matter, light, and how we view the universe.

Hydrogen Emission Spectra

When most substances are heated to high enough temperatures, they give off light of various wavelengths; these are referred to as **emission spectra**. Planck studied the emission spectra of different objects and saw that when certain substances were heated, they emitted only specific wavelengths of light. In other words, the spectra were discontinuous. In particular, the emission spectrum of hydrogen included only four wavelengths within the visible light range, which could be seen separately by passing the emitted light through a prism (**Figure** 5.6).

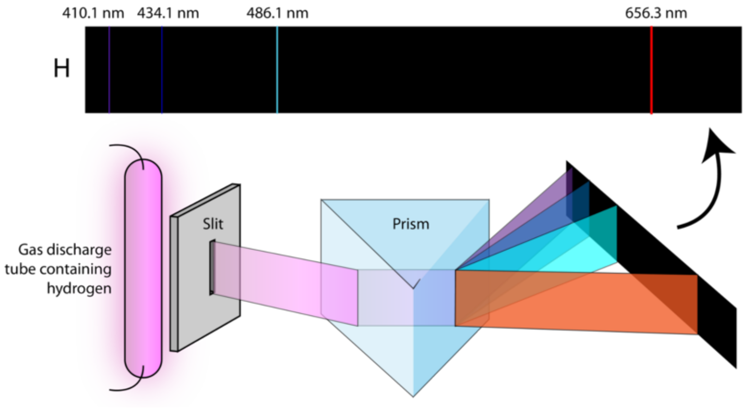


FIGURE 5.6
Hydrogen emission spectrum.

Planck's interpretation of this phenomenon was that the emissions were quantized –they were only emitted in fixed and predictable intervals (Haendler 1982; Goodney 1991). This was described mathematically by the following expression, $E = h\nu$, where E is the energy of a single photon, h is Planck's constant, and ν is the frequency of the electromagnetic wave. Because of this influential work on photons and quanta, Planck was awarded the Nobel Prize in Physics in 1918.

Bohr's Atomic Model

Following the discoveries of hydrogen emission spectra, the Danish physicist Niels Bohr (1885–1962) proposed a new model of the atom in 1915. Bohr suggested that electrons do not radiate energy as they travel around the nucleus but exist in states of constant energy, which he called stationary states (Haendler 1982), orbiting at fixed distances from the nucleus (**Figure** 5.7). Bohr's work was primarily based on the emission spectra of hydrogen, and it won him the Nobel Prize in physics in 1922.

This model, also referred to as the planetary model of the atom, explained emission spectra in terms of electrons moving between different stationary orbits that have different levels of energy. When energy is added, an electron can jump up to a higher energy orbit, and when the electron relaxes back to a lower energy orbit, the difference in energy is emitted as a photon of light. Using the observed frequencies of the emitted photons, the energy differences between orbits in the hydrogen atom could be determined. Since the orbits had set differences in energy, only certain amounts of energy could be released for any single transition. The energy released could not be any arbitrary amount, but was instead quantized (limited to specific values). This formed the basis for what later became known as quantum theory, which accounts for a wide range of physical phenomena that could not previously be explained.

Bohr's work had a strong influence on our modern understanding of the inner workings of the atom. However, although his model worked well for predicting the emissions of the hydrogen atom, it was seriously limited when applied to other atoms. Shortly after Bohr published his planetary model of the atom, several new discoveries were made, which resulted in, yet again, a revised view of the atom.

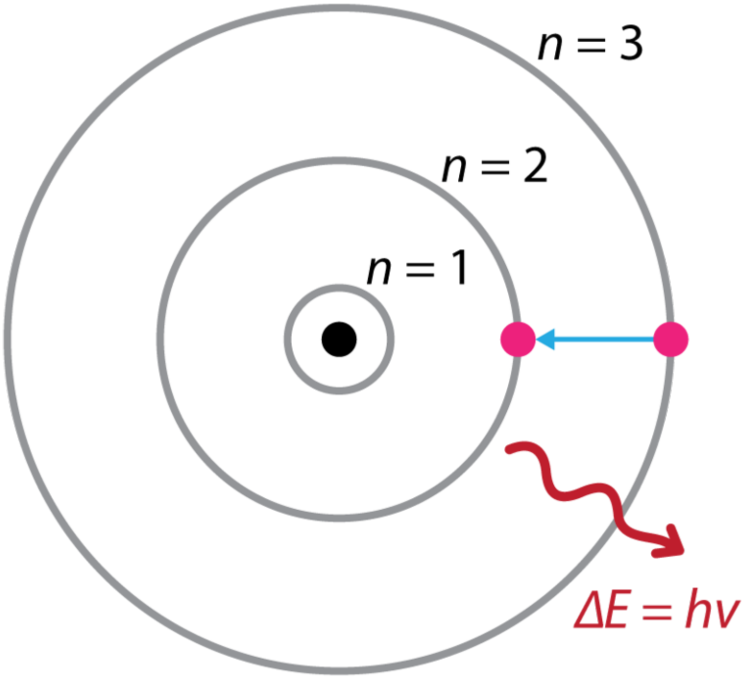


FIGURE 5.7

Bohr's atomic model.

Wave-Particle Duality

French born Physicist Lois de Broglie (1892–1987) studied diffraction patterns of electrons, which seemed to indicate that electrons were behaving as waves, even though they were composed of matter. Further diffraction and interference experiments confirmed these findings. In 1924, de Broglie showed that particles exhibit wavelengths that are inversely proportional to their momentum. Because of this inverse relationship, large objects have wavelengths that are immeasurably small, so wave behavior is not observed. However, the momentum of a very tiny particle, like an electron, can be small enough to detect wave-like behavior during certain types of experiments.

Electrons as Particles

Two years after de Broglie's work, in 1926, the Austrian physicist Erwin Schrödinger (1887–1961) found that the behavior of electrons in atoms could be described by considering them to be standing waves. He was able to incorporate both particle behavior (mass) and wave behavior (an indefinite location in space) into one equation. The mathematical wave function for an electron provided a way to predict the probability of finding the electron in a given region of space. Schrödinger received the Nobel Prize in physics in 1933.

Heisenberg Uncertainty Principle

At about the same time that Schr¨dinger was working out the mathematics of standing waves, the German physicist Werner Heisenberg (1901–1976) showed mathematically that it is impossible to determine simultaneously the exact location and the exact velocity of an electron, or of any other particle. In 1927, Heisenberg presented a paper in which he showed that "the more precisely the position of a particle is determined, the less precisely the momentum is known in this instant, and vice versa" (Hilgevoord and Uffink 2011). This later became known as **Heisenberg's uncertainty principle**.

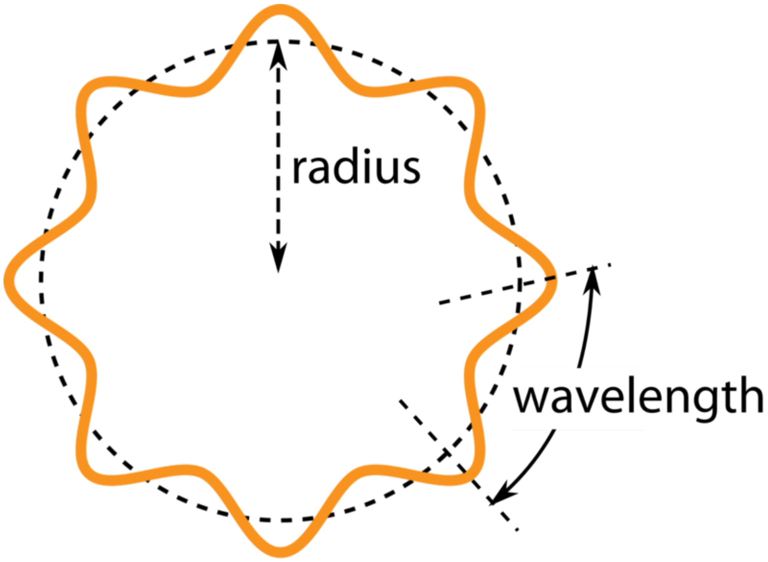


FIGURE 5.8

Electrons exist in atoms as standing waves.

Lesson Summary

- The emission spectrum of hydrogen is discontinuous. The spectrum is made up of discrete lines representing transitions of the hydrogen electron between specific energy levels within the atom.
- In 1915, Bohr proposed a new model of the atom in which electrons exist in states of constant energy, called stationary states, orbiting at fixed distances from the nucleus. Bohr's work was primarily based on the emission spectrum of hydrogen.
- de Broglie proposed in 1924 that any object exhibits a wavelength that is inversely proportional to its momentum. Because of this relationship, only very tiny particles will exhibit measurable wavelengths.
- Two years after de Broglie's work, in 1926, the Austrian physicist Erwin Schr¨dinger described the behavior of electrons in atoms as standing waves.
- Heisenberg showed that it is impossible to determine simultaneously both the exact location and exact velocity of an electron or any other particle. This became known as the Heisenberg uncertainty principle.

Review Questions

1. Describe the Bohr model of the hydrogen atom. What were the shortcomings of this model?
2. What are emission spectra?
3. Hydrogen has four, distinct emission spectra. What does general property of emissions does this indicate?
4. How are emission spectra related to energy levels within an atom?
5. What important property of electrons did de Broglie's experiments demonstrate?
6. What is indicated by the the term, "wave-particle duality"?
7. What are the distinguishing characteristics of wave and particle behavior?
8. Describe the Heisenberg uncertainty principle.

Further Reading / Supplemental Links

- Star Light, Star Bright Teacher Page: Science Background at http://amazing-space.stsci.edu/resources/explorations/light/star-light-science.html

Points to Consider

- In this lesson, we studied the experimental origins for our current understanding of electrons and light. We studied the simplest of atoms, the hydrogen atom, and looked at how electrons behave in this atom. Now, we are going to study the behavior of electrons in atoms of various other elements.

5.3 Electron Arrangement in Atoms

Lesson Objectives

- Define the four quantum numbers and describe how they are used to determine the location (orbital) of an electron in an atom.
- List the total number of electrons needed to fully occupy each main level.
- State the Aufbau principle, the Pauli exclusion principle, and Hund's rule.
- Describe the electron configurations for the atoms of any element using orbital filling diagrams, electron configurations and, when appropriate, noble-gas notation.

Lesson Vocabulary

- **orbital**: The region in space in which an electron is most likely to be found.
- **quantum numbers**: A series of specific numbers used to describe the location of an electron in an associated atom.
- **electron configuration**: The set of orbitals occupied by electrons in a given atom.
- **ground state**: The electron configuration of an atom in its neutral state in which the electrons occupy the lowest possible energy levels.
- **Aufbau principle**: States that all lower energy orbitals must be filled before electrons can be added to a higher energy orbital.
- **Pauli exclusion principle**: States that no two electrons in same atom can have the same set of four quantum numbers.
- **Hund's rule**: States that in a set of orbitals that are energetically equivalent, each orbital is occupied by a single electron before any orbital within the set is occupied by a second electron.
- **noble gas notation**: A shorthand for the electron configuration of an atom in which the elemental symbol of the last noble gas prior to that element in the periodic table is written first, followed by the configuration of the remaining electrons.

Check Your Understanding

- Describe the properties of light.
- What type of relationship have we already seen between light and electrons?

Introduction

In the last lesson, we studied the experimental origins for an area of study called quantum mechanics. We learned that both electrons and light exhibit properties normally associated with both waves and particles, which dramatically affects the way we describe the atomic nature of matter. Our focus in this lesson will be on the arrangement of electrons in atoms. This is important because a great many phenomena in the chemical world can be explained by studying the ways that electrons are arranged in an atom of interest. For example, only a small amount of energy needs to be expended to remove an electron from atoms of some elements, most of which are metallic. Other atoms, such as nitrogen or oxygen, require a much larger energy investment in order to remove an electron. Looking at the arrangement, or configuration, of electrons in a given atom helps us to predict this and other properties that are characteristic of a given atom.

Atomic Orbitals

In the Bohr model, the atom is viewed as a densely packed nucleus comprised of neutrons and protons that is surrounded by electrons at fixed distances, which correspond to specific energy levels. However, the quantum model showed that the distances between electrons and the nucleus are not really fixed. Due to their wave-like nature, we cannot pinpoint the exact location of an electron that is in motion, but we can determine the probability that a given electron will be in a particular region in three-dimensional space. Schr¨dinger's equations are used to determine the position of a specific electron with respect to a nearby nucleus. The region in space in which an electron is most likely to be found is referred to as an **orbital**.

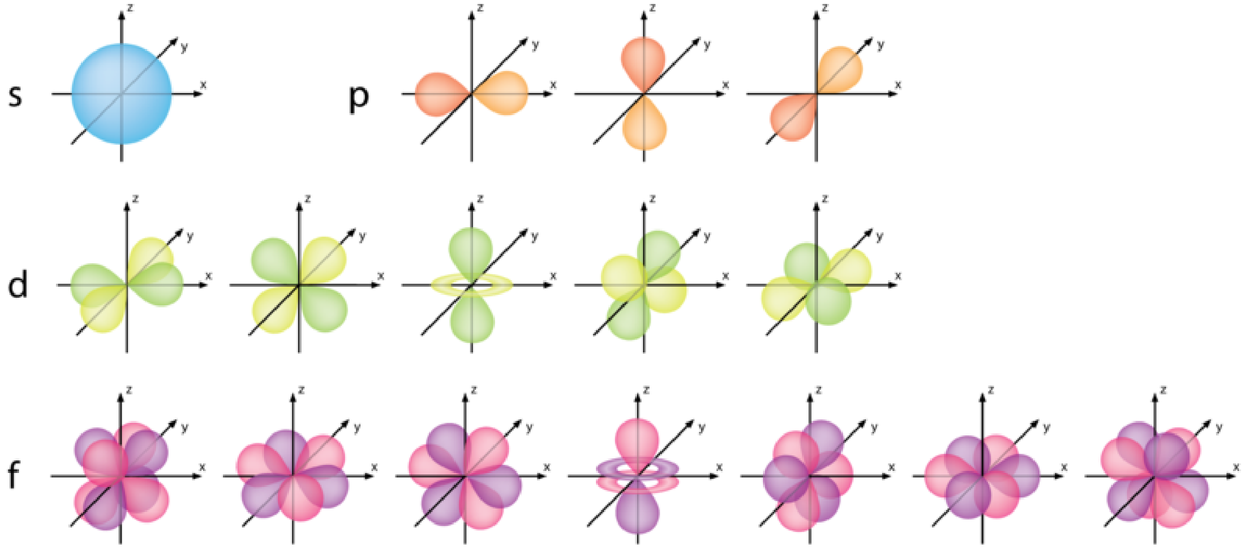


FIGURE 5.9

The images shown here are of simulations of probability density distributions of different electron states in the hydrogen atom. They represent where the electron is most likely to exist relative to the nucleus (Zukav 1979). There are different orbitals which can exist for a given atom and which a given electron can occupy. The four orbital types shown here are: (1) the spherically shaped s-orbital; (2) dumbbell-shaped p-orbitals (which are oriented in three different directions); (3) d-orbitals (which have five different possible orientations); and (4) f-orbitals (which have seven different possible orientations).

Quantum Numbers

We use a series of specific numbers, called **quantum numbers**, to describe the location of an electron in an associated atom. An electron in an atom or ion has four quantum numbers to describe its state. Think of them as important variables in an equation which describes the three-dimensional position of electrons in a given atom.

Principal Quantum Number (n)

The principal quantum number, signified by (n), is the main energy level occupied by the electron. Electrons in orbitals with higher principal quantum numbers are, on average, further from the nucleus and higher in energy. Possible values for the principal quantum number include any positive whole number (e.g., 1, 2, 3, 4, 5, 6, ...). As we will see, the principal quantum number is related to the row in which an element appears on the periodic table.

Angular Momentum Quantum Number (

The angular momentum quantum number, signified by (l), describes the general shape of the region occupied by an electron. The possible value(s) of l depend on the value of the principal quantum number n. The angular momentum quantum number can be any whole number between zero and (n-1). For example, if n = 2, l could be either 0 or 1.

Magnetic Quantum Number (

The magnetic quantum number, signified by (m_l), describes the orientation of an orbital in space. For a given value of the angular momentum quantum number l, there are ($2l$ + 1) possible values for m_l, which are determined as follows:

$-l$, $(-l+1)$ ... 0 ... $(+l-1)$, $+l$

For example:

If n = 2
Then $l = 0$ or 1
for $l = 0$, $m_l = 0$
for $l = 1$, $m_l = -1, 0,$ or $+1$

The **Table** 5.1 shows the possible magnetic quantum number values (m_l) for the corresponding angular momentum quantum number (l).

TABLE 5.1: Relationships among Values of n,

n	Possible Values of l	Subshell Designation	Possible Values of m_l	Number of Orbitals in Subshell	Total Number of Orbitals in Shell
1	0	1s	0	1	1
2	0 1	2s 2p	0 1, 0, -1	1 3	4
3	0 1 2	3s 3p 3d	0 1, 0, -1 2, 1, 0, -1, -2	1 3 5	9

TABLE 5.1: (continued)

n	Possible Values of l	Subshell Designation	Possible Values of m_l	Number of Orbitals in Subshell	Total Number of Orbitals in Shell
4	0 1 2 3	4s 4p 4d 4f	0 1, 0, -1 2, 1, 0, -1, -2 3, 2, 1, 0, -1, -2, -3	1 3 5 7	16

Spin Quantum Number (

The spin quantum number describes the spin for a given electron. An electron can have one of two possible spin values, either $+\frac{1}{2}$ or $-\frac{1}{2}$. An electron cannot have zero spin. We also represent spin with arrows ↑ or ↓, and correspondingly, m_s values of $+\frac{1}{2}$ or $-\frac{1}{2}$ are sometimes referred to as "spin up" and "spin down" electrons. A single orbital can hold a maximum of two electrons, but only if they have opposite spins. Another way to say this is that no two electrons in an atom can have the same four quantum numbers. They cannot occupy the same orbital, designated by the first three numbers, and have the same spin, indicated by the final number.

s, p, d, and f Orbitals

The shapes corresponding to each value of l also go by different names, each designated by a single letter (chosen based on older analyses of atomic emission spectra). For example, an electron for which $l = 0$ is located in an s orbital, regardless of the value of its principal quantum number n. This orbital is spherical in shape, as seen in **Figure** 5.10.

Electrons for which $l = 1$ are located in dumbbell-shaped p orbitals. **Table** 5.1 shows us that p orbitals can have three possible orientations (designated by three values for m_l), each of which is perpendicular to the two others in three-dimensional space (**Figure** 5.11).

When $l = 2$, the possible m_l values include -2, -1, 0, +1, and +2, for a total of five d orbitals. The relative orientations for each of these orbitals are shown in **Figure** 5.12. Note that even though one of the d orbitals appears to have a different shape than the others, it is still mathematically equivalent and exhibits the same properties (such as total energy) as the other d orbitals.

The most complex set of orbitals that we will encounter are the f orbitals. When $l = 3$, possible values for m_l include -3, -2, -1, 0, +1, +2, and +3, for a total of seven distinct orbitals. The relative orientations for each of these orbitals are shown in **Figure** 5.13.

Rules for Determining Electron Configurations

Now that we know about some of the possible locations (orbitals) in an atom that can be occupied by electrons, how can we predict which orbitals will contain electrons and how many each will contain? The set of orbitals occupied by electrons in a given atom is referred to as its **electron configuration**. An electron configuration essentially provides a map of where each electron is likely to be located in a given atom. In the case of a free, electrically neutral atom, the atom is considered to be in a **ground state**. This means its electrons are in the lowest energy locations. Several rules can be used to determine the lowest energy locations of the various electrons in a free atom.

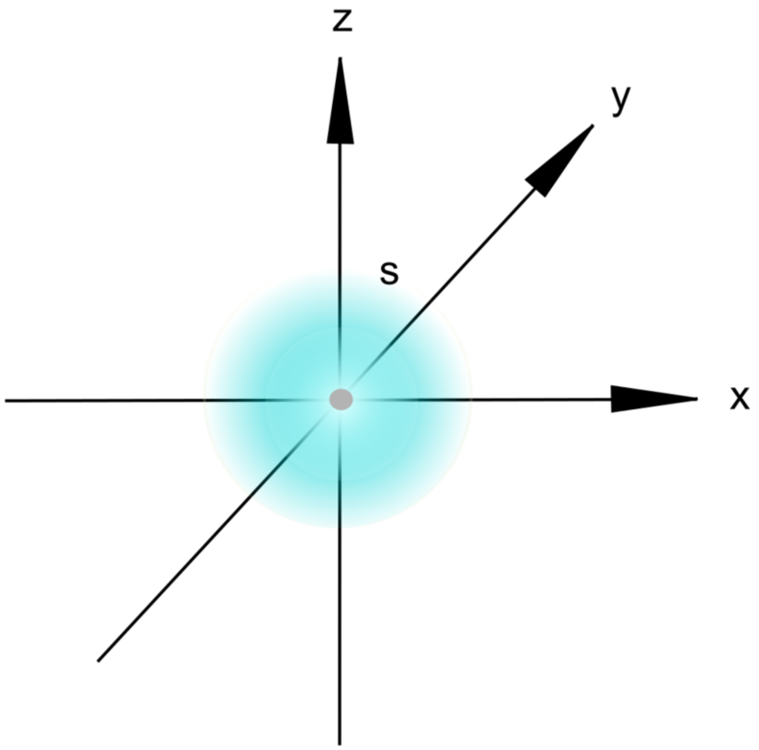


FIGURE 5.10
An s orbital

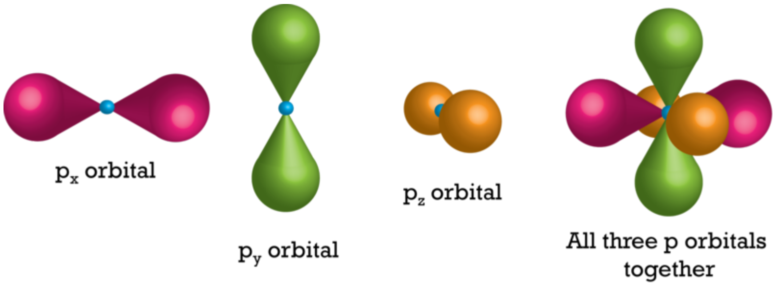


FIGURE 5.11
Three individual p orbitals are centered on the nucleus of the atom. This figure shows them both separately and together.

Aufbau Principle

To determine the lowest energy electron configuration for a given atom, it is first necessary to organize the atomic sublevels in order of increasing energy. **Figure** 5.14 shows the relative energies of various sublevels.

The lowest energy sublevel is always the 1s sublevel, which consists of one orbital. The single electron of the hydrogen atom will occupy the 1s orbital when the atom is in its ground state. As we move on to atoms with more electrons, those electrons are sequentially added to the next lowest sublevels, first 2s, then 2p, then 3s, and so on. The **Aufbau principle** states that all lower energy orbitals must be filled before electrons can be added to a higher energy orbital. The Aufbau principle is sometimes referred to as the "building-up" principle. It is worth noting that, in reality, atoms are not built by adding protons and electrons one at a time. This method is merely a way for us to predict and understand the end result.

As seen in **Figure** 5.14, the energies of the sublevels in different principal energy levels eventually begin to overlap. After the 3p sublevel, it would seem logical that the 3d sublevel should be the next lowest in energy. However, the 4s sublevel is slightly lower in energy than the 3d sublevel, so the 4s orbital fills first. After the 3d sublevel is filled,

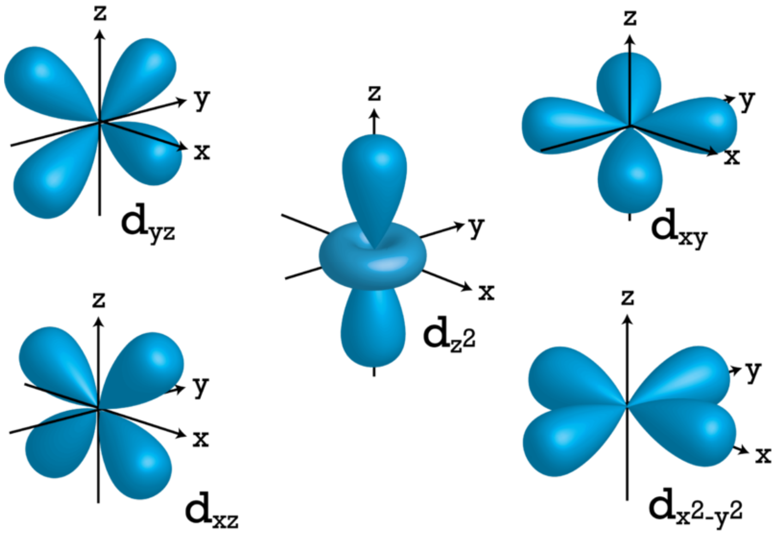


FIGURE 5.12
Relative geometry of the d orbitals

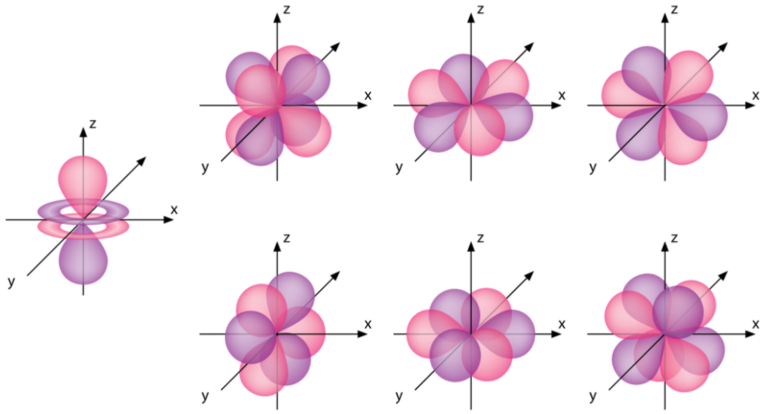


FIGURE 5.13
Relative geometry of the f orbitals

the next lowest sublevels are 4p, 5s, and 4d. Note that the 4f sublevel does not fill until just after the 6s sublevel. **Figure** 5.15 is a useful and simple aid for keeping track of the order in which electrons are first added to each atomic sublevel.

Pauli Exclusion Principle

As pointed out before, no two electrons in same atom can have the same set of four quantum numbers; this concept is referred to as the **Pauli exclusion principle**. If two electrons have the same three values for n, l, and m_l, they would be found in the same orbital. In order to maintain separate identities, two electrons in the same orbital would need to have different spin quantum numbers (m_s). Because there are only two possible spin quantum numbers, each orbital can hold a maximum of two electrons, each of which must have a different spin.

Hund's Rule

Hund's rule states that, in a set of orbitals that are energetically equivalent, each orbital is occupied by a single electron before any orbital within the set is occupied by a second electron. Additionally, all electrons in singly

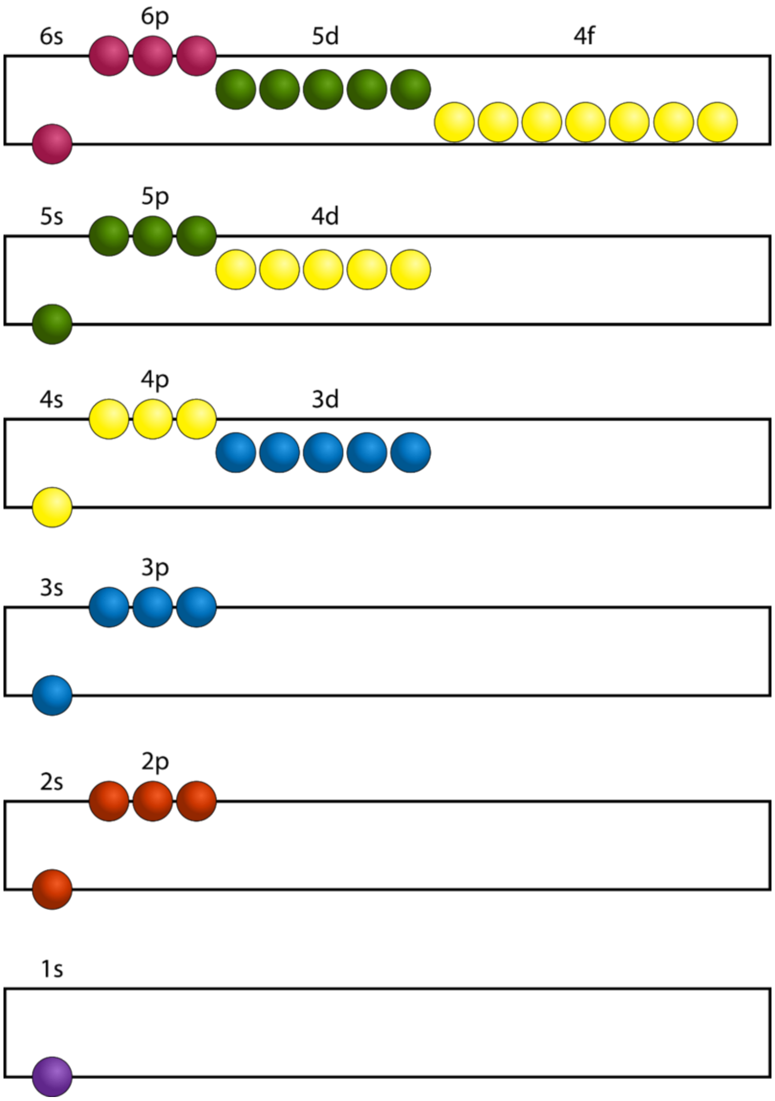


FIGURE 5.14

According to the Aufbau principle, all lower energy orbitals must be filled before electrons can be added to a higher energy orbital. The principal energy levels are color coded in this figure. Sublevels are grouped together by column, and each circle represents an orbital that is capable of holding two electrons.

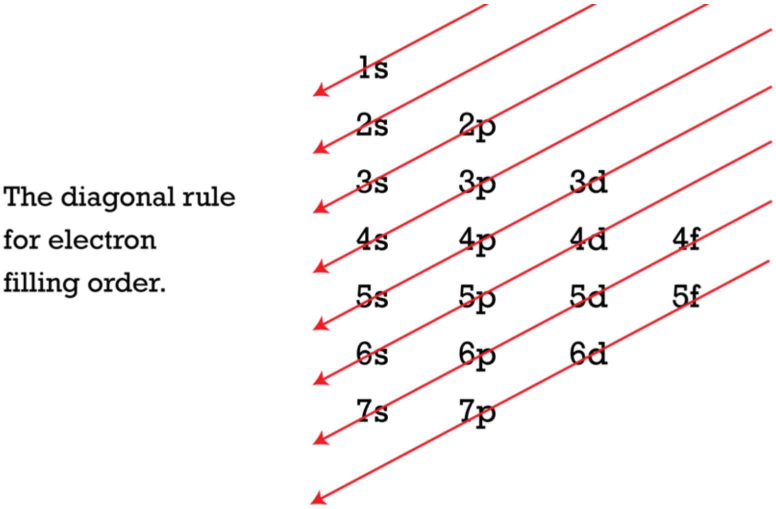


FIGURE 5.15

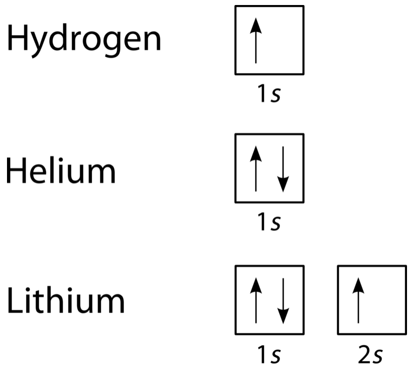
The Aufbau principle is illustrated in the diagram by following each red arrow in order from top to bottom: 1s, 2s, 2p, 3s, etc.

occupied orbitals prefer to have the same spin quantum number. We will see more concrete examples of how this rule works below in our discussion of orbital filling diagrams.

Depicting Electron Configurations

Orbital Filling Diagrams

There are multiple ways to depict the electron configuration of a given atom. An orbital filling diagram provides a visual representation of the way in which an atom's electrons are distributed into various orbitals. Each orbital is shown as a single square (or circle), and orbitals within the same sublevel are drawn directly next to each other. Each sublevel is labeled by its principal quantum number and by its sublevel (which corresponds to a specific value of *l*). Electrons are indicated by arrows inside the circles. An arrow pointing upwards indicates one spin direction, while a downward pointing arrow indicates the other direction. The orbital filling diagrams for hydrogen, helium, and lithium are shown below.



According to the Aufbau principle, sublevels and orbitals are filled with electrons in order of increasing energy. Since the s sublevel consists of just one orbital, the second electron simply pairs up with the first electron, as in helium. The next element, lithium, requires the use of the next available sublevel. The third electron must be placed in a 2s orbital, because the 1s orbital is completely filled.

Electron Configuration Notation

Electron configuration notation is a shorthand version of the information contained in orbital filling diagrams. The squares and arrows are eliminated and replaced with the name of each occupied sublevel and a superscript indicating the number of electrons present in that sublevel. For example, the configuration of a hydrogen atom is $1s^1$, and the configuration of helium is $1s^2$. Multiple occupied sublevels are placed one after another, so the electron configuration of lithium is written $1s^2 2s^1$. The sum of all the superscripts in an electron configuration is equal to the number of electrons in that atom, which is in turn equal to its atomic number.

Noble Gas Notation

The elements that are found in the last column of the periodic table are an important group of elements called the noble gases. They include helium, neon, argon, krypton, xenon, and radon. For elements with large numbers of electrons, electron configurations can become quite long. The electron configuration of an atom can be abbreviated by using **noble gas notation**, in which the elemental symbol of the last noble gas prior to that atom is written first, followed by the configuration of the remaining electrons. Lithium can be used as an example to illustrate this method, even though its configuration ($1s^2 2s^1$) is not especially long. Because helium has a configuration of $1s^2$, that portion of the configuration for neon can be replaced by the symbol for helium written in brackets, [He]. Now, the configuration for lithium can be written as [He]2s^1. This becomes more useful in the case of larger atoms. For example, the full electron configuration for cesium is $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^66s^1$. Using noble gas notation, this becomes [Xe]6s^1. Comparing this to the configuration of lithium, it becomes easy to see the similarity. Each of these elements has a configuration equivalent to a noble gas plus a single electron in an s orbital. This fundamental similarity causes the chemical properties of lithium and cesium to be quite similar. We will revisit this trend when we discuss the structure of the periodic table.

Filling the Orbitals with Electrons - The First 10 Elements

Hydrogen and Helium - The 1s Orbital

Now let's see how electrons are arranged for the first several elements. We start with hydrogen, which has only one electron. According to the Aufbau principle, this should be placed into the 1s orbital, which is the lowest energy orbital. For the 1s orbital, n = 1, $l = 0$, and $m_l = 0$, since that is the only possible m_l value when $l = 0$. Because there are no other electrons, it does not matter whether m_s is $+\frac{1}{2}$ or $-\frac{1}{2}$. The configuration of hydrogen is 1s^1, and possible quantum numbers for this electron would be the following:

TABLE 5.2: **Atomic Number: 1 Element: Hydrogen**

n	l	m_l	m_s	Orbital Type
1	0	0	$+\frac{1}{2}$	1s

Helium has two electrons. The lowest energy orbital (1s) has enough room to accommodate both, so the first three quantum numbers are the same for both electrons. However, in order to follow the Pauli exclusion principle, the spin of the second electron must be different from that of the first. One electron has a spin of $+\frac{1}{2}$ and the other electron has a spin of $-\frac{1}{2}$. Helium has a 1s^2 configuration, with two electrons in the 1s orbital. The quantum numbers for these two electrons are shown below:

TABLE 5.3: **Atomic Number: 2 Element: Helium**

n	l	m_l	m_s	Orbital Type
1	0	0	$+\frac{1}{2}$	1s
1	0	0	$-\frac{1}{2}$	1s

Lithium and Beryllium - The 2s Orbital

Now that we have filled the 1s shell, we move to n = 2 and start to work on the second shell with lithium.

TABLE 5.4: **Atomic Number: 3 Element: Lithium**

n	l	m_l	m_s	Orbital Name
1	0	0	$+\frac{1}{2}$	1s
1	0	0	$-\frac{1}{2}$	1s
2	0	0	$+\frac{1}{2}$	2s

Lithium has a configuration of 1s^{2}2s^1.

There is space for one more electron in the 2s orbital, so we give that second 2s electron a $-\frac{1}{2}$ spin.

TABLE 5.5: **Atomic Number: 4 Element: Beryllium**

n	l	m_l	m_s	Orbital Name
1	0	0	$+\frac{1}{2}$	1s
1	0	0	$-\frac{1}{2}$	1s
2	0	0	$+\frac{1}{2}$	2s
2	0	0	$-\frac{1}{2}$	2s

Beryllium has a configuration of $1s^2 2s^2$.

Boron Through Neon - The 2p Orbitals

Now that the 1s and 2s orbitals are filled, the next lowest energy orbitals are the three 2p orbitals. For p orbitals, l = 1, which means that m_l can have values of -1, 0, or +1. If there is only one electron in a set of p orbitals, it does not matter which of the possible values are used for m_l and m_s. One possible example is shown in the following table:

TABLE 5.6: **Atomic Number: 5 Element: Boron**

n	l	m_l	m_s	Orbital Type
1	0	0	$+\frac{1}{2}$	1s
1	0	0	$-\frac{1}{2}$	1s
2	0	0	$+\frac{1}{2}$	2s
2	0	0	$-\frac{1}{2}$	2s
2	1	-1	$+\frac{1}{2}$	2p

Boron has a configuration of $1s^2 2s^2 2p^1$.

Beginning with carbon, we start to see Hund's rule come into play. The rule states that orbitals of equal energy are each occupied by one electron before any orbital is occupied by a second electron, and all electrons in singly occupied orbitals must have the same spin. So the sixth electron in carbon goes into another p orbital (with a different m_l value), and its value for m_s must match as many of the other 2p electrons as possible. A possible set of quantum numbers that satisfies these criteria is shown below:

TABLE 5.7: **Atomic Number: 6 Element: Carbon**

n	l	m_l	m_s	Orbital Type
1	0	0	$+\frac{1}{2}$	1s
1	0	0	$-\frac{1}{2}$	1s
2	0	0	$+\frac{1}{2}$	2s
2	0	0	$-\frac{1}{2}$	2s
2	1	-1	$+\frac{1}{2}$	2p
2	1	0	$+\frac{1}{2}$	2p

Carbon has a configuration of $1s^2 2s^2 2p^2$.

Nitrogen has a third 2p electron, which should go into an orbital with the third possible value for m_l. Again, the m_s values should be the same for as many 2p electrons as possible, provided it does not violate the Pauli exclusion principle. In this case, all three can have the same spin value. Nitrogen has a configuration of $1s^2 2s^2 2p^3$.

TABLE 5.8: Atomic Number: 7 Element: Nitrogen

n	l	m_l	m_s	Orbital Type
1	0	0	$+\frac{1}{2}$	1s
1	0	0	$-\frac{1}{2}$	1s
2	0	0	$+\frac{1}{2}$	2s
2	0	0	$-\frac{1}{2}$	2s
2	1	-1	$+\frac{1}{2}$	2p
2	1	0	$+\frac{1}{2}$	2p
2	1	+1	$+\frac{1}{2}$	2p

Now that we have no more empty orbitals within this subshell, we need to start putting electrons in orbitals that are already partially occupied. For oxygen, one of the 2p orbitals will contain two electrons, while the others will still each have one. The electrons in the doubly occupied 2p orbital must have different spins to avoid violating the Pauli exclusion principle. Oxygen has a configuration of $1s^22s^22p^4$.

TABLE 5.9: Atomic Number: 8 Element: Oxygen

n	l	m_l	m_s	Orbital Type
1	0	0	$+\frac{1}{2}$	1s
1	0	0	$-\frac{1}{2}$	1s
2	0	0	$+\frac{1}{2}$	2s
2	0	0	$-\frac{1}{2}$	2s
2	1	-1	$+\frac{1}{2}$	2p
2	1	-1	$-\frac{1}{2}$	2p
2	1	0	$+\frac{1}{2}$	2p
2	1	+1	$+\frac{1}{2}$	2p

Adding another 2p electron gives us fluorine's configuration of $1s^22s^22p^5$.

TABLE 5.10: Atomic Number: 9 Element: Fluorine

n	l	m_l	m_s	Orbital Type
1	0	0	$+\frac{1}{2}$	1s
1	0	0	$-\frac{1}{2}$	1s
2	0	0	$+\frac{1}{2}$	2s
2	0	0	$-\frac{1}{2}$	2s
2	1	-1	$+\frac{1}{2}$	2p
2	1	-1	$-\frac{1}{2}$	2p
2	1	0	$+\frac{1}{2}$	2p
2	1	0	$-\frac{1}{2}$	2p
2	1	+1	$+\frac{1}{2}$	2p

Once we reach neon, a noble gas, all of the 2p orbitals will be completely full. Neon has a configuration of $1s^22s^22p^6$. Any further electrons will need to go in the next highest energy orbital, which would be the 3s orbital.

TABLE 5.11: Atomic Number: 10 Element: Neon

n	l	m_l	m_s	Orbital Type

TABLE 5.11: (continued)

n	l	m_l	m_s	Orbital Type
1	0	0	$+\frac{1}{2}$	1s
1	0	0	$-\frac{1}{2}$	1s
2	0	0	$+\frac{1}{2}$	2s
2	0	0	$-\frac{1}{2}$	2s
2	1	-1	$+\frac{1}{2}$	2p
2	1	-1	$-\frac{1}{2}$	2p
2	1	0	$+\frac{1}{2}$	2p
2	1	0	$-\frac{1}{2}$	2p
2	1	+1	$+\frac{1}{2}$	2p
2	1	+1	$-\frac{1}{2}$	2p

Electron configurations and orbital filling diagrams for lithium through neon are provided in **Figure** 5.16.

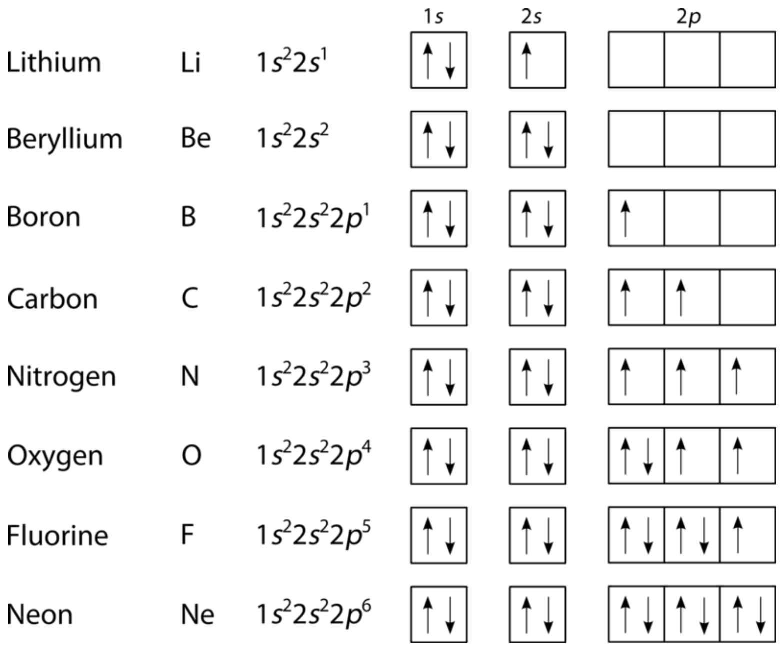


FIGURE 5.16

Electron configurations of lithium through neon.

Lesson Summary

- The locations where electrons are likely to be located around the nucleus are known as orbitals. Each orbital represents a three-dimensional region in which a given electron is most likely to be found.
- We use four quantum numbers to describe the location of an electron within an atom. The first three quantum numbers describe the orbital that the electron occupies, and the fourth indicates the relative spin of the electron.
- The principal quantum number, signified by (n), is the main energy level occupied by the electron.
- The angular momentum quantum number, signified by (l), describes the general shape of the region in which an electron is likely to be found (the shape of its orbital).
- The magnetic quantum momentum quantum number, signified by (m_l), describes the orientation of an orbital.

- The spin quantum number, signified by (m_s), describes the spin for a given electron. Possible values include $+\frac{1}{2}$ or $-\frac{1}{2}$; an electron cannot have zero spin. We also represent spin with arrows: ↑ (spin up) or ↓ (spin down).
- We can apply our knowledge of quantum numbers to describe the arrangement of electrons within an atom. We do this with something called electron configurations, which are effectively a map of the electrons for a given atom.

Review Questions

1. State the four quantum numbers and the possible values they may have.
2. Name the orbitals described by the following quantum numbers
   a. n = 3, l = 0
   b. n = 3, l = 1
   c. n = 3, l = 2
   d. n = 5, l = 0
3. Give the n and l values for the following orbitals
   a. 1s
   b. 3s
   c. 2p
   d. 4d
   e. 5f
4. Place the following orbitals in order of increasing energy: 1s, 3s, 4s, 6s, 3d, 4f, 3p, 7s, 5d, 5p
5. What are the possible m_l values for the following types of orbitals?
   a. s
   b. p
   c. d
   d. f
6. How many possible orbitals are there for n =
   a. 2
   b. 4
7. How many electrons can be accommodated by the full set of n = 4 orbitals?
8. Tabulate all of the possible orbitals (by name, i.e. 4s) for n = 4 and give the three quantum numbers that define each orbital.
9. Write electron configurations for the following atoms:
   a. H
   b. Li
   c. N
   d. F
   e. Br

Further Reading / Supplemental Links

- The History of the Discovery of Radiation and Radioactivity: http://mightylib.mit.edu/Course%20Materials/22.01/Fall%202001/discovery%20of%20radiation.pdf
- Quantum numbers: http://www.etap.org/demo/chem1/instructiontutor_last.html

- Quantum Numbers and Electronic Configurations: http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch6/quantum.html

5.4 References

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4. Christopher Auyeung. CK-12 Foundation . CC BY-NC 3.0
5. Radio antenna: Image copyright Baloncici, 2014; Longwave antenna: User:Junglecat/Wikipedia. Radio antenna: http://www.shutterstock.com; Longwave antenna: http://commons.wikimedia.org/wiki/File:CB_antenna.jpg . Radio antenna: Used under license from Shutterstock.com; Longwave antenna: Public Domain
6. Christopher Auyeung, using emission spectra by User:Merikanto/Wikimedia Commons and User:Adrignola/Wikimedia Commons. CK-12 Foundation; H spectrum: http://commons.wikimedia.org/wiki/File:Emission_spectrum-H.svg . CC BY-NC 3.0 (H emission spectra available under public domain)
7. Zachary Wilson. CK-12 Foundation . CC BY-NC 3.0
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9. Zachary Wilson. CK-12 Foundation . CC BY-NC 3.0
10. Joanna Kośmider. http://commons.wikimedia.org/wiki/File:Orbital_s.svg . Public Domain
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CHAPTER 6 The Periodic Table

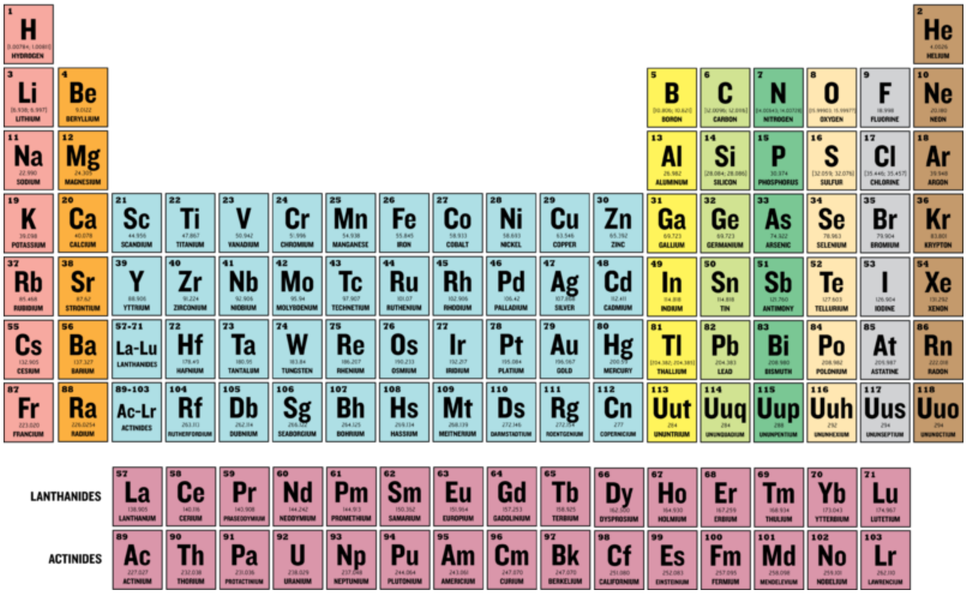
Chapter Outline

6.1 HISTORY OF THE PERIODIC TABLE

6.2 ELECTRON CONFIGURATION AND THE PERIODIC TABLE

6.3 TRENDS IN THE PERIODIC TABLE

6.4 REFERENCES



Humans have had a strong interest in classifying and working with matter throughout recorded history. Many of the elements that we are familiar with today have been known since ancient times, such as gold (aurum), silver (argentum), potassium (kalium), sodium (natrium), lead (plumbum), and copper (cuprium). An element's reactivity, solubility, flame color, compound formation, and luster are just a few of the various characteristics that people have studied and attempted to categorize. We can use our knowledge of atomic number and atomic weight in conjunction with these characteristics to arrange the elements systematically. In fact, this was how the first versions of the periodic table were created in the mid-1800s. Our modern day periodic table, pictured above, is an evolution of these earlier works. In this chapter, we will be studying how the periodic table of elements is organized and how it can be used to predict certain properties about a given element.

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6.1 History of the Periodic Table

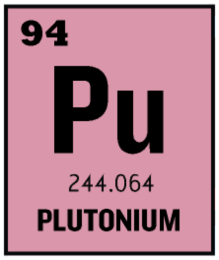
Lesson Objectives

- Describe the history of the periodic table and the contributions of Luther Meyer, John Newlands, Dmitri Mendeleev, Ernest Rutherford, and Henry Moseley.
- Explain how the periodic table was originally organized and the inconsistencies in this first periodic table.
- Describe the relationship between atomic number and atomic mass.
- Describe our modern periodic table and how the elements are arranged.

Lesson Vocabulary

- **periodic law**: States that when elements are arranged in order of increasing atomic number, there is a periodic repetition of their chemical and physical properties.

Check Your Understanding

1. What is the atomic weight and atomic number of the following element?
2. 

3. What do atomic number and atomic mass tell us?

Introduction

The earliest versions of the periodic table of elements emerged in the mid-1800s. At that time, there were approximately 60 known elements. This table has evolved over time as additional elements have been discovered and the known elements were arranged and categorized in slightly different ways. Today, there are 118 known elements, which are generally arranged in the familiar form of a modern periodic table.

Atomic Mass and Periodic Properties

One of the major developments that allowed for what became known as the periodic table was the discovery and measurements of atomic masses. With this discovery, some characteristic properties of the elements could be related to their relative atomic mass. This method for arranging the elements began in the early 1800s when John Dalton (1766–1844) described elements and compounds in terms of relative weights. Using the knowledge available at the time, Dalton prepared an early version of what later became the periodic table (**Figure** 6.1).

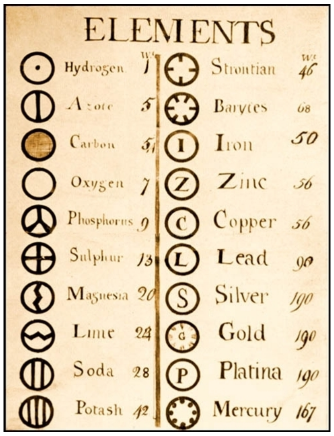


FIGURE 6.1

Dalton's Table of the Elements

Following Dalton's work, scientists began relating chemical properties to atomic weight. This resulted in several major discoveries, which led to the development of what we now know as the modern periodic table.

Other Early Attempts at a Periodic Table

Following the work of Dalton, a German scientist by the name of Julius Lothar Meyer (1830–1895) created a table of elements that was organized based on the concept of valency, which has to do with the ratios in which one element combines with another to make a compound.

Meyer published a textbook in 1864 where he presented his table of elements. Meyer's table showed 28 elements systematically arranged by valence into vertical columns. The atomic weights of these elements increase by similar amounts when going stepwise from left to right across the table. There were, however, some major shortcomings of Meyer's table. Only a fraction of the known elements could be easily categorized by valence, due to the fact that many elements can combine with one another in multiple different ratios (thus creating multiple different chemical compounds).

Shortly after this, in 1865, a similar periodic table was published by English chemist William Odling (1829–1921). Odling's table described a systematic arrangement of 45 elements. However, some elements were omitted without any reasonable explanation, and this version of the periodic table was quickly replaced by subsequent versions.

The Law of Octaves

Also in 1865, an English chemist by the name of John Newlands (1837–1898) published another version of the periodic table (**Table** 6.1). The arrangement was based on his proposed Law of Octaves, which stated that "if the chemical elements are arranged according to increasing atomic weight, those with similar physical and chemical properties occur after each interval of seven elements."

TABLE 6.1: **Newlands' Law of Octaves Octaves**

H	Li	Ga	B	C	N	O
F	Na	Mg	Al	Si	P	S
Cl	K	Ca	Cr	Ti	Mn	Fe
Co, Ni	Cu	Zn	Y	In	As	Se
Br	Rb	Sr	Ce, La	Zr	Di, Mo	Ro, Ru
Pd	Ag	Cd	U	Sn	Sb	Te
I	Cs	Ba, V	Ta	W	Nb	Au
Pt, Ir	Tl	Pb	Th	Hg	Bi	Th

Newlands was one of the first to detect a periodic pattern in the properties of the elements and anticipated later developments of this periodic law. However, Newlands' table, like Meyer's, did not gain widespread acceptance and use, primarily because it required the omission of several known elements without any real explanation, and few testable predictions could be made from his proposals.

Dmitri Mendeleev's Periodic Table

At this point in history, the sharing of scientific information was not as systematic as it is today, so multiple scientists could be working on the same ideas in different parts of the world without even realizing it. In 1869, Russian chemist Dmitri Mendeleev (1834–1907) independently described an arrangement of about 60 elements based on increasing atomic weight (**Figure** 6.2).

Mendeleev's table was similar to some of the other ones mentioned above, but it gained more widespread acceptance, due in part to its predictions of properties for elements that were not yet known. Rather than omitting elements where the periodic trends did not seem to fit, he left placeholders for elements that he predicted would eventually be discovered. The predicted properties (including atomic mass, valence, and melting points) of "eka-boron", "eka-aluminum", and "eka-silicon" were found to be very close to those of the subsequently discovered elements scandium (1879), gallium (1875), and germanium (1886). The discoveries of these elements provided very strong evidence in support of Mendeleev's table, and it provided the basis for our modern periodic table of the elements.

Here is a short video describing Mendeleev's discovery: http://www.youtube.com/watch?v=rBroXfaavw0 (4:05).

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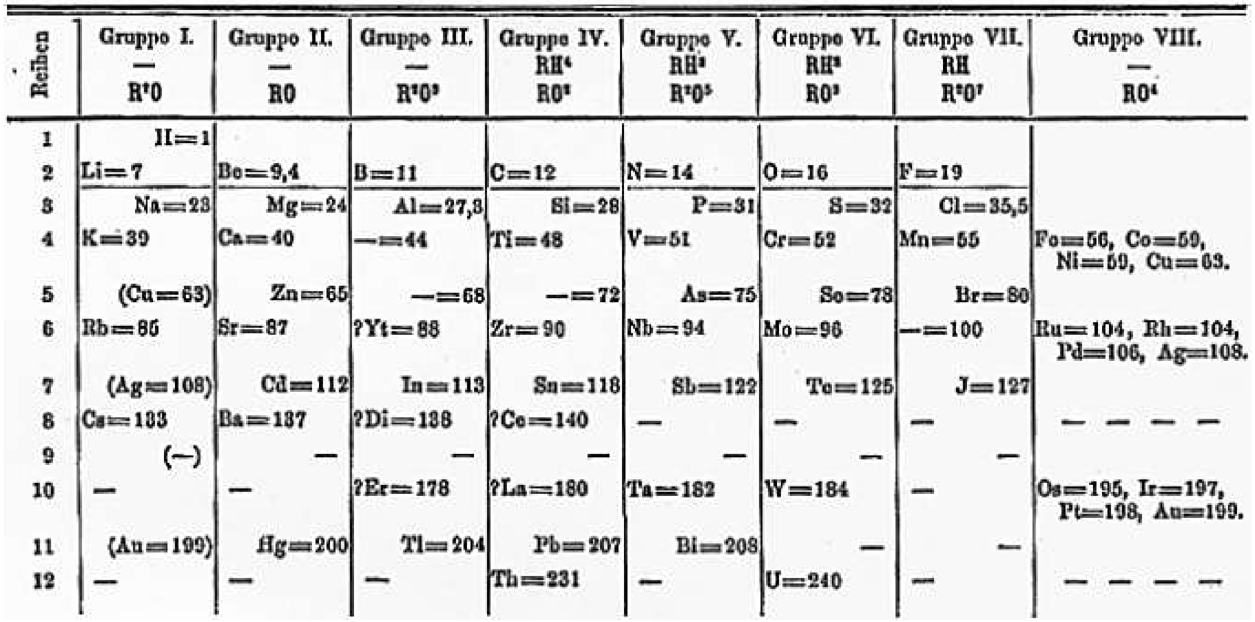
The Modern Periodic Table

In Mendeleev's table, atomic mass increases from top to bottom of vertical columns, with successive columns going left to right. Elements that are in the same horizontal row are groups of elements that were known to exhibit similar



Reihen	Gruppo I. — R^2O	Gruppo II. — RO	Gruppo III. — R^2O^3	Gruppo IV. RH^4 RO^2	Gruppo V. RH^3 R^2O^5	Gruppo VI. RH^2 RO^3	Gruppo VII. RH R^2O^7	Gruppo 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=140	—	—	—	— — — —
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	—	— — — —

FIGURE 6.2

Mendeleev's Periodic Table

chemical properties. However, even with the use of placeholders, there were some elements that did not quite fit the pattern. For example, Mendeleev listed tellurium before iodine even though its atomic mass is higher, because he knew that the properties of iodine were much more similar to those of fluorine (F), chlorine (Cl), and bromine (Br) than they were to oxygen (O), sulfur (S), and selenium (Se). He simply assumed that there was an error in the determination of one or both of the atomic masses. This turned out not to be the case, but Mendeleev was indeed correct to group these two elements as he did.

Recall that Rutherford's experiments leading to the discovery of the nucleus occurred in 1911, long after Mendeleev's periodic table was developed. Just two years later, in 1913, English physicist Henry Moseley (1887-1915) examined the x-ray spectra of a number of chemical elements. His results led to the definition of atomic number as the number of protons contained in the nucleus of each atom. He then realized that the elements of the periodic table should be arranged in order of increasing atomic number instead of increasing atomic mass.

When ordered by atomic number, the discrepancies within Mendeleev's table disappeared. Tellurium has an atomic number of 52, while iodine has an atomic number of 53. Even though tellurium does indeed have a greater average atomic mass than iodine, it is properly placed before iodine in the periodic table. Mendeleev and Moseley are credited with formulating the modern **periodic law**, which states that when elements are arranged in order of increasing atomic number, there is a periodic repetition of their chemical and physical properties. We will discuss some of these chemical and physical properties later on in this chapter. The result is the periodic table as we know it today.

Lesson Summary

- The early versions of the periodic table included approximately 60 known elements, while our current version includes 118.
- An early version of the periodic table was first published by Julius Lothar Meyer in 1864, where he used the concept of valence to group similar elements together.
- In 1865, Newlands described a periodic pattern in the properties of the elements that he referred to as the Law of Octaves. This anticipated later developments in our understanding of the periodic law.
- Between 1869 and 1871, Russian chemist Dmitri Mendeleev systematically arranged 60 elements based on increasing atomic weight.
- Mendeleev's table became widely accepted, primarily because he predicted the characteristics and placement of elements which were yet to be discovered.
- One of the major developments that allowed for what became known as the periodic table was the idea of atomic mass, which is attributed to John Dalton.
- Characteristic properties of the elements could be related to atomic mass and atomic number.
- Ordering the elements by atomic number instead of atomic mass cleared up some of the discrepancies found in older periodic tables and provided the basis for our current table of the elements.

Review Questions

1. Create a timeline that shows the contributions from the various scientists which led to the evolution of the periodic table.
2. What were some of the limitations of the early versions of the periodic table?
3. What were some aspects of Mendeleev's table that helped convince the scientific community to adopt its use?
4. How was Mendeleev's table arranged? What was systematic about it?
5. What predictions did Mendeleev make with his table that were later confirmed?
6. What contributions did Moseley make to the modern periodic table?
7. The periodic table has evolved over time. Do you suppose it is a completed table at this point? In other words, will it evolve further in the future?

Further Reading / Supplemental Links

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Points to Consider

- Even though the modern periodic table is a work in progress, there have been many other competing tables which have not been widely accepted. Research different periodic tables and see how they describe the periodic nature of the elements compared to the one with which we are most familiar.

6.2 Electron Configuration and the Periodic Table

Lesson Objectives

- Distinguish between core and valence electrons
- Understand the relationship between the number of orbitals in various energy sublevels and the length of the periods in the periodic table.
- Identify each block of the periodic table and be able to determine which block each element belongs to based on its electron configuration.
- Describe the relationship between outer electron configuration and group number. Be able to determine the number of valence electrons for any element.
- Locate the following groups of elements on the periodic table: alkali metals, alkaline earth metals, halogens, noble gases, transition elements, lanthanides, and actinides.

Lesson Vocabulary

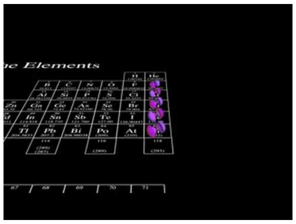
- **valence electrons**: The electrons that are in the highest occupied principal energy level (n).
- **core electrons**: The electrons that are closer to the nucleus and less available for interaction with other atoms.
- **representative (main-group) elements**: elements that have the s and p sublevels for a given principal energy level.
- **alkali metals**: The elements in Group 1 (lithium, sodium, potassium, rubidium, cesium, and francium).
- **alkaline earth metals**: The elements in Group 2 (beryllium, magnesium, calcium, strontium, barium, and radium).
- **noble gases**: The elements of Group 18 (helium, neon, argon, krypton, xenon, and radon).
- **halogens**: The elements of Group 17 (fluorine, chlorine, bromine, iodine, and astatine).
- **transition elements**: The elements that are found in Groups 3-12 on the periodic table.
- **lanthanides**: The 14 elements from cerium (atomic number 58) to lutetium (atomic number 71).
- **actinides**: The 14 elements from thorium (atomic number 90) to lawrencium (atomic number 103).

Check Your Understanding

- How to atoms form chemical bonds with one another? Are some elements more chemically reactive than others?

Introduction

The development of the periodic table was largely based on elements that display similar chemical behavior. In the modern table, these elements are found in vertical columns called groups. In this lesson, you will see how the form of the periodic table is related to electron configurations, which in turn influences chemical reactivity. We will first start with the following introductory video: http://www.youtube.com/watch?v=5MMWpeJ5dn4 (3:51).



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Periods and Blocks

There are seven horizontal rows, or periods, on the periodic table. The length of each period is determined by electron capacity of the sublevels that fill during that period, as seen in **Table** 6.2.

TABLE 6.2: Period Length and Sublevels in the Periodic Table

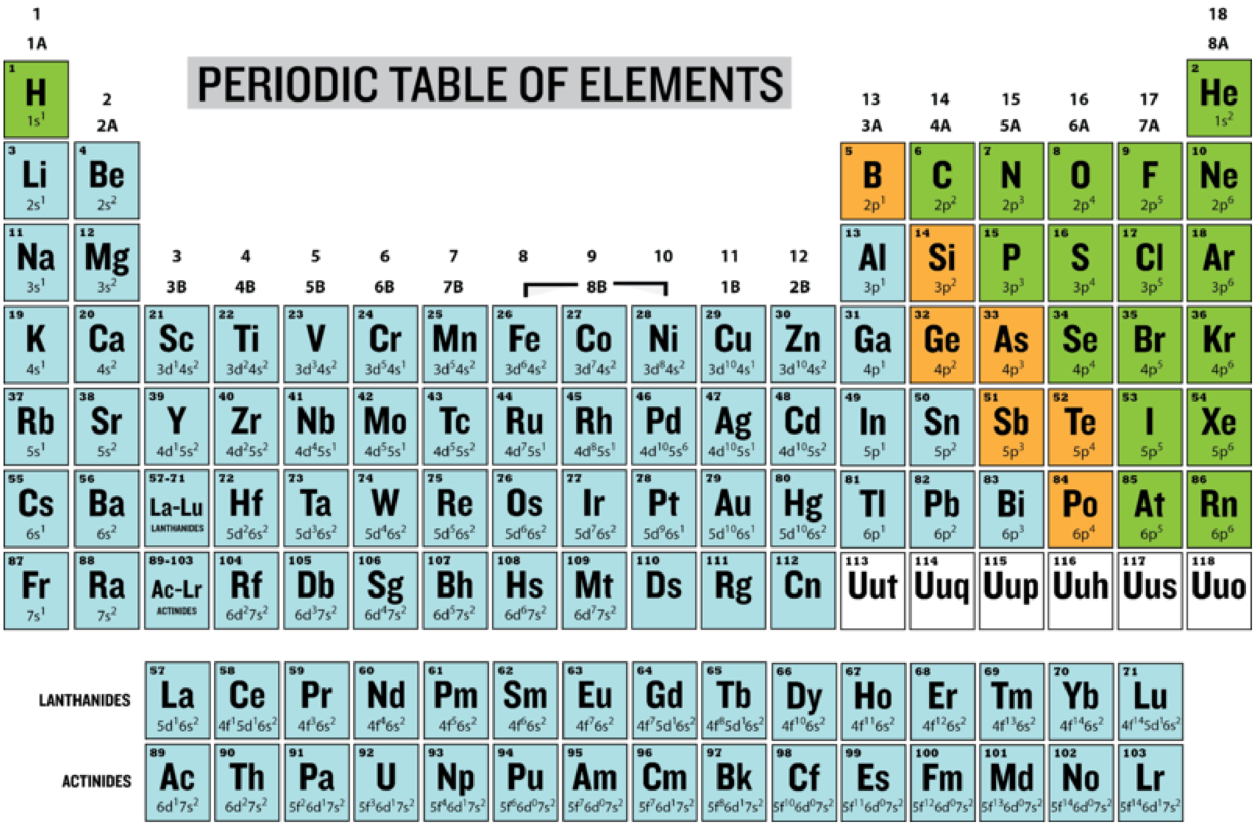
Period	Number of Elements in Period	Sublevels in Order of Filling
1	2	1s
2	8	2s 2p
3	8	3s 3p
4	18	4s 3d 4p
5	18	5s 4d 5p
6	32	6s 4f 5d 6p
7	32	7s 5f 6d 7p

Recall that the four different sublevels (s, p, d, and f) each consist of a different number of orbitals. The s sublevel has one orbital, the p sublevel has three orbitals, the d sublevel has five orbitals, and the f sublevel has seven orbitals. In the first period, only the 1s sublevel is being filled. Since all orbitals can hold two electrons, the entire first period consists of just two elements. In the second period, the 2s sublevel, with two electrons, and the 2p sublevel, with six electrons, are being filled. Consequently, the second period contains eight elements. The third period is similar to the second, except the 3s and 3p sublevels are being filled. Because the 3d sublevel does not fill until after the 4s sublevel, the fourth period contains 18 elements, due to the 10 additional electrons that can be accommodated by the 3d orbitals. The fifth period is similar to the fourth. After the 6s sublevel fills, the 4f sublevel is populated with up to 14 electrons. This is followed by the 5d and the 6p sublevels. The total number of elements in the sixth period is 32. The seventh period also contains 32 elements, most of which are too unstable to be found in nature. All 32 have been detected or synthesized, although for some of the later elements in this period, only a handful of atoms have ever been made.

The period to which a given element belongs can easily be determined from its electron configuration. As an example, consider the element nickel (Ni). Its electron configuration is $[Ar]3d^84s^2$. The highest occupied principal energy level is the fourth, as indicated by the 4 in the $4s^2$ portion of the configuration. Therefore, nickel can be found in the fourth period of the periodic table. **Figure** 6.3 shows a version of the periodic table that includes abbreviated electron configurations.

Based on electron configurations, the periodic table can be divided into blocks denoting which sublevel is in the process of being filled. The s, p, d, and f blocks are illustrated below in **Figure** 6.4.

Figure 6.4 also illustrates how the d sublevel is always one principal level behind the period in which that sublevel



PERIODIC TABLE OF ELEMENTS

1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8	9 8B	10	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1 H $1s^1$																	2 He $1s^2$
3 Li $2s^1$	4 Be $2s^2$											5 B $2p^1$	6 C $2p^2$	7 N $2p^3$	8 O $2p^4$	9 F $2p^5$	10 Ne $2p^6$
11 Na $3s^1$	12 Mg $3s^2$											13 Al $3p^1$	14 Si $3p^2$	15 P $3p^3$	16 S $3p^4$	17 Cl $3p^5$	18 Ar $3p^6$
19 K $4s^1$	20 Ca $4s^2$	21 Sc $3d^14s^2$	22 Ti $3d^24s^2$	23 V $3d^34s^2$	24 Cr $3d^54s^1$	25 Mn $3d^54s^2$	26 Fe $3d^64s^2$	27 Co $3d^74s^2$	28 Ni $3d^84s^2$	29 Cu $3d^{10}4s^1$	30 Zn $3d^{10}4s^2$	31 Ga $4p^1$	32 Ge $4p^2$	33 As $4p^3$	34 Se $4p^4$	35 Br $4p^5$	36 Kr $4p^6$
37 Rb $5s^1$	38 Sr $5s^2$	39 Y $4d^15s^2$	40 Zr $4d^25s^2$	41 Nb $4d^45s^1$	42 Mo $4d^55s^1$	43 Tc $4d^55s^2$	44 Ru $4d^75s^1$	45 Rh $4d^85s^1$	46 Pd $4d^{10}5s^6$	47 Ag $4d^{10}5s^1$	48 Cd $4d^{10}5s^2$	49 In $5p^1$	50 Sn $5p^2$	51 Sb $5p^3$	52 Te $5p^4$	53 I $5p^5$	54 Xe $5p^6$
55 Cs $6s^1$	56 Ba $6s^2$	57-71 La-Lu LANTHANIDES	72 Hf $5d^26s^2$	73 Ta $5d^36s^2$	74 W $5d^46s^2$	75 Re $5d^56s^2$	76 Os $5d^66s^2$	77 Ir $5d^76s^2$	78 Pt $5d^96s^1$	79 Au $5d^{10}6s^1$	80 Hg $5d^{10}6s^2$	81 Tl $6p^1$	82 Pb $6p^2$	83 Bi $6p^3$	84 Po $6p^4$	85 At $6p^5$	86 Rn $6p^6$
87 Fr $7s^1$	88 Ra $7s^2$	89-103 Ac-Lr ACTINIDES	104 Rf $6d^27s^2$	105 Db $6d^37s^2$	106 Sg $6d^47s^2$	107 Bh $6d^57s^2$	108 Hs $6d^67s^2$	109 Mt $6d^77s^2$	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo

LANTHANIDES	57 La $5d^16s^2$	58 Ce $4f^15d^16s^2$	59 Pr $4f^36s^2$	60 Nd $4f^46s^2$	61 Pm $4f^56s^2$	62 Sm $4f^66s^2$	63 Eu $4f^76s^2$	64 Gd $4f^75d^16s^2$	65 Tb $4f^85d^16s^2$	66 Dy $4f^{10}6s^2$	67 Ho $4f^{11}6s^2$	68 Er $4f^{12}6s^2$	69 Tm $4f^{13}6s^2$	70 Yb $4f^{14}6s^2$	71 Lu $4f^{14}5d^16s^2$
ACTINIDES	89 Ac $6d^17s^2$	90 Th $6d^27s^2$	91 Pa $5f^26d^17s^2$	92 U $5f^36d^17s^2$	93 Np $5f^46d^17s^2$	94 Pu $5f^66d^07s^2$	95 Am $5f^76d^07s^2$	96 Cm $5f^76d^17s^2$	97 Bk $5f^86d^17s^2$	98 Cf $5f^{10}6d^07s^2$	99 Es $5f^{11}6d^07s^2$	100 Fm $5f^{12}6d^07s^2$	101 Md $5f^{13}6d^07s^2$	102 No $5f^{14}6d^07s^2$	103 Lr $5f^{14}6d^17s^2$

FIGURE 6.3

This periodic table shows the outer electron configurations of the elements.

occurs. In other words, the 3d sublevels fills during the fourth period. The f sublevel is always two levels behind. The 4f sublevel belongs to the sixth period.

Numbering the Periodic Groups

The vertical columns, or groups, of the periodic table contain elements that exhibit similar properties. Two different ways of numbering the groups are commonly in use. The currently preferred convention is to number each column of the periodic table from 1-18. Group 1 includes hydrogen, lithium and sodium, and group 18 includes helium, neon, argon, and krypton. An older method is to skip the d and f blocks and utilize Roman numerals from IA to VIIIA. The letter A differentiates these groups from the d block groups, which are numbered using the letter B (from IB to VIIIB). For example, the element carbon could be described as being part of group 14 or group IVA, while scandium is in group 3 or group IIIB.

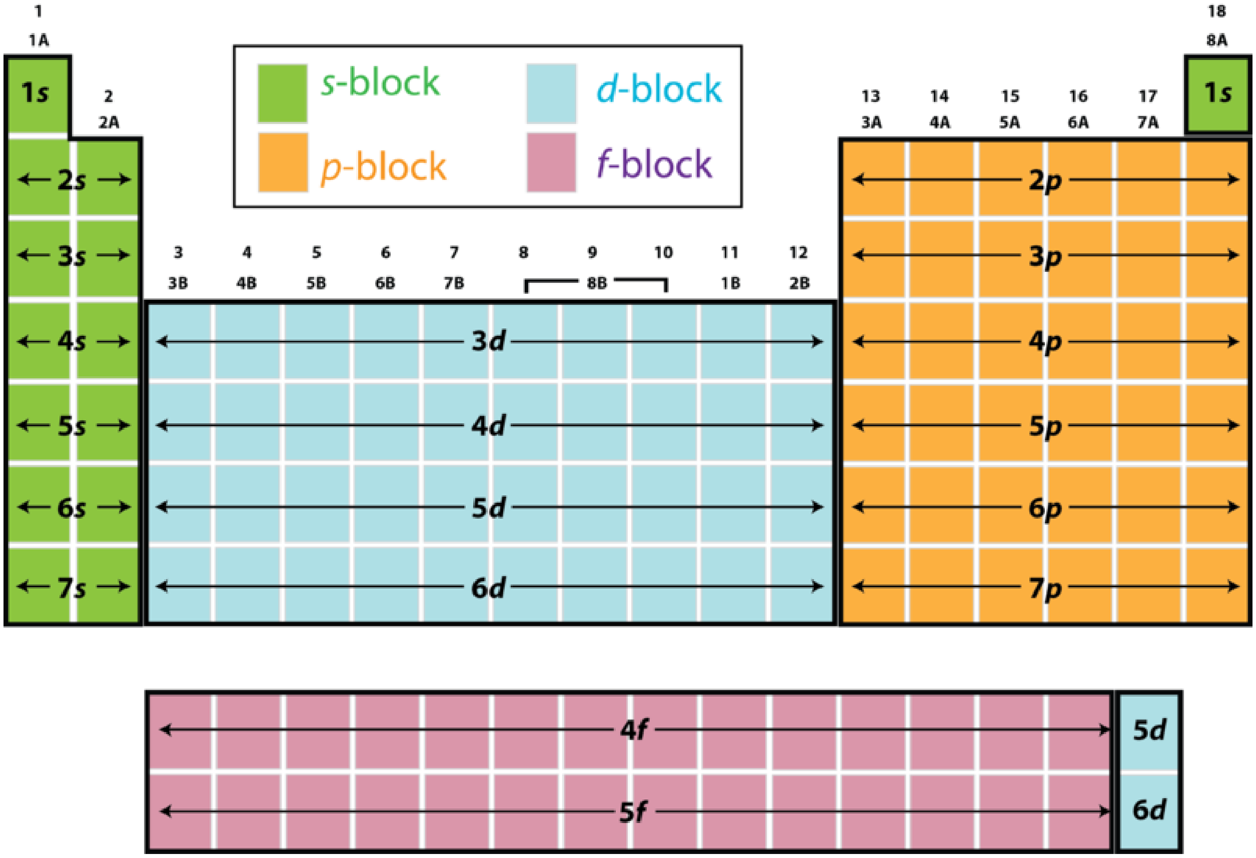


FIGURE 6.4

A block diagram of the periodic table shows which sublevels are being filled at any point.

Valence Electrons

Because they are held more loosely to the nucleus than the inner electrons, it is the outermost electrons that dictate the chemical behavior of a given element. Specifically, much can be predicted about the chemical reactivity of a given element based solely on the number of electrons in its highest occupied principal energy level (n). These electrons are referred to as **valence electrons**. The remaining electrons, which are closer to the nucleus and less available for interaction with other atoms, are referred to as **core electrons**.

Consider the element magnesium, which has 12 electrons in a configuration of $1s^2 2s^2 2p^6 3s^2$. The highest occupied principal energy level is 3, so all electrons with a quantum number of n = 3 are valence electrons. Thus, magnesium has two valence electrons. The other 10 electrons (in the n = 1 and n = 2 levels) are its core electrons.

Representative Elements

We will now examine each block of the periodic table in more detail. The s and p sublevels for a given principal energy level are filled during the correspondingly numbered period. For example, the 2s and 2p sublevels fill during the second period. The s-block elements and the p-block elements are together called the **representative** or **main-group elements**.

The s-block

The s-block consists of the elements in Group 1 and Group 2, which are primarily composed of highly reactive metals. The elements in Group 1 (lithium, sodium, potassium, rubidium, cesium, and francium) are called the **alkali metals**. All of the alkali metals have a single s electron in their valence energy level. The general form for the electron configuration of each alkali metal is ns^1, where the n refers to the highest occupied principal energy level. For example, the electron configuration of lithium (Li), the alkali metal of Period 2, is $1s^2 2s^1$. This single valence electron is what gives the alkali metals their extreme reactivity. **Figure** 6.5 shows the alkali metal element sodium.

FIGURE 6.5

Like all alkali metals, sodium is very soft. A fresh surface, which can be exposed by cutting the sample, exhibits a luster that is quickly lost as the sodium reacts with air.

All alkali metals are very soft and can be cut easily with a knife. Due to their high reactivity, they must be stored under oil to prevent them from reacting with oxygen or water vapor in the air. The reactions between alkali metals and water are particularly vigorous and include the rapid production of large quantities of hydrogen gas. Alkali metals also react easily with most nonmetals. All of the alkali metals are far too reactive to be found in nature in their pure elemental form. For example, all naturally occurring sodium exists as a compound, such as sodium chloride (table salt).

The elements in Group 2 (beryllium, magnesium, calcium, strontium, barium, and radium) are called the **alkaline earth metals** (see **Figure** 6.6). These elements have two valence electrons, both of which reside in the outermost s sublevel. The general electron configuration of all alkaline earth metals is ns^2. The alkaline earth metals are still too reactive to exist in nature as free elements, but they are less reactive than the alkali metals. They tend to be harder, stronger, and denser than the alkali metals, and they also form numerous compounds with nonmetals.

Hydrogen and Helium

Looking at the block diagram (**Figure** 6.4), you may be wondering why hydrogen and helium were not included in our discussion of the alkali metal and alkaline earth metal groups. Though hydrogen, with its $1s^1$ configuration, appears as though it should be similar to the rest of Group 1, it does not share the properties of that group. Hydrogen is a unique element that cannot be reasonably included in any single group of the periodic table. Some periodic tables even separate hydrogen's square from the rest of Group 1 to indicate its solitary status.

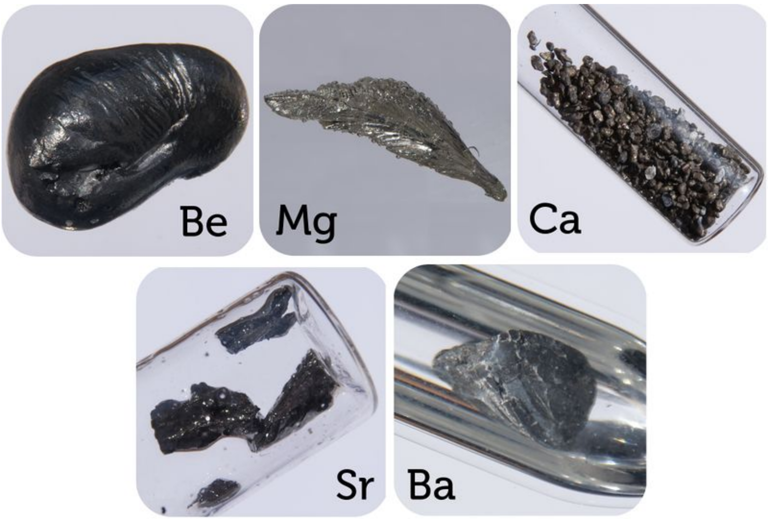


FIGURE 6.6

The alkaline earth metals include beryllium, magnesium, calcium, strontium, and barium. Strontium and barium react with air and must be stored in oil.

Helium has a configuration of $1s^2$, which would seem to place it with the alkaline earth metals. However, it is instead placed in Group 18 at the far right of the periodic table. The elements in this group, called the noble gases, are very unreactive because their outermost s and p sublevels are completely filled. Since it is part of the first period, helium does not have a p sublevel. Its filled 1s sublevel makes it very similar to the other members of Group 18.

The p-block

The p-block consists of the elements in groups 13-18. The p sublevel always fills after the s sublevel of a given principal energy level. Therefore, the general electron configuration for an element in the *p*-block is ns^2np^{1-6}. For example, the electron configuration of elements in Group 13 is ns^2np^1, the configuration of elements in Group 15 is ns^2np^3, and so on. The elements of Group 18 (helium, neon, argon, krypton, xenon, and radon) are called the **noble gases**. They are an especially important group of the periodic table because they are almost completely unreactive, due to their completely filled outermost s and p sublevels. As noted above, helium might at first seem to be out of place, because it has a configuration of $1s^2$ instead of the ns^2np^6 configuration that is characteristic of the other noble gases. However, because there are no 1p orbitals, helium also has a completely filled outermost energy level, which leads to the various chemical properties exhibited by the other noble gases.

Note that the noble gases were not a part of Mendeleev's periodic table because they had not yet been discovered. In 1894, English physicist Lord Rayleigh and Scottish chemist Sir William Ramsay detected argon as a small percentage of the atmosphere. Discovery of the other noble gases soon followed. The group was originally called the *inert gases* because they were believed to be completely unreactive and unable form compounds. However, beginning in the early 1960s, several compounds of xenon were synthesized by treating it with highly reactive fluorine gas. The name of the group was later changed to noble gases.

The number of valence electrons in elements of the p-block is equal to the group number minus 10. As an example, sulfur is located in Group 16, so it has 16 –10 = 6 valence electrons. Since sulfur is located in period 3, its outer electron configuration is $3s^23p^4$. In the older system of labeling groups, the representative elements are designated IA through VIIIA. Using this system, the number of valence electrons is equal to the number preceding the letter A. Using the same example, sulfur is a member of Group VIA, so it has 6 valence electrons.

The elements of Group 17 (fluorine, chlorine, bromine, iodine, and astatine) are called the **halogens**. The halogens all have the general electron configuration ns^2np^5, giving them seven valence electrons. They are one electron short of having full outer s and p sublevels, which makes them very reactive. They undergo especially vigorous reactions with the reactive alkali metals. In their pure elemental forms, chlorine and fluorine are gases at room temperature, bromine is a dark orange liquid, and iodine is a dark purple-gray solid. Astatine is so rare that its properties are mostly unknown.

Transition Elements

Transition elements are the elements that are found in Groups 3-12 on the periodic table. The d sublevel, which becomes increasingly filled from left to right across the period, is in a lower principal energy level than the s sublevel filled before it. For example, the electron configuration of scandium, the first transition element, is $[Ar]3d^1 4s^2$. Remember that the configuration is not written in the same order as the sublevels are filled; the 4s sublevel gets filled before electrons are placed into 3d orbitals. Because they are all metals, the transition elements are often called the transition metals (**Figure** 6.7). As a group, they display typical metallic properties but are less reactive than the metals in Groups 1 and 2. Some of the more familiar transition metals are unreactive enough to be found in nature as pure elements, such as platinum, gold, and silver.

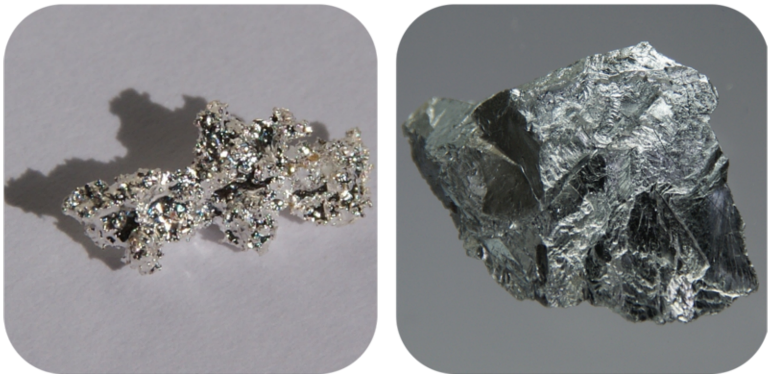


FIGURE 6.7

Silver (*left*) and chromium (*right*) are two typical transition metals.

Many transition elements make compounds that are distinctive for being vividly colored. Electron transitions that occur within the d sublevel absorb some of the wavelengths present in white light, and the wavelengths that are not absorbed are perceived by observers as the color of the compound (**Figure** 6.8).

FIGURE 6.8

Transition metal compounds dissolved in water exhibit a wide variety of bright colors. From left to right are shown solutions of cobalt(II) nitrate, potassium dichromate, potassium chromate, nickel(II) chloride, copper(II) sulfate, and potassium permanganate.

The d-block

The transition elements found in Groups 3-12 are also referred to as the d-block, since the d sublevel is in the process of being filled across the d-block from left to right. Since there are five d orbitals, each of which can accommodate two electrons, there are ten elements in each period of the d-block. The general electron configuration for elements in the d-block is $(n - 1)d^{1-10}ns^2$. The d sublevel being filled belongs to a principal energy level that is one lower than the s sublevel that has just been filled. For example, the configuration of zirconium (Zr) is $[Kr]4d^25s^2$. The group number can easily be determined from the combined number of electrons in the *s* and *d* sublevels. Zirconium is in Period 5 and Group 4.

Because electrons in the d sublevel do not belong to the outermost principal energy level, they are not valence electrons. Most d-block elements have two valence electrons, which are the two electrons from the outermost s sublevel.

The f-block

The first of the f sublevels is the 4f sublevel. It fills after the 6s sublevel, meaning that f sublevels are two principal energy levels behind. The general electron configuration for elements in the f-block is $(n - 2)f^{1-14}ns^2$. The seven orbitals of the f sublevel can each accommodate two electrons, so the f-block is 14 elements in length. It is usually shown pulled out of the main body of the periodic table and is placed at the very bottom. Because of that, the elements of the f-block do not belong to any of the numbered groups; they are wedged in between Groups 3 and 4. The **lanthanides** are the 14 elements from cerium (atomic number 58) to lutetium (atomic number 71). Most lanthanides have a partially filled 4f sublevel. They are all metals and are similar in reactivity to the Group 2 alkaline earth metals.

The **actinides** are the 14 elements from thorium (atomic number 90) to lawrencium (atomic number 103). Most actinides have a partially filled 5f sublevel. The actinides are all radioactive elements, and only the first four have been found to occur naturally on Earth. All of the others have only been artificially made in the laboratory.

Lesson Summary

- An element's placement in the periodic table is determined by its electron configuration.
- Valence electrons (those in the outermost principal energy level) dictate the chemical behavior of each element. Their relatively large distance from the nucleus makes them more available to interact with other atoms.
- Core electrons are the electrons that are closer to the nucleus and therefore do not participate in bonding.
- The periodic table is divided into 4 blocks (s, p, d, and f) based on which sublevel is in the process of being filled.
- Alkali metals, alkaline earth metals, halogens, and noble gases are the common names of groups 1, 2, 17, and 18.
- Transition elements are members of the d-block, while the f-block consists of the lanthanides and the actinides.

Review Questions

1. Sketch a periodic table, labeling the s, p, d and f blocks.
2. What can be said about the elements within a given group of the periodic table?
3. How do valence electrons and core electrons differ?
4. What blocks of the periodic table make up the representative elements?
5. Describe the relationship between the electron configuration of the alkali earth metals and their reactivity.
6. How do alkaline earth metals differ from the alkali metals?
7. Describe the properties of hydrogen and helium?
8. Why are the noble gases almost completely unreactive?
9. What are some unique properties of transition metals?

10. What block to the lanthanides and actinides belong to?
11. Use a periodic table to identify the block in which each of the following elements would be found.
    a. rubidium
    b. holmium
    c. palladium
    d. tellurium
12. Write the electron configurations for the following elements:
    a. Na
    b. Cl
    c. Zr

Further Reading / Supplemental Links

- Winter, M. (1993-2011). WebElements: the periodic table on the WWW, from http://www.webelements.com/

Points to Consider

- Archaeological evidence suggests that people have been using tin for at least 5500 years. Tin is used to form many useful alloys (mixtures of two or more metals). Bronze is an alloy of tin and copper, while solder is an alloy of tin and lead.
- Gallium melts near room temperature and has one of the largest liquid ranges of any metal, so it has found use in high temperature thermometers.
- Lead is a soft, malleable, and corrosion resistant material. The ancient Romans used lead to make water pipes, some of which are still in use today.
- Can you think of other elements which have similar uses to those listed here?

6.3 Trends in the Periodic Table

Lesson Objectives

- Describe what a noble gas configuration is and explain how elements react by losing, gaining, or sharing electrons to achieve a noble gas configuration.
- Define cation and anion, and explain the relationship between the number of electrons typically lost for a particular element and its position on the periodic table.
- Describe how ions are formed, and explain why it is easier to remove valence electrons than core electrons.
- Define atomic radius and describe the trend of atomic radius across a period and down a group of the periodic table.
- Define ionic radius and describe how and why ionic radius differs for cations and anions. Describe the trends in ionic radius.
- Define ionization energy and describe how and why ionization energy differs for cations and anions. Describe the trend in ionization energy across a period and down a group of the periodic table.

Lesson Vocabulary

- **atomic radius**: The distance from an atom's nucleus to the electrons in the outermost orbitals.
- **ion**: An atom or group of bonded atoms that has a positive or negative charge.
- **cation**: A positively charged ion.
- **anion**: A negatively charged ion.
- **ionization energy**: The energy required to remove an electron from an atom.
- **electron shielding**: When outer electrons are partially shielded from the attractive force of the protons in the nucleus by inner electrons.
- **isoelectronic**: Two atoms or ions with the same number number of electrons and therefore the same electron configurations.
- **electron affinity**: The amount of energy required for an electron to be added to a neutral atom in gas form.
- **ionic radius**: A measure of the size of an atom that is helpful in comparing the size of an ion to that of the parent atom.
- **electronegativity**: A measure of the ability of an atom to attract shared electrons when the atom is part of a compound.
- **metal**: An element that is a good conductor of heat and electricity.
- **nonmetal**: An element that is generally a poor conductor of heat and electricity.
- **metalloid**: An element with properties that are intermediate between those of metals and nonmetals.

Check Your Understanding

1. Write the electron configurations for the following atoms:
   a. Xe

  b. Pb

2. How do you determine the number of valence electrons for a given atom?

Introduction

In the last section, we studied the relationship between an element's behavior and its location on the periodic table. The characteristics of an element are largely described by the configuration of its valence electrons. In this section, we are going to look at specific properties that can be predicted by an element's position on the periodic table. Additionally, we will look at the formation of ions, including how to predict which ions are likely to form and which are not.

Atomic Radius

One important characteristic that determines the way in which elements behave is the total size of each atom. Free atoms are spherical in shape, so the relative sizes of the elements can be compared by looking at each atom's **atomic radius**, which is the distance from an atom's nucleus to the electrons in the outermost orbitals. You might expect atoms to generally grow larger as they go up in atomic number (which is equal to the total number of electrons in the neutral atom). Indeed, if you look at a single group of the periodic table, this trend holds true. Iodine is larger than bromine, which is in turn larger than chlorine and fluorine. In the case of a single group, each successive row places electrons in a higher principal energy level. Since higher energy levels are farther from the nucleus on average, this results in a larger total volume occupied by the atom.

However, when going across a period from left to right, the atomic radius actually tends to decrease. Why is this so? Each successive electron is going into the same principal energy level as the previous one, so the total amount of occupied space does not really go up significantly. Additionally, because protons are also added to the nucleus as you go across the row, the pull of the positively charged nucleus on the negatively charged electrons increases. This tighter pull leads to a slight decrease in atomic radius. As a result, the atomic radii of the elements exhibit a periodic trend, gradually tending downward, but with a sharp spike up whenever electrons are added to a new principal energy level (**Figure** 6.9).

Forming Ions

An **ion** is an atom or group of bonded atoms that has a positive or negative charge. Ions are formed when an atom gains or loses electrons from its valence shell (**Figure** 6.10). This process causes an imbalance between the number of positively charged protons and negatively charged electrons, so the overall ion will carry a net positive or negative charge.

When an atom loses one or more electrons, it becomes positively charged, because it now has more protons than electrons. A positively charged ion is called a **cation**. The charge for a cation is written as a numerical superscript after the chemical symbol, followed by a plus sign. If the ion carries a single unit of charge, the number "1" is assumed and is not written. For example, a sodium atom that loses one electron becomes a sodium ion, which is written as Na^+. A magnesium atom that loses two electrons becomes a magnesium ion, which is written as Mg^{2+}. This magnesium ion carries a 2+ charge because it now has two more protons than electrons.

When an atom gains one or more electrons, it becomes negatively charged, because it now has more electrons than protons. A negatively charged ion is called an **anion**. The charge of an anion is written in the same way as the charge

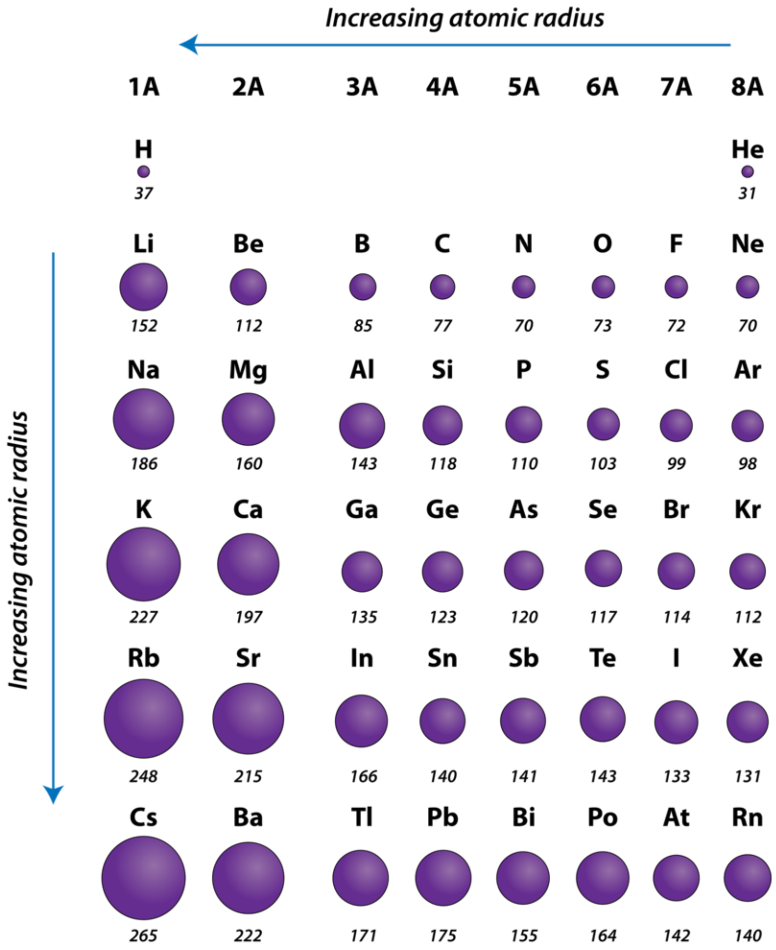


FIGURE 6.9
Atomic radii of the main group elements (pm).

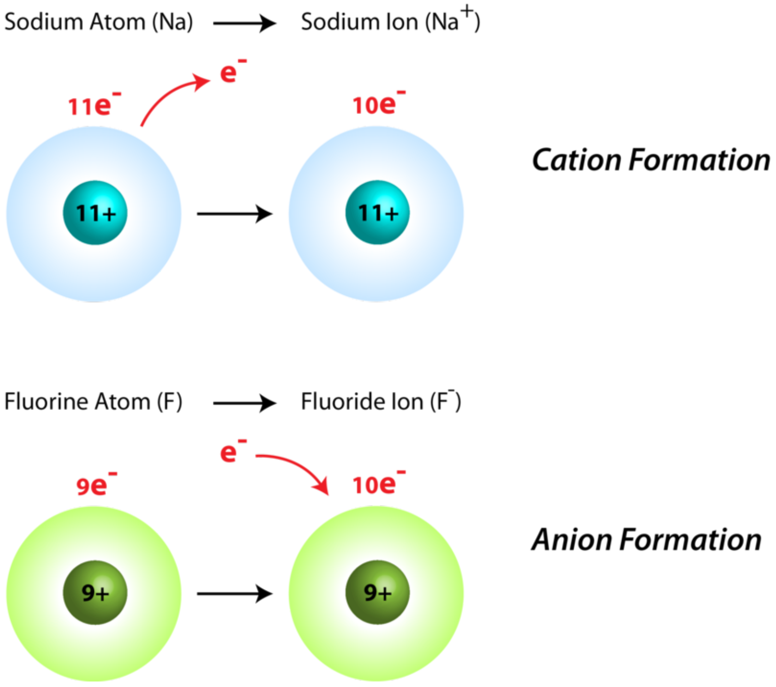


FIGURE 6.10

of a cation, except a minus sign is used instead of a plus sign. A chlorine atom that gains one electron becomes Cl^-, and a sulfur atom that gains two electrons becomes S^{2-}.

It is important to realize that atoms become ions only when the number of electrons increases or decreases. The number of protons and neutrons is not changing. Therefore the reactivity of the element may change as the valence shell configuration is changing, but the element itself remains the same.

Noble Gas Configurations

How can we predict the number of electrons that an element is likely to gain or lose in order to form a stable ion? To answer that, we look to the noble gases. Certain physical and chemical properties were found to repeat themselves in a regular pattern when the elements are arranged by their atomic number. For example, the elements on the far left of the periodic table (groups 1 and 2) tend to be quite reactive in their pure form, whereas the elements in group 18 (the noble gases) are almost completely unreactive. Because they are so unlikely to react with other chemical substances, most of them were discovered quite a bit later than the elements just before and after them on the periodic table. This lack of reactivity can largely be explained by electron configurations. The configurations of the noble gas elements are shown in **Table** 6.3.

TABLE 6.3: **Electron Configurations of the Noble Gases**

Element (Symbol)	Electron configuration
helium (He)	$1s^2$
neon (Ne)	$1s^2 2s^2 2p^6$
argon (Ar)	$1s^2 2s^2 2p^6 3s^2 3p^6$
krypton (Kr)	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$
xenon (Xe)	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$
radon (Rn)	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 4f^{14} 5d^{10} 6s^2 6p^6$

Except for helium, each of these elements has a configuration of $ns^2 np^6$ in its highest occupied principal energy level. In other words, each noble gas has 8 valence electrons, sometimes referred to as a complete octet. Having completely filled s and p orbitals in the outermost energy level represents an especially stable configuration, so noble gases have very little driving force to react any further. Conversely, other elements will readily gain, lose, or share electrons in order to achieve a stable octet of valence electrons. The number of electrons that needs to be lost or gained in order for this to occur helps us to predict the charges of ions formed by the main group elements.

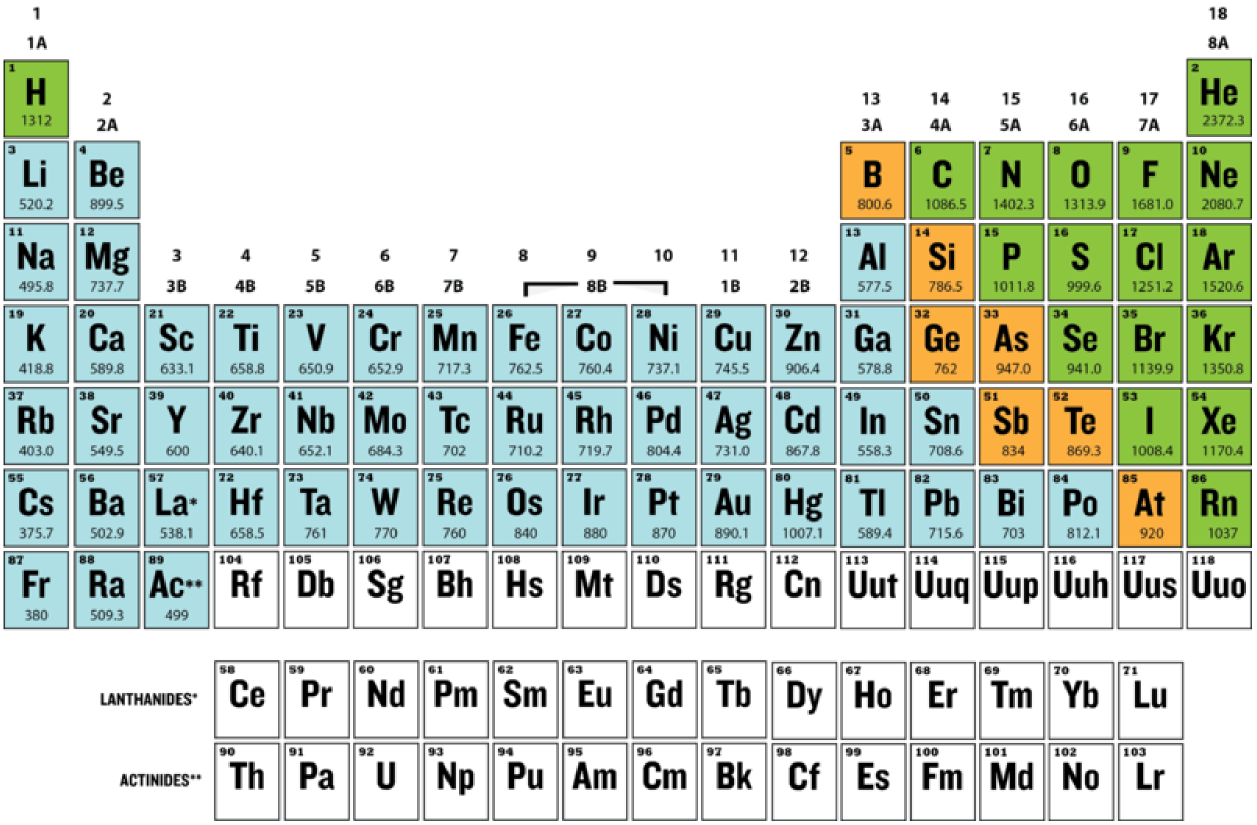
Helium may seem to be an exception, since it has only two valence electrons. This has to do with the fact that the n = 1 energy level has one s orbital and no p orbitals. As a result, the first energy level can be completely filled by just two electrons. It is the presence of a filled valence shell that gives noble gases their unusual stability, not anything intrinsic about the number 8. In addition to helium, the first few elements such as lithium, beryllium, and boron, have a particularly stable configuration with a pair of valence electrons rather that an octet.

Ionization Energy (X $\rightarrow$ X

To make an electron jump from a lower energy level to a higher energy level, there must be an input of energy. Removing the electron from the atom entirely requires even more energy. This is called an ionization process. **Ionization energy** is the energy required to remove an electron from an atom. An equation can be written to illustrate this process for a sodium atom.

$$\text{Na} + \text{energy} \rightarrow \text{Na}^+ + e^-$$

The equation shows that energy added to a sodium atom results in a sodium ion plus the removed electron (e^-). The lost electron is always a valence electron. This is because the electrons in the outermost principal energy level are furthest from the nucleus and are therefore the easiest to remove. The ionization energies of various elements (**Figure** 6.11) are influenced by the size of the atom, the nuclear charge, and the electron energy levels. Ionization energies are measured in units of kilojoules per mole (kJ/mol).



1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8	9 8B	10	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1 H 1312																	2 He 2372.3
3 Li 520.2	4 Be 899.5											5 B 800.6	6 C 1086.5	7 N 1402.3	8 O 1313.9	9 F 1681.0	10 Ne 2080.7
11 Na 495.8	12 Mg 737.7											13 Al 577.5	14 Si 786.5	15 P 1011.8	16 S 999.6	17 Cl 1251.2	18 Ar 1520.6
19 K 418.8	20 Ca 589.8	21 Sc 633.1	22 Ti 658.8	23 V 650.9	24 Cr 652.9	25 Mn 717.3	26 Fe 762.5	27 Co 760.4	28 Ni 737.1	29 Cu 745.5	30 Zn 906.4	31 Ga 578.8	32 Ge 762	33 As 947.0	34 Se 941.0	35 Br 1139.9	36 Kr 1350.8
37 Rb 403.0	38 Sr 549.5	39 Y 600	40 Zr 640.1	41 Nb 652.1	42 Mo 684.3	43 Tc 702	44 Ru 710.2	45 Rh 719.7	46 Pd 804.4	47 Ag 731.0	48 Cd 867.8	49 In 558.3	50 Sn 708.6	51 Sb 834	52 Te 869.3	53 I 1008.4	54 Xe 1170.4
55 Cs 375.7	56 Ba 502.9	57 La* 538.1	72 Hf 658.5	73 Ta 761	74 W 770	75 Re 760	76 Os 840	77 Ir 880	78 Pt 870	79 Au 890.1	80 Hg 1007.1	81 Tl 589.4	82 Pb 715.6	83 Bi 703	84 Po 812.1	85 At 920	86 Rn 1037
87 Fr 380	88 Ra 509.3	89 Ac** 499	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
		LANTHANIDES*	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
		ACTINIDES**	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

FIGURE 6.11

A periodic table showing the first ionization energies of the elements in units of kJ/mol.

As can be seen from **Figures** 6.11 and 6.12, the ionization energy of atoms generally increases from left to right across each row of the periodic table. The reason for this increase in ionization energy is the increase in nuclear charge. A nucleus containing more protons has a larger total positive charge, which results in a greater attractive force being applied to each electron. If the valence electrons are held more tightly to the nucleus by this stronger force, they are more difficult to remove, and more ionization energy is required.

However, there are periodic drops in ionization energy that correspond to electrons being added into a new, higher principal energy level. This is due to a concept called **electron shielding**. Outer electrons are partially shielded from the attractive force of the protons in the nucleus on inner electrons (**Figure** 6.13).

To explain how shielding works, consider a lithium atom, which has three protons and three electrons. Two of its electrons are in the first principal energy level, and its valence electron is in the second. The valence electron is partially shielded from the attractive force of the nucleus by the two inner electrons. Removing that valence electron is easier because of this shielding effect.

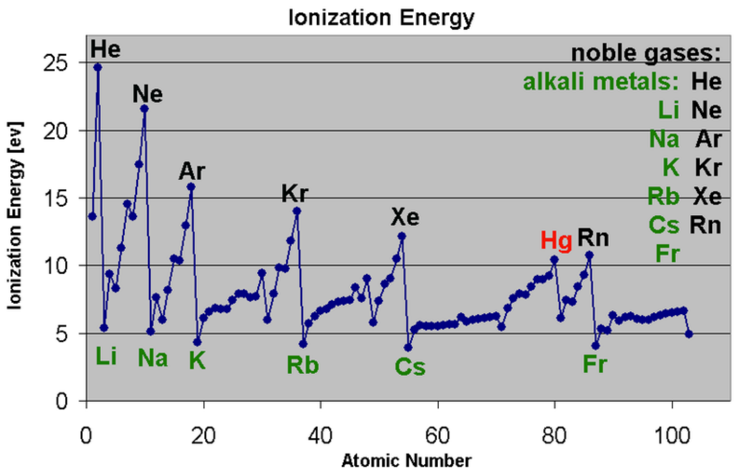


FIGURE 6.12

Graph of first ionization energy plotted against atomic number.

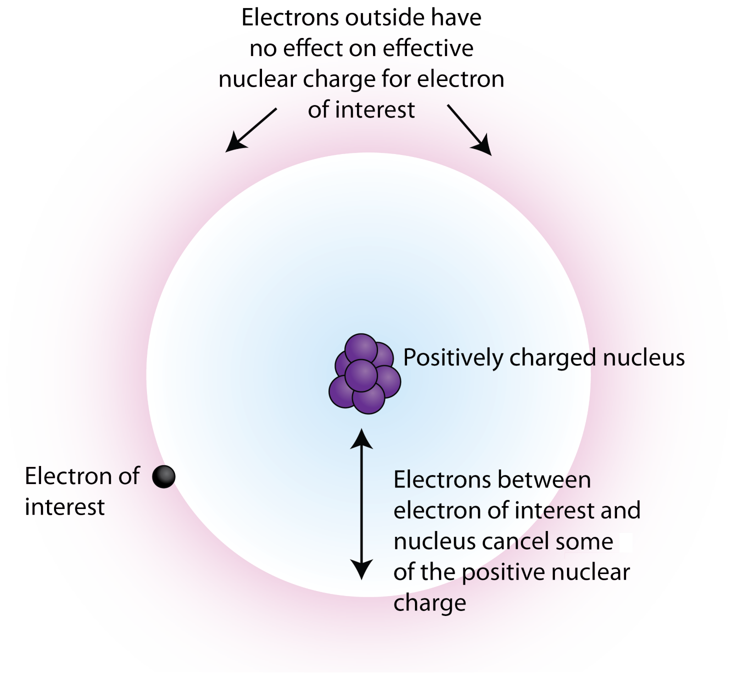


FIGURE 6.13

The interior electron cloud (in green) shields the outer electrons from the full attractive force of the nucleus. A larger shielding effect results in a decrease in ionization energy.

The ionization energies of the representative elements generally decrease from top to bottom within a group. This trend is explained by the increase in size of the atoms within a group. The valence electron that is being removed is further from the nucleus in the case of a larger atom. The attractive force between the valence electron and the nucleus weakens as the distance between them increases and as the shielding effect increases, resulting in a lower ionization energy for the larger atoms within a group. Although the nuclear charge is increased for larger atoms, the shielding effect also increases due to the presence of a larger number of inner electrons. This is particularly easy to see in the alkali metals, where the single valence electron is shielded by all of the inner core electrons.

Multiple Ionizations

So far, we have described first ionization energy and its trends for various atoms. However, in many cases, multiple electrons can be removed from an atom. If an atom loses two electrons, it acquires a 2+ charge. If an atom loses three electrons, it acquires a 3+ charge, and so on. The energies required for subsequent ionizations are called the second ionization energy (IE_2), the third ionization energy (IE_3), and so on. The first six ionization energies are shown for the elements of the first three periods in **Table** 6.4.

TABLE 6.4: **Ionization Energies (kJ/mol) of the First 18 Elements**

Element	IE_1	IE_2	IE_3	IE_4	IE_5	IE_6
H	1312					
He	2373	5251				
Li	520	**7300**	11,815			
Be	899	1757	**14,850**	21,005		
B	801	2430	3660	**25,000**	32,820	
C	1086	2350	4620	6220	**38,000**	47,261
N	1400	2860	4580	7500	9400	**53,000**
O	1314	3390	5300	7470	11,000	13,000
F	1680	3370	6050	8400	11,000	15,200
Ne	2080	3950	6120	9370	12,200	15,000
Na	496	**4560**	6900	9540	13,400	16,600
Mg	738	1450	**7730**	10,500	13,600	18,000
Al	578	1820	2750	**11,600**	14,800	18,400
Si	786	1580	3230	4360	**16,000**	20,000
P	1012	1904	2910	4960	6240	**21,000**
S	1000	2250	3360	4660	6990	8500
Cl	1251	2297	3820	5160	6540	9300
Ar	1521	2666	3900	5770	7240	8800

Notice that the second ionization energy of an element is always higher than the first, the third is always higher than the second, and so on. This is because after one ionization, a positively charged ion is formed. At this point, there is a greater overall attractive force on the remaining electrons, because the protons now outnumber the electrons. Removing a second electron is therefore more difficult.

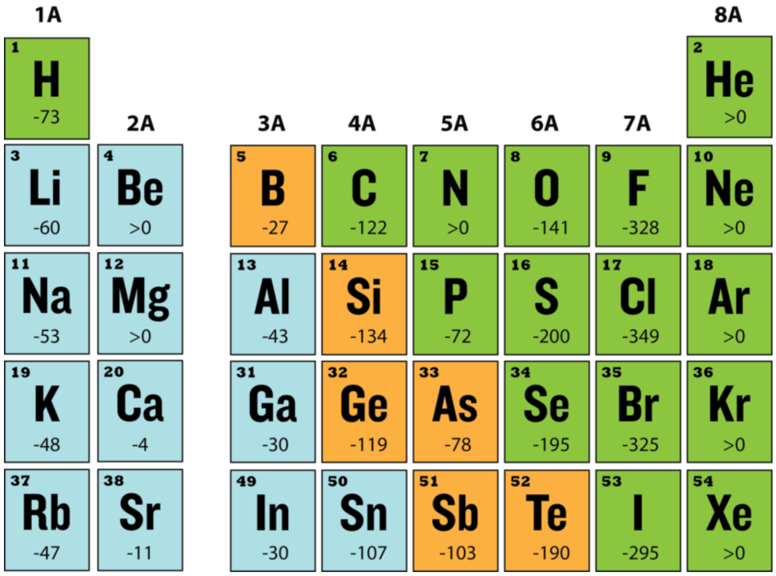
The first ionization energies for the noble gases (He, Ne, Ar) are higher than those of any other element within that period. The noble gases have full outer s and p sublevels, which gives them extra stability and makes them mostly unreactive. As we discussed above, the stability of the noble gas electron configuration applies to other elements as well. Consider the element lithium, which has a configuration of $1s^2 2s^1$. As an alkali metal, its first ionization energy is very low. After it loses its valence electron (the 2s electron), it becomes a lithium ion, Li^+, which has an electron configuration of $1s^2$. This is the electron configuration of the noble gas helium. We say that the Li^+ ion and the helium atom are **isoelectronic**, indicating that they have the same electron configuration. The second ionization energy of lithium (shaded above) shows an extremely large jump compared to the first because the removal of a second electron requires breaking apart the noble gas electron configuration. The pattern continues across each period of the table. Beryllium shows a large jump after IE_2, boron after IE_3, and so on.

Electron Affinity (X + e

Electron affinity is the amount of energy required for an electron to be added to a neutral atom in gas form. In most cases, the formation of an anion by the addition of an electron to a neutral atom releases energy. This can be shown for chloride ion formation below:

$$\mathrm{Cl} + e^- \rightarrow \mathrm{Cl}^- + \text{energy}$$

When energy is released in a chemical reaction or process, that energy is expressed as a negative number. **Figure** 6.14 shows electron affinities in kJ/mol for the main group elements.



1A	2A	3A	4A	5A	6A	7A	8A
1 H -73							2 He >0
3 Li -60	4 Be >0	5 B -27	6 C -122	7 N >0	8 O -141	9 F -328	10 Ne >0
11 Na -53	12 Mg >0	13 Al -43	14 Si -134	15 P -72	16 S -200	17 Cl -349	18 Ar >0
19 K -48	20 Ca -4	31 Ga -30	32 Ge -119	33 As -78	34 Se -195	35 Br -325	36 Kr >0
37 Rb -47	38 Sr -11	49 In -30	50 Sn -107	51 Sb -103	52 Te -190	53 I -295	54 Xe >0

FIGURE 6.14

Electron affinities (in kJ/mol) for representative elements in the first five periods. Electron affinities are written as negative numbers because energy is being released.

The elements of the halogen group (Group 17) gain electrons most readily, as can be seen from their large negative electron affinities. This means that more energy is released in the formation of a halide ion than for the anions of any other elements. Considering electron configuration, it is easy to see why. The outer configuration of all halogens is ns^2np^5. The addition of one more electron gives the halide ions the same electron configuration as a noble gas, which we have seen is particularly stable.

Period and group trends for electron affinities are not nearly as regular as those for ionization energy. In general, electron affinities increase (become more negative) from left to right across a period and decrease (become less negative) from top to bottom down a group. However, there are many exceptions.

Ionic Radius

The **ionic radius** is helpful in comparing the size of an ion to the size of its parent atom. **Figure** 6.15 compares the radii of commonly formed ions to the sizes of their parent atoms for Groups 1, 2, 13, 16 and 17. The atoms are shown in gray. Groups 1, 2, and 13 are metals that lose electrons to form cations, which are shown in green. Groups 16 and 17 are nonmetals that gain electrons to form anions, which are shown in purple.

The removal of electrons always results in a cation that is smaller than the parent atom. This is true for any cation because the remaining electrons are drawn closer to the nucleus, now that the protons outnumber the electrons. Additionally, if all of the valence electrons from a given atom are removed, the resulting ion has one fewer occupied principal energy levels, so the electron cloud that remains is considerably smaller.

The addition of electrons always results in an anion that is larger than the parent atom. More electrons results

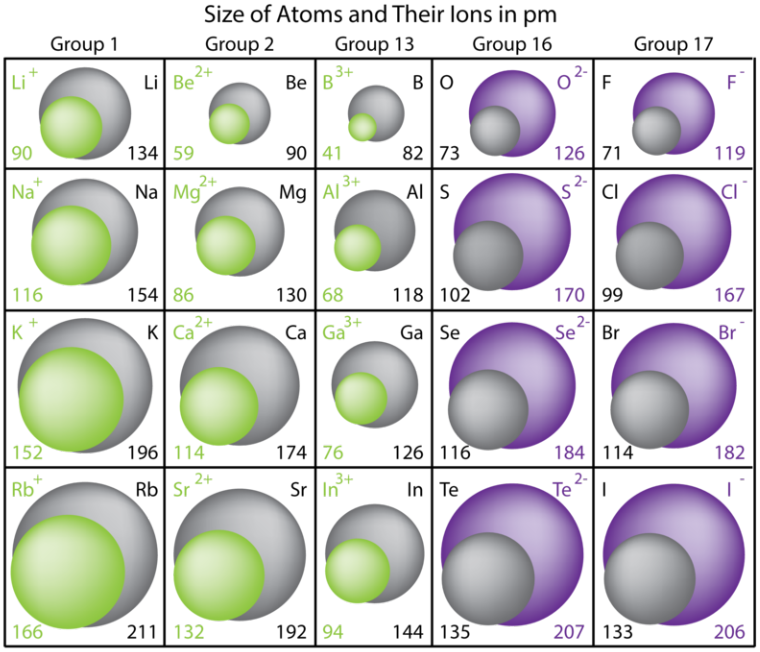


FIGURE 6.15

Atomic and ionic radii of the first five elements in Groups 1, 2, 13, 16, and 17. Atoms are shown in gray. The most common ion for each element is shown in either green (for cations) or purple (for anions).

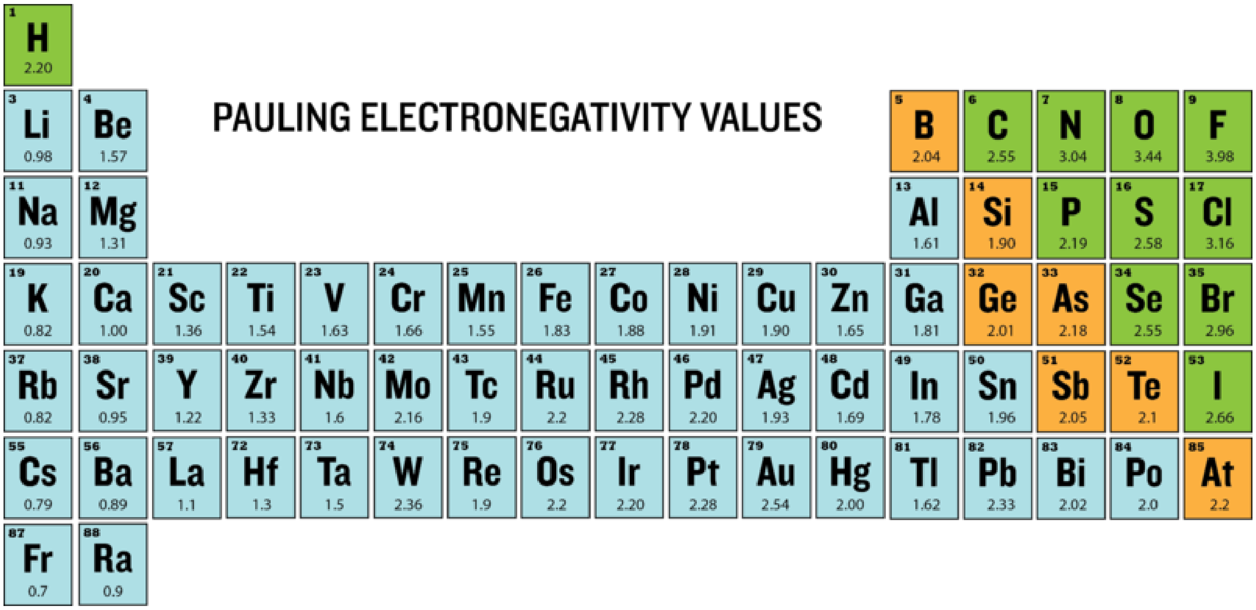
in greater electron-electron repulsions, and without any additional protons to cancel this effect, the electron cloud spreads out over a larger volume to minimize repulsive interactions.

Electronegativity

Valence electrons of both atoms are always involved when those two atoms come together to form a chemical bond. Chemical bonds are the basis for how elements combine with one another to form compounds. When these chemical bonds form, atoms of some elements have a greater ability to attract the valence electrons involved in the bond than other elements. **Electronegativity** is a measure of the ability of an atom to attract shared electrons when the atom is part of a compound. Electronegativity differs from electron affinity because electron affinity is a measure of the actual energy released when an atom gains an electron. In contrast, electronegativity is a relative scale, so it is not measured in units of energy. All elements are compared to one another, and the most electronegative element, fluorine, is assigned an electronegativity value of 3.98. Fluorine attracts shared electrons better than any other element. **Figure** 6.16 shows the electronegativity values of most elements.

Since metals have few valence electrons, they tend to increase their stability by losing electrons to become cations. Consequently, the electronegativities of metals are generally low. Nonmetals have more valence electrons and increase their stability by gaining electrons to become anions. The electronegativities of nonmetals are generally high.

Electronegativities generally increase from left to right across a period. This is due to an increase in nuclear charge because of the greater number of protons in the nucleus. Alkali metals have the lowest electronegativities, while halogens have the highest. Because most noble gases do not form compounds, they are generally not assigned electronegativity values. Note that there is little variation among the transition metals. Electronegativities generally decrease from top to bottom within a group due to the larger atomic size.



PAULING ELECTRONEGATIVITY VALUES

1 H 2.20																
3 Li 0.98	4 Be 1.57											5 B 2.04	6 C 2.55	7 N 3.04	8 O 3.44	9 F 3.98
11 Na 0.93	12 Mg 1.31											13 Al 1.61	14 Si 1.90	15 P 2.19	16 S 2.58	17 Cl 3.16
19 K 0.82	20 Ca 1.00	21 Sc 1.36	22 Ti 1.54	23 V 1.63	24 Cr 1.66	25 Mn 1.55	26 Fe 1.83	27 Co 1.88	28 Ni 1.91	29 Cu 1.90	30 Zn 1.65	31 Ga 1.81	32 Ge 2.01	33 As 2.18	34 Se 2.55	35 Br 2.96
37 Rb 0.82	38 Sr 0.95	39 Y 1.22	40 Zr 1.33	41 Nb 1.6	42 Mo 2.16	43 Tc 1.9	44 Ru 2.2	45 Rh 2.28	46 Pd 2.20	47 Ag 1.93	48 Cd 1.69	49 In 1.78	50 Sn 1.96	51 Sb 2.05	52 Te 2.1	53 I 2.66
55 Cs 0.79	56 Ba 0.89	57 La 1.1	72 Hf 1.3	73 Ta 1.5	74 W 2.36	75 Re 1.9	76 Os 2.2	77 Ir 2.20	78 Pt 2.28	79 Au 2.54	80 Hg 2.00	81 Tl 1.62	82 Pb 2.33	83 Bi 2.02	84 Po 2.0	85 At 2.2
87 Fr 0.7	88 Ra 0.9															

FIGURE 6.16

The electronegativity scale was developed by Nobel Prize winning American chemist Linus Pauling. The largest electronegativity (3.98) is assigned to fluorine, and all other electronegativity measurements are made relative to that value.

Metals and Nonmetals

Physical Properties

Elements can be classified in a number of different ways. Classifying by period and/or group is useful because it is based on electron configuration. Another way is to classify elements based on physical properties. Three broad classes of elements that are categorized in this way include metals, nonmetals, and metalloids.

A **metal** is an element that is a good conductor of heat and electricity. Metals are also malleable, which means that they can be hammered into very thin sheets without breaking, and ductile, which means that they can be drawn into wires. When a fresh surface of any metal is exposed, it will be very shiny, because it reflects light well. This property is referred to as luster. All metals are solid at room temperature except mercury (Hg), which is a liquid. The melting points of different metals vary widely. Mercury has the lowest melting point of all pure metals (−39°C), and tungsten (W) has the highest (3422°C). On the periodic table in **Figure** 6.16, the metals are shaded blue and are located to the left of the bold stair-step line. About 80 percent of the elements are metals (see examples in **Figure** 6.17).

Properties of Metals

- shiny 'metallic' appearance
- solids at room temperature (except mercury)
- high melting points
- high densities

FIGURE 6.17

The elements mercury, gold, and copper display properties that are common of metals. Mercury (*left*) is the only metal that is a liquid at room temperature. Even in its liquid form, it still has a high luster. Gold (*middle*) is malleable and can be formed into very thin sheets called gold leaf. Because copper (*right*) is ductile, inexpensive, and a good conductor, it is used extensively in electrical wiring.

- large atomic radii
- low ionization energies
- low electronegativities
- generally high deformation
- malleable (can easily be hammered out without breaking)
- ductile (can be draw out into thin wire)
- thermal conductors (transfer heat well)
- electrical conductors (transfer electricity well)

A **nonmetal** is an element that is generally a poor conductor of heat and electricity. Many properties of nonmetals are the opposite of those seen in metals. There is a wider variation in properties among the nonmetals than among the metals, as seen in **Figure** 6.18. Nonmetals exist in all three states of matter at room temperature. The majority are gases, such as nitrogen and oxygen. Bromine is a liquid, and a few are solids, such as carbon and sulfur. In the solid state, nonmetals are brittle, meaning that they will shatter if struck with a hammer. The solids are not lustrous, and their melting points are generally much lower than those of metals. On the periodic table above, the nonmetals are shaded green and appear to the right of the stair-step line.

FIGURE 6.18

Nonmetals have properties that are unlike those of metals. Sulfur (*left*) is brittle, and its distinctive yellow color lacks luster. Bromine (*center*) is the only liquid nonmetal and must be carefully handled due to its toxicity. Helium (*right*), a colorless and unreactive gas, is lighter than air and thus is used in blimps.

Properties of Nonmetals

- typically good oxidizing agents
- form acidic oxides
- have higher electronegativities

- non-lustrous
- non-conductors
- non-ductile (few exceptions)

A **metalloid** is an element with properties that are intermediate between those of metals and nonmetals. Silicon is a typical metalloid (**Figure** 6.19). It has luster like a metal, but is brittle like a nonmetal. Silicon is used extensively in computer chips and other electronics because its electrical conductivity is in between that of a metal and a nonmetal. Metalloids can also be called semimetals. On the periodic table above, the elements that are shaded orange are considered to be metalloids, and they include most of the elements that border the stair-step line. Notice that aluminum also borders the line, but it is considered to be a metal because its properties most closely resemble those of metals.

FIGURE 6.19

Elemental Silicon

Properties of Metalloids

- electronegativities between those of metals and nonmetals
- ionization energies between those of metals and nonmetals
- possess some characteristics of metals and some of nonmetals
- reactivity depends on properties of other components of the particular reaction
- often make good semiconductors

Periodic Trends in Metallic Character

Pure elements with a high metallic character, meaning those that have chemical properties most similar to properties of metals, are generally very reactive. Metals tend to lose electrons in chemical reactions, as indicated by their low ionization energies. Within a compound, metal atoms have a relatively low attraction to shared electrons, as indicated by their low electronegativity values. By following the trend summary in **Figure** 6.20, you can see that the most reactive metals would reside in the lower left portion of the periodic table. The most reactive metal that occurs naturally in reasonable quantities is cesium, which is always found in nature as a compound, never as a free element. It reacts explosively with water and will ignite spontaneously in air. Francium is below cesium in the alkali metal group, but it is so rare that many of its properties have never even been observed.

Nonmetals tend to gain electrons in chemical reactions and have a high attraction to electrons within a compound. The most reactive nonmetals reside in the upper right portion of the periodic table. Since the noble gases are an unusually unreactive group, the element fluorine is the most reactive nonmetal. It is also not found in nature as a free element. Fluorine gas reacts explosively with many other elements and compounds and is considered to be one of the most dangerous known substances.

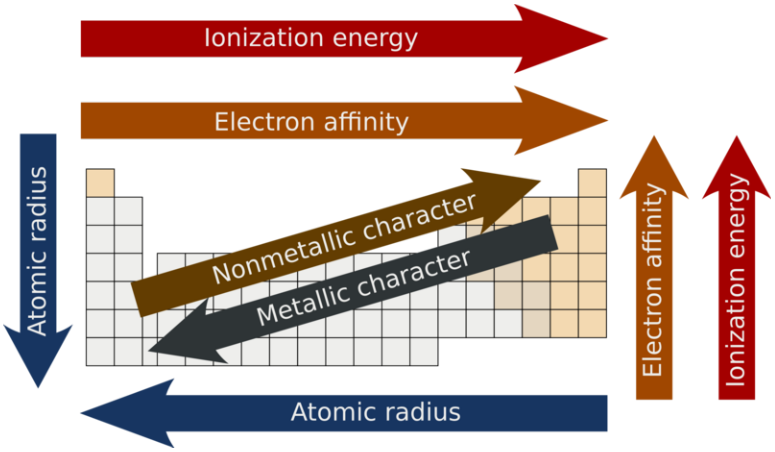


FIGURE 6.20
Summary of periodic trends within periods and groups.

Lesson Summary

- The chemical behavior of elements can largely be explained by electron configurations.
- The elements on the far left of the periodic table (groups 1 and 2) are very reactive as pure metals, while the noble gases (group 18) are almost totally unreactive.
- Ionization energy is the energy required to remove an electron from a specific atom. Ionization energy generally increases as you move left to right across the table or from bottom to top.
- Electron affinity is the energy required for an electron to be added to a neutral atom in its gaseous form. Because most atoms release energy when an electron is added, most electron affinity values are negative. These values generally become more negative (more energy is released) as you move left to right across the table or from bottom to top.
- Ionic radius helps to indicate the size of an ion as compared to its parent atom. Cations always have a smaller atomic radius than the parent atom; anions always have a larger atomic radius than the parent atom.
- When an atom gains an electron, its radius increases. Conversely, when an atom loses an electron, its radius decreases. The radius of an anion is larger than the radius of a neutral isoelectronic atom because there are fewer protons available to attract the same number of electrons. The reverse is true for cations.
- Electronegativity is a measure of the relative tendency of an atom to attract electrons to itself when chemically combined with another atom. In general, electronegativity increases as you move left to right across the table and from bottom to top.
- Periodic trends in metallic and nonmetallic characteristics mirror those of the other properties that we have discussed; the most metallic elements are at the lower left of the table, and the most nonmetallic elements are at the upper right.

Review Questions

1. Compare and contrast the characteristics of metals and nonmetals.
2. Write the electron configurations for the following ions:
   a. Li^+
   b. Be^{2+}
   c. N^{3-}
   d. O^{2-}

   e. F^-

3. Which configuration corresponds to an atom with a larger radius: $1s^22s^22p^1$ or $1s^22s^22p^6$? Identify these elements.
4. Which configuration corresponds to an atom with a larger radius: $1s^22s^22p^6$ or $1s^22s^22p^63s^23p^6$? Identify these elements.
5. Using only the periodic table, arrange each set of atoms in order of increasing atomic radius:
   a. Rb, Cs, Li
   b. B, Li, F
   c. Cl, F, Ba
   d. Rb, Be, K
   e. Cl, Al, Ba
6. Arrange each set of atoms and ions in order of increasing radius:
   a. O, O^-, O^{2-}
   b. Li^+, Li, Be^{2+}
   c. Na^+, Mg^{2+}, Al^{3+}
   d. F^-, Br^-, O^{2-}
   e. Cs^+, Ba^{2+}, Al^{3+}
7. Arrange each set of atoms in order of increasing electron affinity (least negative to most negative):
   a. Li, K, F
   b. F, O, N
   c. S, Cl, Ca
   d. I, Ba, Tl
   e. Br, Al, I
8. Pick the largest ionization energy for each set:
   a. IE_1(Li), IE_2(Li), IE_1(Be)
   b. IE_2(Cs), IE_1(Rb), IE_7(Na)
   c. IE_1(Y), IE_1(Zr), IE_3(Zr)

Further Reading / Supplemental Links

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CHAPTER 7 Chemical Nomenclature

Chapter Outline

7.1 IONIC COMPOUNDS

7.2 MOLECULAR COMPOUNDS

7.3 ACIDS AND BASES

7.4 REFERENCES

The opening image shows crystals of the mineral cinnabar, which is the most common mercury-containing ore. It is primarily composed of the compound mercuric sulfide, HgS. Cinnabar has been mined since the Stone Age for its uses as a pigment and as a source of pure mercury. Mercury can be easily harvested from cinnabar by roasting cinnabar powder (vermillion), which actually vaporizes the mercury metal. The hot mercury vapor can then be recondensed to yield pure liquid mercury.

Cinnabar is one of thousands of minerals that occur naturally on earth. Some minerals are common (like cinnabar) while others are rarer (like ores of gold and silver). Another less common mercury-containing mineral is montroydite, which is composed primarily of mercuric oxide (HgO). The composition of mercuric oxide was first determined in 1774 by the English chemist Joseph Priestley. Priestley showed that heating montroydite powder produced mercury metal and a gas, which he called phlogiston-free air. The gas was later determined to be oxygen. The revised name, based on information gained from experiments, allowed chemists to have a better understanding of chemical composition and chemical reactions. Clear unambiguous naming makes communication much easier and more reliable.

Parent Gry. commons.wikimedia.org/wiki/File:Cinabre_macl%C3%A9_%28Chine%29_.jpg. Public Domain.

7.1 Ionic Compounds

Lesson Objectives

- Define and give examples of chemical formulas for ionic compounds.
- Be able to name and write the formulas for both monatomic and polyatomic ions.
- Explain and use the Stock system for naming ionic compounds, when necessary.
- Memorize the list of polyatomic ions, including both the formulas and the charges.
- When given the chemical formula for an ionic compound, be able to write its name.
- When given the name of an ionic compound, be able to write its chemical formula.

Lesson Vocabulary

- **empirical formula**: The lowest whole-number ratio between two ions.
- **binary ionic compound**: A compound made up of a cation and an anion.
- **ternary ionic compound**: An ionic compound that is composed of more than two elements.
- **monatomic ion**: Form when a single atom gains or loses electrons.
- **polyatomic ion**: An ion composed of more than one atom.
- **oxoanion**: Anions in which one or more oxygen atoms are all bonded to a central atom of some other element.

Introduction

As we saw in the previous chapter, ions are formed when atoms gain or lose electrons. If an atom loses one or more electrons, the resulting ion has a positive charge (more protons are present than electrons). If the atom gains one or more electrons, the resulting ion has a negative charge (more electrons are present than protons). Positive ions are called cations, and negative ions are called anions. Because opposite charges attract one another, cations and anions are held together by strong electromagnetic forces. An ionic compound consists of a large three-dimensional array of alternating cations and anions. For example, sodium chloride (NaCl) is composed of Na^+ and Cl^- ions arranged into a structure like the one shown in **Figure** 7.1.

The most straightforward way to describe this structure with a chemical formula is to give the lowest whole-number ratio between the two ions, which is known as an **empirical formula**. In the case of NaCl, there are equal numbers of sodium ions and chloride ions in the salt crystal. In contrast, a crystal of magnesium chloride has twice as many chloride ions as magnesium ions, so it has a formula of $MgCl_2$.

Naming Ionic Compounds

Ionic compounds are composed of one type of cation and one type of anion. The name of an ionic compound can be formed by writing the name of the cation followed by the name of the anion. For example, NaCl is composed

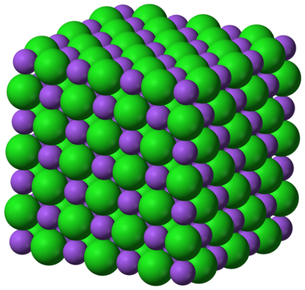


FIGURE 7.1

A crystal of table salt, sodium chloride, is a large array of alternating positive and negative ions. The purple spheres represent the Na^+ ions, while the green spheres represent the Cl^- ions.

of sodium ions (Na^+) and chloride ions (Cl^-), so its name is sodium chloride. Ionic compounds like NaCl that are composed of only two elements are referred to as **binary ionic compounds**. Similarly, KOH is composed of potassium ions (K^+) and hydroxide ions (OH^-), so its name is potassium hydroxide. Ionic compounds like KOH that are composed of more than two elements are referred to as **ternary ionic compounds**. To learn how to name various ionic compounds, we simply need to learn the names of individual ions.

Monatomic Ions

Monatomic ions form when a single atom gains or loses electrons. For the main group elements, cations are generally formed by removing all of the valence electrons from the atom. Since the numbers of valence electrons for the representative elements are constant within a particular group, all we need is the group number of a given element to know its charge when it becomes a cation. Group 1 elements form ions with a 1+ charge, Group 2 metal ions have a 2+ charge, and the ions of Group 13 elements tend to have a 3+ charge. Heavier p-block metals such as tin and lead are special cases and will be discussed with the transition metal ions. The name of a monatomic cation is the same as the name of the neutral element. For example, the sodium atom (Na) loses a single electron to form the sodium ion (Na^+), while Al^{3+} is an aluminum ion.

Anions form when an atom gains electrons. Nonmetallic atoms typically gain enough electrons to obtain the same electron configuration as the nearest noble gas. All the elements in Group 17 have seven valence electrons, which are arranged into a outer configuration of ns^2np^5. To achieve a noble gas configuration (ns^2np^6), each of these elements needs to gain just one electron, resulting in an anion with a $1-$ charge. Similarly, Group 16 elements can obtain an ns^2np^6 valence configuration by forming ions with a $2-$ charge, and the Group 15 nonmetals will form ions with a $3-$ charge. Naming anions is slightly different than naming cations. The end of the element's name is dropped and replaced with the *–ide* suffix. For example, when the chlorine atom (Cl) gains one electron, it becomes the chloride ion (Cl^-). This structure has the same electron configuration as the noble gas argon. Similarly, sulfur can gain two electrons to become the sulfide ion (S^{2-}), which also has a noble gas configuration.

Most main group elements, particularly those in groups 1, 2, 16, and 17, gain or lose enough electrons to form ions that have the same electron configuration as that of the nearest noble gas. **Table** 7.1 shows the names and charges for common monatomic ions of the representative elements:

TABLE 7.1: **Common Monatomic Ions**

1+	2+	3+	3-	2-	1-
lithium, Li^+	beryllium, Be^{2+}	aluminum, Al^{3+}	nitride, N^{3-}	oxide, O^{2-}	fluoride, F^-
sodium, Na^+	magnesium, Mg^{2+}	gallium, Ga^{3+}	phosphide, P^{3-}	sulfide, S^{2-}	chloride, Cl^-
potassium, K^+	calcium, Ca^{2+}		arsenide, As^{3-}	selenide, Se^{2-}	bromide, Br^-

TABLE 7.1: (continued)

1+	2+	3+	3-	2-	1-
rubidium, Rb^+	strontium, Sr^{2+}			telluride, Te^{2-}	iodide, I^-
cesium, Cs^+	barium, Ba^{2+}				

Transition Metal Ions

Most transition metals differ from the metals of Groups 1, 2, and 13 in that they are capable of forming more than one type of stable cation. For example, iron sometimes loses two electrons to form the Fe^{2+} ion, but it is also common for iron to lose three electrons to form the Fe^{3+} ion. Although they are members of the p block and not the d block, tin and lead also form more than one type of ion. Because the charges of these ions cannot simply determined by looking at the periodic table, they must have names that also indicate their charge. The Stock system, proposed by Alfred Stock (1876-1946), denotes the charge of these ions by using a Roman numeral in parentheses after the name of the ion. For example, the previously mentioned iron ions are named the iron (II) ion and the iron (III) ion. When said out loud, "iron (II) ion" should be read, “iron two ion.” **Table** 7.2 lists the names and formulas of some of the more common transition metal ions:

TABLE 7.2: Common Transition Metal Ions

1+	2+	3+	4+
copper (I), Cu^+	cadmium, Cd^{2+}	chromium (III), Cr^{3+}	lead (IV), Pb^{4+}
gold (I), Au^+	chromium (II), Cr^{2+}	cobalt (III), Co^{3+}	tin (IV), Sn^{4+}
silver, Ag^+	cobalt (II), Co^{2+}	gold (III), Au^{3+}	
	copper (II), Cu^{2+}	iron (III), Fe^{3+}	
	iron (II), Fe^{2+}		
	lead (II), Pb^{2+}		
	manganese (II), Mn^{2+}		
	mercury (II), Hg^{2+}		
	nickel (II), Ni^{2+}		
	platinum (II), Pt^{2+}		
	tin (II), Sn^{2+}		
	zinc, Zn^{2+}		

Notice in **Table** 7.2 that there are three cations whose names do not include a Roman numeral. Silver, cadmium, and zinc only form one common type of ion, so the charges on ions of these elements are considered to be implied by the name (1+ for silver, and 2+ for zinc and cadmium). By convention, the Stock system is not used for these elements, and their cations are named in the same way as those of the representative elements.

There is also an older system for naming some of these cations that is still occasionally used. The Latin root of the metal name is written with one of two suffixes: (1) *–ic* for the ion with a higher charge, and (2) *–ous* for the ion with a lower charge. For example, the Latin name for iron is ferrum, so the Fe^{3+} ion is called the ferric ion, and the Fe^{2+} ion is called the ferrous ion. The primary disadvantage of this system is that the suffixes do not tell you exactly what the charge is for a given ion. For copper, the two most common charges are 1+ and 2+, so Cu^{2+} is called the cupric ion and Cu^+ is the cuprous ion. The Stock system is a much more informative system and will be used as the primary method for naming transition metal compounds throughout this book.

Example 7.1

What are the names of the following compounds?

1. CuCl (composed of Cu^+ and Cl^-)

2. HgO (composed of Hg^{2+} and O^{2-})
3. Fe_2O_3 (composed of Fe^{3+} and O^{2-})
4. MnO_2 (composed of Mn^{4+} and O^{2-})

Answers:

1. copper (I) chloride
2. mercury (II) oxide
3. iron (III) oxide
4. manganese (IV) oxide

In the above example, we gave you the charges of the cations, but what if all you had was the formula? Ionic compounds must be electrically neutral, so if the charge on the anion is known, the charge of the cation can be determined from the ratio given by the formula. For example, we know that chlorine forms an ion with a charge of -1. If we see the formula CuCl, we know that copper must have a charge of +1, because in order for the charges to cancel, we would need to combine these ions in a 1:1 ratio. Similarly, the formula $CuCl_2$, we would know that copper has a charge of +2, because two Cl^- ions are required to balance out the charge of each Cu^{2+} ion. In general, the charge on the anion can be determined from inspection, and the charge on the cation can be indirectly determined from the ratio by which the cation and anion combined.

Polyatomic Ions

A **polyatomic ion** is an ion composed of more than one atom. For example, the ammonium ion consists of one nitrogen atom and four hydrogen atoms. Together, they comprise a single ion with a 1+ charge and a formula of $NH_4{}^+$. The carbonate ion consists of one carbon atom and three oxygen atoms, and it carries an overall charge of 2−. The formula of the carbonate ion is $CO_3{}^{2-}$. The atoms of a polyatomic ion are tightly bonded together, so the entire ion behaves as a single unit. **Figure** 7.2 shows several models, and **Table** 7.3 lists many of the most common polyatomic ions.

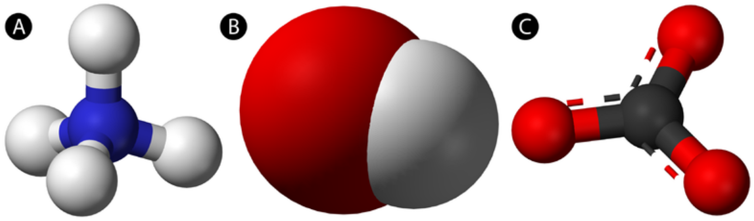


FIGURE 7.2

(A) The ammonium ion ($NH_4{}^+$) is a nitrogen atom (blue) bonded to four hydrogen atoms (white). (B) The hydroxide ion (OH^-) is an oxygen atom (red) bonded to a hydrogen atom. (C) The carbonate ion ($CO_3{}^{2-}$) is a carbon atom (black) bonded to three oxygen atoms.

TABLE 7.3: **Common Polyatomic Ions**

1-	2-	3-	1+
acetate, CH_3COO^-	carbonate, $CO_3{}^{2-}$	arsenate, $AsO_3{}^{3-}$	ammonium, $NH_4{}^+$
bromate, $BrO_3{}^-$	chromate, $CrO_4{}^{2-}$	phosphite, $PO_3{}^{3-}$	
chlorate, $ClO_3{}^-$	dichromate, $Cr_2O_7{}^{2-}$	phosphate, $PO_4{}^{3-}$	

TABLE 7.3: (continued)

1-	2-	3-	1+
chlorite, $ClO_2{}^-$	hydrogen phosphate, $HPO_4{}^{2-}$		
cyanide, CN^-	peroxide, $O_2{}^{2-}$		
dihydrogen phosphate, $H_2PO_4{}^-$	sulfate, $SO_4{}^{2-}$		
hydrogen carbonate, $HCO_3{}^-$	sulfite, $SO_3{}^{2-}$		
hydrogen sulfate, $HSO_4{}^-$			
hydrogen sulfide, HS^-			
hydroxide, OH^-			
hypochlorite, ClO^-			
nitrate, $NO_3{}^-$			
nitrite, $NO_2{}^-$			
perchlorate, $ClO_4{}^-$			
permanganate, $MnO_4{}^-$			

Oxoanions

Note that the vast majority of polyatomic ions are anions, many of which end in *–ate* or *–ite*. In some cases, such as nitrate ($NO_3{}^-$) and nitrite ($NO_2{}^-$), there are multiple anions that consist of the same two elements. This is particularly common for **oxoanions**, which are anions in which one or more oxygen atoms are all bonded to a central atom of some other element. A given element may form several oxoanions that all have the same charge but differ in the number of oxygen atoms present. When there are two common oxoanions for a particular element, the one with the greater number of oxygen atoms gets an *–ate* suffix, while the one with the lower number of oxygen atoms gets an *–ite* suffix. Some elements form more than two common oxoanions, such as chlorine:

- ClO^-, hypochlorite
- $ClO_2{}^-$, chlorite
- $ClO_3{}^-$, chlorate
- $ClO_4{}^-$, perchlorate

For larger families of oxoanions, the ion with one more oxygen atom than the *–ate* anion is given a *per-* prefix, and the ion with one fewer oxygen atom than the *–ite* anion is given a *hypo-* prefix. Organizing oxoanions in the following format (in **Table** 7.4) may help with memorization:

TABLE 7.4: **Common Oxoanions**

Central Atom	Root	1 more oxygen	"normal"	1 less oxygen	2 less oxygens
Chlorine	chlor-	$ClO_4{}^-$ *perchlorate*	$ClO_3{}^-$ chlor*ate*	$ClO_2{}^-$ chlor*ite*	ClO^- *hypo*chlor*ite*
Bromine	brom-	$BrO_4{}^-$	$BrO_3{}^-$	$BrO_2{}^-$	BrO^-
Iodine	iod-	$IO_4{}^-$	$IO_3{}^-$		
Sulfur	sulf-	$SO_5{}^{2-}$	$SO_4{}^{2-}$	$SO_3{}^{2-}$	$SO_2{}^{2-}$
Nitrogen	nitr-		$NO_3{}^-$	$NO_2{}^-$	
Phosphorus	phosph-		$PO_4{}^{3-}$	$PO_3{}^{3-}$	$PO_2{}^{3-}$
Carbon	carbon-		$CO_3{}^{2-}$		

Writing Formulas from Names

Binary Ionic Compounds

If you know the name of a binary ionic compound, you can write its formula. Start by writing the metal ion and its charge, followed by the nonmetal ion with its charge. The overall compound must be electrically neutral, so the ions must combine in a ratio that allows the positive and negative charges to cancel each other out. Consider the compound aluminum nitride. The charges on each of these ions can be determined by looking at the groups in which aluminum and nitrogen are found. The ions are:

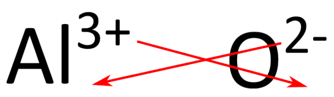
$$Al^{3+} \quad N^{3-}$$

Since the ions have charges that are equal in magnitude, 1:1 is the lowest ratio of ions that will produce a neutral compound. As a result, the formula of aluminum nitride is AlN. Another compound, lithium oxide, contains the following ions:

$$Li^{+} \quad O^{2-}$$

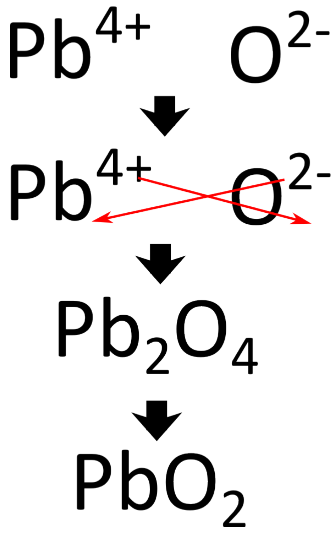
In this case, two lithium ions are required to balance out the charge of each oxide ion. The formula of lithium oxide is Li_2O.

For compounds in which the ratio of ions is not as obvious, an alternative way to determine the correct formula is to use the crisscross method. In this method, the numerical value of each charge crosses over to become the subscript of the opposite ion. The signs of the charges are dropped. The crisscross method is demonstrated below for aluminum oxide.



The red arrows indicate that the 3 from the 3+ charge will cross over to become the subscript for O, while the 2 from the 2− charge will cross over to become the subscript for Al. The formula for aluminum oxide is Al_2O_3.

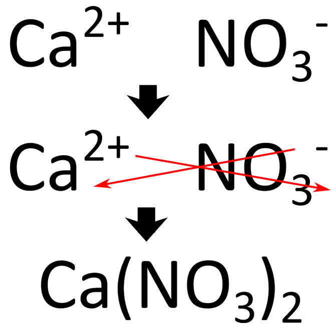
For aluminum oxide, the crisscross method directly produces the correct formula, but in some cases, another step is required. Because ionic compounds are always described by their empirical formulas, they must be written as the lowest whole-number ratio of the ions. In the case of aluminum nitride, the crisscross method would yield a formula of Al_3N_3, which is not correct. A second step must be performed in which the subscripts are reduced but the ratio is kept the same. Al_3N_3 can be reduced to AlN, because both formulas describe a 1:1 ratio of aluminum ions to nitride ions. Following the crisscross method to write the formula for lead(IV) oxide would involve the following steps:



The crisscross method first yields Pb_2O_4 for the formula, but that must be reduced to PbO_2, which is the correct formula.

Ternary Ionic Compounds

Writing a formula for a ternary ionic compound involves the same steps as for a binary ionic compound. Write the symbol and charge of the cation followed by the symbol and charge of the anion. Use the crisscross method to ensure that the final formula is neutral. For example, calcium nitrate is composed of calcium cations and nitrate anions.



The charge is balanced by the presence of two nitrate ions and one calcium ion. Parentheses are used around the nitrate ion because more than one of the polyatomic ion is needed. If only one polyatomic ion is present in a formula, parentheses are not used. For example, the formula for calcium carbonate is $CaCO_3$. The carbonate ion carries a 2− charge, so it exactly balances the 2+ charge of the calcium ion.

Lesson Summary

- Ionic compounds are composed of cations and anions, which combine in a ratio that makes the overall compound electrically neutral.
- Ionic compounds are named by writing the name of the cation followed by the name of the anion.
- Monatomic cations have the same name as their parent element, whereas monatomic anions end in *-ide*.
- For main group elements, the charges of monatomic cations and anions can be determined by looking at which group the element belongs to on the periodic table.

- Cations that can possess more than one possible charge are named by the Stock system, in which the charge is indicated in the name with Roman numerals.
- Polyatomic ions consist of more than one atom and act as a single unit. Their names and charges must be memorized.

Review Questions

1. What is the purpose of an empirical formula?
2. Define binary and ternary ionic compounds.
3. What is the difference between a monatomic and a polyatomic ion?
4. For each of the following ionic compounds, what ions are present and in what ratio?
    a. $MgBr_2$
    b. Li_2CO_3
    c. $Fe_2(SO_4)_3$
5. Predict the compound that forms when gallium combines with oxygen. What would the name of this compound be?
6. Give the formula for each of the following ionic compounds:
    a. ammonium nitrate
    b. cobalt (II) sulfate
    c. nickel (II) cyanide
    d. vanadium (III) oxide
    e. barium oxide
    f. calcium hypochlorite
7. Name the following ionic compounds:
    a. $MgBr_2$
    b. Li_2CO_3
    c. $KHSO_3$
    d. $KMnO_4$
    e. $(NH_4)_2S$
    f. CuCl
    g. $CuCl_2$
8. Write the correct formulas for the following ionic compounds:
    a. barium chloride
    b. chromium(III) oxide
    c. potassium sulfate
    d. zinc phosphate

Further Reading / Supplemental Links

- Martín-Gil, J., F. J. Martín-Gil, G. Delibes-de-Castro, P. Zapatero-Magdaleno, and F. J. Sarabia-Herrero. 1995. The first known use of vermillion. Cellular and Molecular Life Sciences 51 (8):759-761.
- "Chemical Nomenclature. Chem Team 2012." Available from http://www.chemteam.info/Nomenclature/Nomenclature.html .

Points to Consider

- Ionic compounds result from the transfer of electrons from metal atoms to nonmetal atoms, but not all compounds are ionic. A great many molecules are formed by the “sharing” of electrons rather than the complete exchange of electrons.

7.2 Molecular Compounds

Lesson Objectives

- Define a molecule and give examples of molecules.
- Be able to name a molecular compound when given its formula.
- Be able to write the formula for a molecular compound when given its name.
- Know the common names for some simple molecular compounds, such as methane (CH_4), ammonia (NH_3), phosphine (PH_3), water (H_2O), and hydrogen sulfide (H_2S).

Lesson Vocabulary

- **covalent bond**: Two or more atoms bonded together by sharing electrons.
- **molecule**: A group of atoms are joined together by covalent bonds.
- **molecular formula**: Designates how many of each atom are in a single molecule of that substance.
- **binary molecular compound**: A molecular compound that is composed of two elements.

Check Your Understanding

- Give an example of a cation and an anion.
- Give an example of an ionic compound.
- Name the following compounds: MgO, CuO.

Introduction

So far we have looked at ionic compounds, in which atoms of various elements gain or lose electrons to produce ions. The resulting ions are held together by strong attractions between oppositely charged particles. However, this only works for bonds between atoms in which one partner (the metal) has a tendency to lose electrons, and the other (the nonmetal) has a tendency to gain them. Then how might two nonmetals, such as nitrogen and oxygen, form chemical bonds? Neither is likely to lose electrons and become a cation, but both require more electrons to reach a noble gas configuration. Instead of a complete transfer of electrons, these atoms can bond by sharing electrons, producing what is called a **covalent bond**. When a group of atoms are joined together by covalent bonds, the resulting structure is called a **molecule**. Molecules are generally much smaller than the extended three-dimensional networks of ions that are seen in ionic compounds. We will look much more at covalent bonding and molecules in future chapters, but for now, we will focus on the ways in which molecules are named.

Naming Binary Molecular Compounds

A **binary molecular compound** is a molecular compound that is composed of two elements. In general, the elements that combine to form binary molecular compounds are both nonmetals. This contrasts with ionic compounds, which usually involve bonds between metal ions and nonmetal ions. Because ionic charges cannot be used to name these compounds or to write their formulas, a different naming system must be used for molecular compounds. Another difference between ionic and molecular compounds is that two nonmetal atoms will frequently combine with one another in a variety of ratios. For example, nitrogen and oxygen combine to make several binary compounds, including NO, NO_2, and N_2O. Obviously they can't all be called nitrogen oxide! How would someone know which one you were talking about? Each of the three compounds has very different properties and reactivity. A system to distinguish between compounds such as these is necessary.

Prefixes are used in the names of binary molecular compounds to identify the number of atoms of each element. **Table** 7.5 shows the prefixes for one to ten atoms:

TABLE 7.5: **Numerical Prefixes**

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

The rules for using the prefix system of nomenclature of binary molecular compounds can be summarized as follows:

1. Generally, the less electronegative element is written first in the formula, though there are a few exceptions. Carbon is almost always first in a molecular formula, and hydrogen is usually written after nitrogen in a formula such as NH_3. The order in which common nonmetals are written in binary compound formulas is the same as their order in the following series: C, P, N, H, S, I, Br, Cl, O, F.
2. The first element in the formula is written first in the name of the compound, along with the appropriate prefix. No prefix is used if there is only one atom of the first element.
3. The second element is named after the first, but the ending of the element's name is changed to -*ide*. The appropriate prefix is always used for the second element, even if there is only one atom of that element. Even though the -*ide* suffix is also used to name anions, it is important to remember that molecules are held together by covalent bonds and do not contain cations and anions.
4. The *a* or *o* at the end of a prefix is usually dropped from the name when the name of the element begins with a vowel. As an example, four oxygen atoms is tetroxide instead of tetraoxide.

Some examples of molecular compounds are listed in **Table** 7.6:

TABLE 7.6: **Examples of Molecular Compounds**

Formula	Name
NO	nitrogen monoxide

TABLE 7.6: (continued)

Formula	Name
N_2O	dinitrogen monoxide
S_2Cl_2	disulfur dichloride
Cl_2O_7	dichlorine heptoxide

Notice that the mono- prefix is not used with the nitrogen in the first compound, but is used with the oxygen in both of the first two examples. Also, the *o* of mono- and the *a* of hepta- are dropped from the name when paired with oxide.

The example S_2Cl_2 emphasizes another difference between ionic and molecular substances. Because ionic substances exist as extended networks, we simply give the lowest whole-number ratio of cations to anions, which is the empirical formula. A molecular formula is not simply a ratio. Rather, the **molecular formula** designates how many of each atom are in a single molecule of that substance. S_2Cl_2 cannot be reduced to SCl, because each molecule of disulfur dichloride contains two sulfur atoms and two chlorine atoms.

Example 7.2

Name the following binary compounds.

1. BF_3
2. NO
3. N_2O_5
4. PCl_5
5. P_4O_6

Answer:

1. boron trifluoride
2. nitrogen monoxide
3. dinitrogen pentoxide
4. phosphorous pentachloride
5. tetraphosphorous hexoxide

Writing Formulas for Binary Molecular Compounds

When you know the name of a molecular compound, the prefixes directly tell you which subscript to place with that element in the formula. If there is no prefix, only one atom of that element is present and no subscript is used. For example, if given the name diboron hexahydride, you would realize that the molecule must contain two atoms of boron and six atoms of hydrogen. Its formula is B_2H_6. Notice that metalloids like boron generally form molecular compounds instead of ionic compounds.

Other Ways of Naming Molecules

Common Names

Some compounds (generally very common ones) are better known by names that are different than the "official" names, which are designated by the International Union of Pure and Applied Chemistry (IUPAC). A few examples can be found in the following **Table** 7.9:

TABLE 7.7: Common Names of Covalent Compounds

Formula	Common name	IUPAC Name
NO	nitric oxide	nitrogen monoxide
N_2O	nitrous oxide (laughing gas)	dinitrogen monoxide
N_2H_4	hydrazine	dinitrogen tetrahydride
H_2O	water	dinitrogen monoxide
NH_3	ammonia	nitrogen trihydride
PH_3	phosphine	phosphorus trihydride
H_2S	hydrogen sulfide	dihydrogen monosulfide
H_2O_2	hydrogen peroxide	dihydrogen dioxide

Nomenclature for Organic Molecules

Carbon has a unique ability to form an extremely large variety of molecules with just a few other common elements. In fact, most of the molecules that make up living beings are composed of just carbon, hydrogen, oxygen, and nitrogen (with a little sulfur and phosphorus as well). Knowing only the molecular formula for an organic molecule is not enough to identify it; we also need to indicate how the atoms are arranged within the molecule. For example, dimethyl ether and ethanol are two molecules with very different properties that both have the molecular formula C_2H_6O. One is an extremely flammable gas, and the other is the intoxicating liquid found in alcoholic beverages. As a result, most carbon-based molecules have a separate, more complex system of naming that we will cover in another chapter. However, the formulas for a few common organic compounds can be found in the **Table** 7.11:

TABLE 7.8: Names of Common Organic Compounds

Formula	Name
CH_4	methane
CH_3OH	methanol
C_2H_6	ethane
C_2H_5OH	ethanol
C_3H_7OH	isopropanol (rubbing alcohol)
$C_6H_{12}O_6$	glucose
$C_{12}H_{22}O_{11}$	sucrose

Lesson Summary

- Molecular compounds are formed when atoms are held together by covalent bonds, which involve sharing electrons rather than transferring them.
- The formula of a binary molecular compound shows how many of each atom are present in the molecule. The less electronegative element is generally written first.
- Prefixes are used in the names of molecular compounds to designate how many of each atom are in the molecule.

Review Questions

1. How is a covalent bond characterized?

2. What differs between ionic compounds and molecules?
3. What are binary molecular compounds?
4. What differs between a molecular formula and an empirical formula?
5. Give the formula for each of the following binary covalent compounds:
    a. carbon dioxide
    b. phosphorus triiodide
    c. sulfur dichloride
    d. boron trifluoride
    e. dioxygen difluoride
    f. xenon trioxide
6. Name the following binary covalent compounds:
    a. N_2F_4
    b. HBr
    c. SF_4
    d. BCl_3
    e. P_2O_5
    f. ClF_3
7. Is "nitrogen oxide" an appropriate name for the compound NO? Why or why not?
8. Is "calcium oxide" an appropriate name the compound CaO? Why or why not?

Further Reading / Supplemental Links

- Winter, M. (1993-2011). WebElements: the periodic table on the WWW, from http://www.webelements.com/

7.3 Acids and Bases

Lesson Objectives

- Define and give examples for the following terms: acid, base, binary acid, oxoacid.
- Determine the name of an inorganic acid or base when given the formula.
- Determine the formula of an inorganic acid or base when given its name.

Lesson Vocabulary

- **acid**: Any compound that produces hydrogen ions (H+) when dissolved in water.
- **binary acid**: Acids in which one or more acidic hydrogen atoms are bound directly to a single atom.
- **oxoacid**: A strong acid produced by combining oxoanions with one or more hydrogen ions.
- **base**: A compound that produces the hydroxide (OH-) ion when dissolved in water.

Check Your Understanding

1. Name the following compounds:
    a. $NaNO_3$
    b. BF_3
    c. $FeSO_3$
2. Are the following compounds molecular or ionic?
    a. H_2O
    b. CH_4
    c. $BaSO_4$

Introduction

In this chapter, we first looked at the naming conventions for ionic compounds, which exist as extended networks of cations and anions. For most of the compounds that we considered, the cation was a monatomic metal (e.g., Na^+, Mg^{2+}, Fe^{3+}), and the anion was a monatomic nonmetal (e.g., Cl^-, O^{2-}, N^{3-}) or a polyatomic ion, which often contains multiple oxygen atoms (e.g., ${SO_4}^{2-}$). We then looked at molecular compounds, in which atoms are held together into individual molecules by covalent bonds. Now we are going to consider acids and bases, which share characteristics with both ionic and molecular compounds.

Acids

There are multiple ways to define what an acid is, but for the purposes of this book, we will define an **acid** as any compound that produces hydrogen ions (H^+) when dissolved in water. Based on this definition, all acids contain at least one hydrogen atom, but not all hydrogen-containing compounds are acids. When isolated as a pure material, most acids exist as molecular substances. However, when dissolved in water, one or more of the hydrogen atoms acts as an H^+ ion that transfers to water, leaving behind the remainder of the molecule as an anion. This reaction with water can be represented by the following generic equation, where HA represents an acid:

$$HA_{(aq)} + H_2O_{(l)} \rightarrow A^-_{(aq)} + H_3O^+_{(aq)}$$

As you can see, the acid reacts with a molecule of water to produce a hydronium ion (H_3O^+) and the A^- anion. (Note: The H^+ ion is sometimes referred to as a proton. This makes sense when you consider that the most common form of the hydrogen atom consists of one proton and one electron. When the single electron is removed to make a cation, only a proton is left behind. As a result, the above reaction is sometimes referred to as a proton transfer.) A specific example of this process can be seen in the following animation:

http://group.chem.iastate.edu/Greenbowe/sections/projectfolder/animations/HCl(aq).html

In this animation, hydrochloric acid (HCl) reacts with water to produce the hydronium ion and the chloride ion. Even though HCl exists as a molecular gas in the absence of water, it produces ions when water is present. Acids have some unique properties and reactivity patterns that we will discuss in future chapters. For now, we will focus on the ways in which they are named.

Binary Acids

Binary acids are acids in which one or more acidic hydrogen atoms are bound directly to a single atom. As a result, the anion left behind when a binary acid is dissolved in water is a monatomic anion. Examples include hydrogen chloride ($HCl_{(g)}$ and hydrogen sulfide ($H_2S_{(g)}$). Both of these substances are molecular gases in their pure form, but change their properties and their names when dissolved in water. To name a binary acid, start with the name of the anion left behind after the acidic hydrogens have been removed. Then, add the prefix *hydro-* and replace the suffix *-ide* with *-ic acid*. For example, HCl produces Cl^- ions when dissolved in water, so it would therefore be named hydrochloric acid. Some other common binary acids are shown in the following **Table** 7.9:

TABLE 7.9: **Common Binary Acids**

Formula	Name	Anion	Name
$HF_{(aq)}$	hydrofluoric acid	F^-	fluoride
$HCl_{(aq)}$	hydrochloric acid	Cl^-	chloride
$HBr_{(aq)}$	hydrobromic acid	Br^-	bromide
$HI_{(aq)}$	hydroiodic acid	I^-	iodide
$H_2S_{(aq)}$	hydrosulfuric acid	S^{2-}	sulfide

Most of the binary acids listed here are monoprotic, because they have only one acidic hydrogen. Hydrosulfuric acid, on the other hand is diprotic. Its hydrogen ions are transferred to two water molecules in two subsequent reactions.

Oxoacids

So far we have looked at acids that leave behind monatomic anions. However, many strong acids leave behind polyatomic anions as well. In particular, many of the oxoanions we looked at earlier can combine with one or more hydrogen ions (enough to make a neutral molecule) to produce strong acids called **oxoacids**. A common example of an oxoacid is nitric acid (HNO_3), which can be thought of as a hydrogen ion (H^+) combining with a nitrate ion ($NO_3{}^-$). If we simply named this as an ionic compound, we could name the compound hydrogen nitrate. However, because nitric acid exists as individual molecules and not an ionic structure, we use a different convention. To name an oxoacid, look at the anion that will be left behind when all acidic hydrogens have been removed. If it ends in *-ate*, replace that suffix with *-ic acid*. If it ends in *-ite*, replace that suffix with *-ous acid*. The following **Table** 7.10 lists some common oxoacids and their formulas:

TABLE 7.10: **Common Oxoacids**

Formula	Name	Anion	Name
$HClO_4$	*per*chlor*ic* acid	$ClO_4{}^-$	*per*chlor*ate*
$HClO_3$	chlor*ic* acid	$ClO_3{}^-$	chlor*ate*
$HClO_2$	chlor*ous* acid	$ClO_2{}^-$	chlor*ite*
$HClO$	*hypo*chlor*ous* acid	ClO^-	*hypo*chlor*ite*
HNO_3	nitr*ic* acid	$NO_3{}^-$	nitr*ate*
HNO_2	nitr*ous* acid	$NO_2{}^-$	nitr*ite*
H_2SO_4	sulfur*ic* acid	$SO_4{}^{2-}$	sulfate
H_2SO_3	sulfur*ous* acid	$SO_3{}^{2-}$	sulf*ite*
H_2CO_3	carbon*ic* acid	$CO_3{}^{2-}$	carbon*ate*
H_3PO_4	phosphor*ic* acid	$PO_4{}^{3-}$	phosph*ate*

Example 7.3

Name the following compounds:

1. HIO_3
2. $NaBrO_2$
3. $Ca_3(PO_4)_2$
4. H_3PO_3

Answer:

1. iodic acid
2. sodium bromite
3. calcium phosphate
4. phosphorous acid

Bases

Bases can also be defined in multiple ways, but for now, we will define a **base** as a compound that produces the hydroxide (OH^-) ion when dissolved in water. Most of the common strong bases that you will need to deal with are simply ionic compounds in which a metal cation is combined with the hydroxide anion. These bases are named in the same way as any other ionic compound. For example, NaOH would be named sodium hydroxide, and $Ca(OH)_2$ is calcium hydroxide.

Some common bases are listed in the **Table** 7.11:

TABLE 7.11: **Examples of Bases**

Formula	Name
NaOH	sodium hydroxide
$Ca(OH)_2$	calcium hydroxide
NH_4OH	ammonium hydroxide

Lesson Summary

- Acids are molecular compounds that dissolve in water to produce hydronium ions and an anion.

$$HA_{(aq)} + H_2O_{(l)} \rightarrow A^-_{(aq)} + H_3O^+_{(aq)}$$

- The naming rules for acids are based on the suffix of the anion. Formulas for acids are written by balancing out the charge of the anion with the appropriate number of hydrogen ions.
- Bases are ionic compounds consisting of hydroxide ions and a cation. Naming and formula writing for bases follows the same guidelines as for other ionic compounds.

Review Questions

1. How do acids behave in water?
2. What defines a binary acid?
3. What defines an oxoacid?
4. How do bases behave in water?

5. Complete the following **Table** 7.12:

TABLE 7.12: **Review Question 1**

#	Acid Name	Formula of Acid	Name of Anion
1.	hydrobromic acid	HBr	bromide
2.	carbonic acid	H_2CO_3	carbonate
3.		HCl	
4.			sulfite
5.	chlorous acid		
6.	nitric acid		
7.			sulfide
8.		HNO_2	
9.	chromic acid		
10.			phosphate

6. Name the following acids:

   (a) HF
   (b) HI

   (c) H_2S
   (d) H_3PO_4
   (e) H_2SO_4

7. Write the formulas for the following acids:
   (a) sulfurous acid
   (b) hydrosulfuric acid
   (c) nitric acid
   (d) carbonic acid
   (e) chloric acid

Further Reading / Supplemental Links

- Chemical Nomenclature. (2012), from http://www.chemteam.info/Nomenclature/Nomenclature.html
- Video on acid-base nomenclature: http://www.youtube.com/watch?v=CVgi74kswPA

Points to Consider

- Vinegar is an acid that can be produced from the aerobic fermentation of wine. In fact, vinegar is most likely the oldest known acid. It is commonly used as a food additive (to give things an acidic or sour taste) and as a mild cleaning agent.

7.4 References

1. Ben Mills (User:Benjah-bmm27/Wikimedia Commons). http://commons.wikimedia.org/wiki/File:Sodium-chloride-3D-ionic.png . Public Domain
2. Ben Mills (User:Benjah-bmm27/Wikimedia Commons). (A) http://commons.wikimedia.org/wiki/File:Ammonium-3D-balls.png; (B) http://commons.wikimedia.org/wiki/File:Hydroxide-3D-vdW.png; (C) http://commons.wikimedia.org/wiki/File:Carbonate-3D-balls.png . Public Domain

CHAPTER 8 Ionic and Metallic Bonding

Chapter Outline

8.1 IONS
8.2 IONIC BONDS AND IONIC COMPOUNDS
8.3 METALS AND METALLIC BONDS
8.4 REFERENCES

The image above shows the largest gold nugget ever discovered in California, weighing 156 ounces. Gold is widely used for money, decorative purposes, and various practical applications in fields such as dentistry, electronics, and medicine. Its high malleability, ductility, ability to conduct electricity, and resistance to corrosion and most other chemical reactions make it a highly desirable material in things like electric wiring, colored-glass production, and corrosion-resistant jewelry and dishes. Gold is also one of the few metals that occurs naturally in its pure form. Due to their tendency to form cations, most naturally occurring metals are found as part of ionic compounds. For example, aluminum is the most abundant metal on earth, but it is rarely found in its elemental form. Instead, it is found as the mineral bauxite, an ionic substance composed of aluminum cations and oxygen anions. Pure aluminum must be extracted from minerals like bauxite through chemical means. Pure metals have very different properties than the ionic compounds that they can form with various nonmetals. Additionally, metals can be mixed together to make alloys that have different properties than either parent metal. In this chapter, we will investigate and compare some of these different types of substances.

Chris Ralph (User:Reno Chris/Wikipedia). commons.wikimedia.org/wiki/File:Stringer156_nugget.jpg. Public Domain.

8.1 Ions

Lesson Objectives

- Explain how the periodic table can be used to predict the likely charges for ions of a given element.
- Depict atoms and ions using electron dot notation.
- Describe the octet rule and how it is used to explain chemical behavior.
- Define and describe the arrangement of the valence electrons for a given chemical species.

Lesson Vocabulary

- **octet rule**: States that elements tend to form compounds in ways that give each atom eight valence electrons.
- **Lewis electron dot structure**: A diagram for a chemical substance in which each element is represented by its symbol and each valence electron is represented by a single dot.
- **isoelectronic**: Two atoms or ions with the same number of electrons.
- **cation**: A positively charged ion.
- **anion**: A negatively charged ion.

Check Your Understanding

- How do ions differ from atoms? What types of elements form cations, and what types of elements form anions?

Introduction

As we studied in our chapter on the periodic table, we saw that elements share a number of important properties with other elements found in the same group. The chemical behavior of a given element is largely dictated by the configuration of its valence electrons. Many elements have a tendency to gain or lose electrons in order to achieve a more stable configuration. When a neutral atom gains or loses electrons, it becomes an ion. In this lesson, we will look at ways to predict what type of ion a given element is likely to form.

Octet Rule

The noble gases are unreactive because of their electron configurations. American chemist Gilbert Lewis (1875-1946) used this observation to explain the types of ions and molecules that are formed by other elements. He called his explanation the octet rule. The **octet rule** states that elements tend to form compounds in ways that give each atom eight valence electrons. An exception to this rule is the elements in the first period, which are particularly stable when they have two valence electrons. A broader statement that encompasses both the octet rule and this exception is that atoms react in order to achieve the same valence electron configuration as that of the nearest noble gas. Most noble gases have eight valence electrons, but because the first principal energy level can hold a maximum of two electrons, the first noble gas (helium) needs only two valence electrons to fill its outermost energy level. As a result, the nearby elements hydrogen, lithium, and beryllium tend to form stable compounds by achieving a total of two valence electrons.

There are two ways in which atoms can satisfy the octet rule. One way is by sharing their valence electrons with other atoms, which will be covered in the next chapter. The second way is by transferring valence electrons from one atom to another. Atoms of metallic elements tend to lose all of their valence electrons, which leaves them with an octet from the next lowest principal energy level. Atoms of nonmetallic elements tend to gain electrons in order to fill their outermost principal energy level with an octet.

Electron Dot Diagrams

A common way to keep track of valence electrons is with **Lewis electron dot structures**. In an electron dot structure, each atom is represented by its chemical symbol, and each valence electron is represented by a single dot. Note that only valence electrons are shown explicitly in these diagrams. For the main group elements, the number of valence electrons for a neutral atom can be determined by looking at which group the element belongs to. In the s block, Group 1 elements have one valence electron, while Group 2 elements have two valence electrons. In the p block, the number of valence electrons is equal to the group number minus ten. Group 13 elements have three valence electrons, Group 14 elements have four, and so on. The noble gases in Group 18 have eight valence electrons, and the full outer s and p sublevels are what give these elements their special stability. Representative dot diagrams are shown in the **Figure** 8.1:

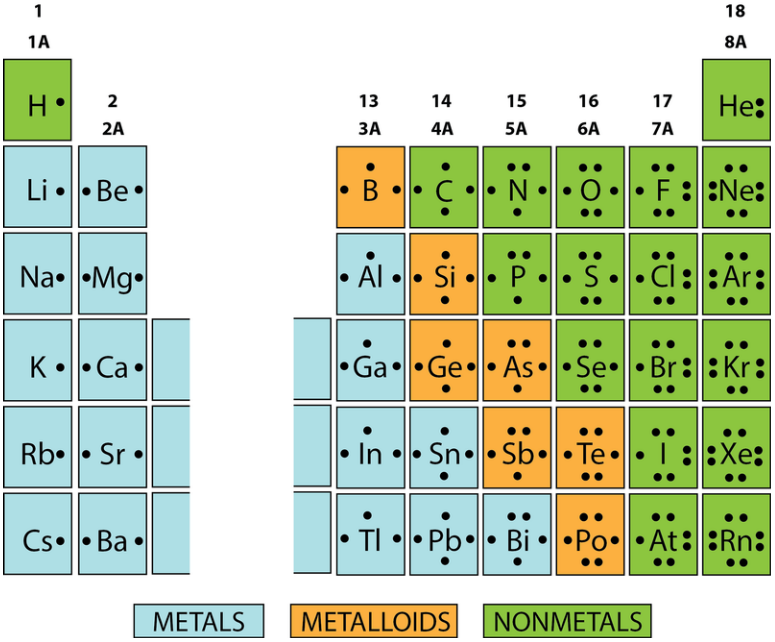


FIGURE 8.1

The image shown here displays dots circling each elemental symbol. Elements will typically gain, lose or share electrons to achieve an octet. Only one group of elements (the noble gases) has a complete octet as neutral atoms.

Cations and Anions

Metals will typically lose electrons to achieve stability, while non-metals typically gain electrons to achieve stability. Two atoms or ions with the same number of electrons are referred to as **isoelectronic**.

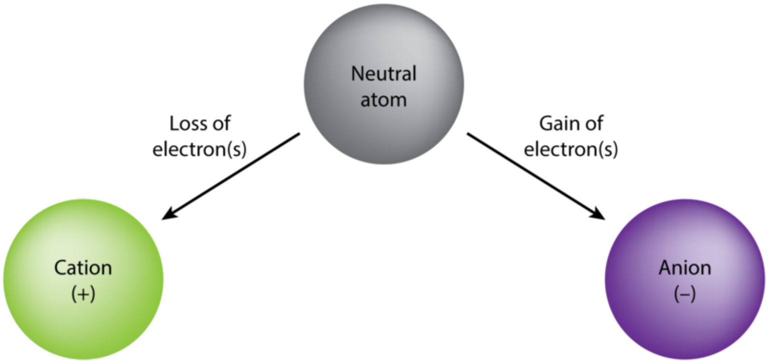


FIGURE 8.2

Cations and Anions

Cations

A positively charged ion is called a **cation**. Main group metals will typically form ions by losing enough electrons to become isoelectronic with the nearest noble gas. For example, lithium, whose configuration is [1s^{2}2s^1], will typically lose one electron to become isoelectronic with helium, which has a configuration of [1s^2] (see **Figure** 8.1).

$$\underset{[He]2s^1}{Li} \rightarrow \underset{[He]}{Li^+} + \mathrm{e}^-$$

Similarly, beryllium has 4 electrons (with the configuration [1s^{2}2s^2]), so it prefers to lose two electrons, in order to become isoelectronic with helium (again, [1s^2]).

$$\underset{[He]2s^2}{Be} \rightarrow \underset{[He]}{Be^{2+}} + 2\mathrm{e}^-$$

Transition Metal Cations

As we saw in our chapter on the periodic table, the valence electrons for transition metals are variable, and electrons in the highest occupied d orbitals (which are not part of the valence shell) may or may not be lost in the formation of a transition metal cation. As a result, many transition metals commonly form more than one type of cation, depending on how many d electrons are lost. **Figure** 8.3 depicts some of the typical electron arrangements for the transition elements.

Anions

A negatively charged ion is called an **anion**. Nonmetals will typically form ions by gaining enough electrons to become isoelectronic with the nearest noble gas. For example, fluorine has 7 valence electrons and is one electron away from being isoelectronic with neon, which has a stable noble gas electron configuration (see **Figure** 8.1).

$$\underset{[He]2s^2 2p^5}{F} + \mathrm{e}^- \rightarrow \underset{[He]2s^2 2p^6\ or\ [Ne]}{F^-}$$

Oxygen has 6 valence electrons in its ground state. Remember that ground state refers to the neutral atom in which the electrons occupy the lowest possible energy positions. Oxygen is two electrons away from being isoelectronic

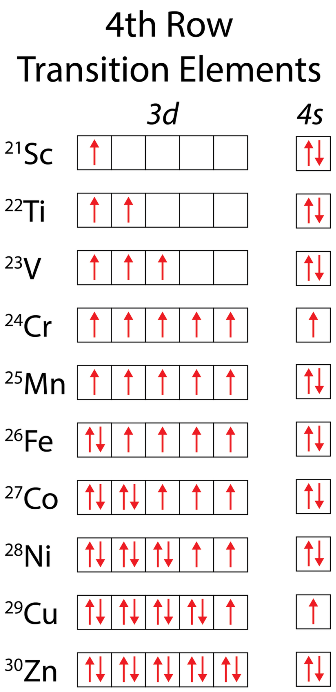


FIGURE 8.3

This image shows the arrangement of electrons in their native, chemically neutral state. Notice that chromium and manganese have a half-filled d shell. Copper and zinc have fully filled d shells.

with the nearest noble gas. Oxygen will therefore form ions by gaining two electrons to become isoelectronic with neon, as shown below:

$$\underset{[He]2s^2 2p^4}{O} + 2e^- \rightarrow \underset{[He]2s^2 2p^6 \text{ or } [Ne]}{O^{2-}}$$

Similarly, nitrogen has five valence electrons in it ground state, which is three electrons away from the nearest noble gas. Nitrogen can gain three electrons to become isoelectronic with neon:

$$\underset{[He]2s^2 2p^3}{N} + 3e^- \rightarrow \underset{[He]2s^2 2p^6 \text{ or } [Ne]}{N^{3-}}$$

Example 8.1

Write the ground state configuration for the nonmetal sulfur, and predict the ion it must form to be isoelectronic with the nearest noble gas.

Answer:

The ground state configuration for the nonmetal sulfur is written as: $1s^2 2s^2 2p^6 3s^2 3p^4$. Sulfur has 16 electrons. The nearest noble gas to sulfur is argon, which has an electron configuration of: $1s^2 2s^2 2p^6 3s^2 3p^6$. To be isoelectronic with argon, which has 18 electrons, sulfur must gain two electrons. Therefore sulfur will form a 2- ion, becoming S^{2-}.

Lesson Summary

- Atoms or groups of atoms that carry an overall electrical charge are referred to as ions. Cations can be formed when a neutral species loses electrons, while anions are formed when a neutral species gains electrons.
- Particularly for main group elements, the number of electrons a given element has in its outer (valence) shell largely determines the chemical behavior of that element.
- The octet rule states that atoms will lose, gain, or share electrons to achieve the electron configuration of the

nearest noble gas (8 valence electrons, except for helium, which has 2).

- Electron dot diagrams are used to help us visualize the arrangement of valence electrons in a given chemical species.
- When an element loses one or more electrons, a cation is formed. Metals typically become cations when they interact with other chemical species.
- Some transition metals can produce ions with multiple different charges due to the optional participation of d electrons.
- When an element gains one or more electrons, an anion is formed. Nonmetals typically become anions when they interact with other chemical species.

Review Questions

1. Draw electron dot diagrams for one metal and one nonmetal.
2. Predict whether each of the following is more likely to become a cation or an anion.
    (a) Ca
    (b) Na
    (c) F
    (d) Br
    (e) S
3. Write the ground state electron configurations for the following elements, and predict the ion that will form when each atom becomes isoelectronic with the nearest noble gas.
    (a) Be
    (b) Mg
    (c) O
    (d) Al
4. Describe the change that is happening when Li → Li^+.
5. What would be the electron configuration for Mg^-? Use the octet rule to explain why this is not likely to be a very stable ion.
6. What would be the electron configuration for F^+? Use the octet rule to explain why this is not likely to be a very stable ion.
7. Element X has a total of 16 electrons.
    (a) Write the electron configuration for element X.
    (b) How many electrons away from a complete octet is this element?
    (c) Make a prediction about the ion that this element might form in an ionic compound.
8. Element Z has a total of 12 electrons.
    (a) Write the electron configuration for element Z.
    (b) How many electrons away from a complete octet is this element?
    (c) Make a prediction about the ion that this element might form in an ionic compound.
9. Write the ground state configuration for the following elements. Then, show how the element ionizes to become isoelectronic with the nearest noble gas. Example: Mg [$1s^22s^22p^63s^2$]
10. $\underset{[Ne]2s^2}{Mg} \rightarrow \underset{[Ne]}{Mg^{2+}} + 2e^-$
    1. Na
    2. Ca
    3. N
    4. Br
    5. Al

6. Se

Further Reading / Supplemental Links

- Pough, Frederick. 1988. Rocks and Minerals, Peterson Field Guides. Boston: Houghton Mifflin.

Points to Consider

- So far, we have been discussing the fact that cations and anions form when electrons are lost or gained, respectively. However, the electrons must be lost to something or gained from something. Where are electrons lost to, and where do they originate from?

8.2 Ionic Bonds and Ionic Compounds

Lesson Objectives

- Describe the general properties that distinguish ionic compounds from other substances.
- Define and give examples of ionic compounds. Be able to predict which elements are likely to form ionic compounds with each other.
- Describe the crystal lattice structures adopted by ionic compounds.
- Define lattice energy and explain what it measures.

Lesson Vocabulary

- **ionic bond**: The resulting attraction between the positively charged cations and negatively charged anions
- **crystal lattice**: A three-dimensional sturcture formed by ions in order to maximize the number of attractive interactions while minimizing the repulsive ones.
- **lattice energy**: The amount of energy needed to completely pull apart an ionic substance into isolated ions.
- **dissolution**: Occurs when water interacts with the ions in the crystal lattice, causing the lattice to break apart.

Check Your Understanding

1. Give some examples of commonly encountered ions.
2. Draw electron dot diagrams for atoms of the following elements:
    a. calcium
    b. oxygen

Introduction

In the last section, we saw that elements may lose or gain electrons to become isoelectronic with the nearest noble gas. Where do the electrons go when an element loses them to become a cation? Where do electrons come from when an element gains them to become an anion? For an atom to gain or lose electrons, there must be an interaction between two different chemical species. If electrons are fully exchanged, then we consider this interaction to be ionic. The resulting attractions between the positively charged cations and the negatively charged anions are referred to as **ionic bonds**.

Ionic Bonds

As we saw in earlier chapters, the electrons in the outermost (valence) shell of an atom are largely responsible for the ways in which that atom will interact with other elements. For example, **Figure** 8.4 shows the electron configurations of sodium (11 e^-, 1 valence e^-), neon (10 e^-, 8 valence e^-), and fluorine (9 e^-, 7 valence e^-).

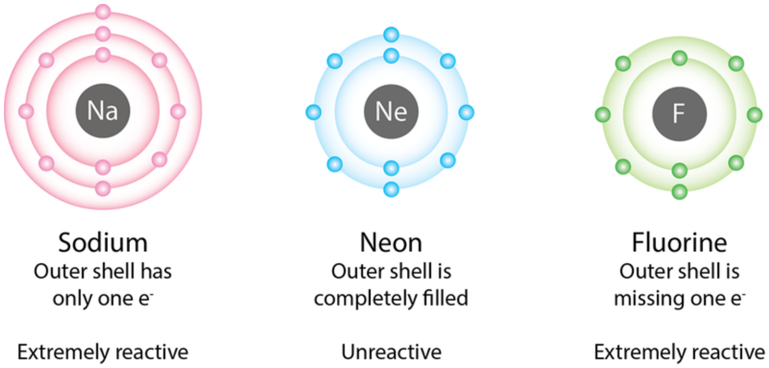


FIGURE 8.4

This image shows the arrangement of electrons in their ground states for sodium, neon, and fluorine.

Our model of ionic bonding and chemical reactivity states that sodium and fluorine have a strong driving force to become isoelectronic with the nearest noble gas, neon. Because sodium needs to lose one electron and fluorine needs to gain one for this to occur, one atom of sodium can give up its valence electron to a fluorine atom, resulting in two ions with noble gas configurations matching that of neon (**Figure** 8.5). The positive and negative ion are held tightly together by electrostatic forces, which are strong forces between oppositely charged particles. When large groups of sodium and fluorine atoms react in this way, the result is the ionic compound, sodium fluoride.

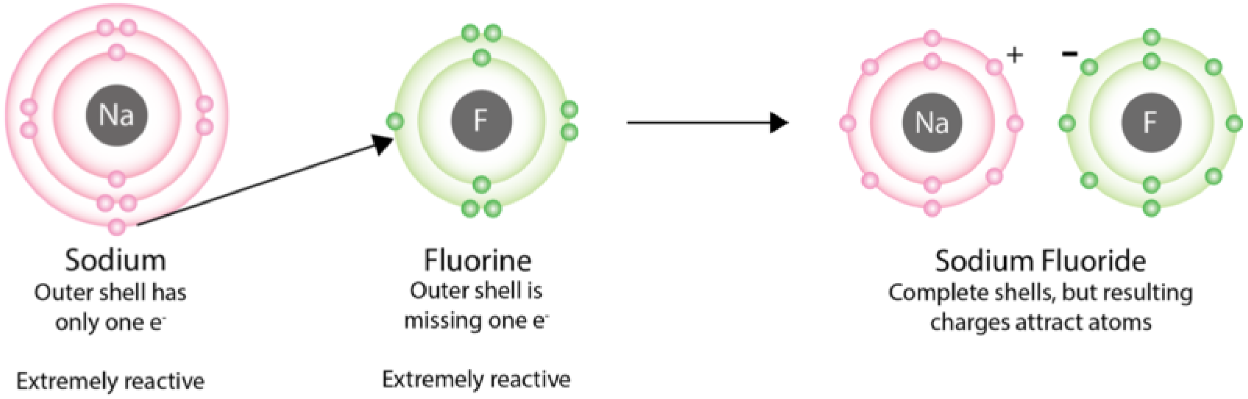


FIGURE 8.5

Electron arrangements for sodium fluoride.

Crystal Lattices

Any ionic compound is composed of extremely large numbers of cations and anions. Each cation is attracted by all of the anions but repelled by all the other cations, and vice versa. In order to maximize the number of attractive interactions while minimizing the repulsive ones, the ions form a three-dimensional structure known as a **crystal lattice**. There are a variety of lattice forms that ionic compounds can exhibit, but all of them involve a regular, repeating pattern in which cations and anions are held rigidly in place by various neighboring ions. For example, sodium fluoride takes the form of a cubic lattice, shown here (**Figure** 8.6):

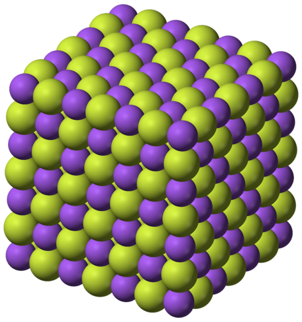


FIGURE 8.6
Crystal Lattice for Sodium Fluoride

Some properties of the crystal form that are exhibited at the atomic level can also be seen at the macroscopic level. Due to the cubic arrangement of ions in sodium fluoride, a single pure crystal of this compound will tend to have smooth faces at right angles to one another (**Figure** 8.7).

FIGURE 8.7
Crystals of Villiaumite, a rare mineral composed of sodium fluoride.

Lattice Energy

There are a number of different ways to measure the strength of a given crystal lattice. One way would be to measure the amount of energy needed to completely pull apart an ionic substance into isolated ions. This value, known as the **lattice energy**, cannot be measured directly, but it can be calculated based on measured energy changes for other more feasible processes. The lattice energy of an ionic solid provides us with one way to measure the relative strength of the ionic bonds in that compound. **Table** 8.1 shows the lattice energies for various ionic substances:

TABLE 8.1: **Lattice Energies for Some Ionic Compounds**

Compound	Lattice Energy (kJ/mol)	Compound	Lattice Energy (kJ/mol)
LiF	1030	KBr	671
LiCl	834	CsCl	657
LiI	730	CsI	600
NaF	910	$MgCl_2$	2326
NaCl	788	$SrCl_2$	2127
NaBr	732	MgO	3795
NaI	682	CaO	3414
KF	808	SrO	3217
KCl	701	ScN	7547

Properties of Ionic Compounds

Ionic compounds exhibit certain properties, some of which are listed below:

- All ionic compounds form crystals.
- Ionic compounds tend to have high melting points and boiling points.
- Ionic compounds are very hard and very brittle.
- Ionic compounds conduct electricity when dissolved in water.

The last property above requires some additional explanation. We are all familiar with the process of dissolution on a large scale. If you stir a spoonful of salt into a glass of water, the salt crystals are broken down and seem to disappear into the water. On the atomic level, the **dissolution** of an ionic compound occurs when water interacts with the ions in the crystal lattice, causing the lattice to break apart (**Figure** 8.8):

Once the ions are dissolved, the presence of charged particles distributed throughout the liquid allows the solution to conduct electricity (**Figure** 8.9). The more ions that are freed from the lattice, the more conductive the solution will be.

Below is a summary of some common ionic compounds and their practical applications (**Table** 8.2):

TABLE 8.2: **Common Examples of Ionic compounds**

Formula	Name	Common name	Uses
NaCl	Sodium chloride	Table salt	Food additive
$NaHCO_3$	Sodium hydrogen carbonate	Baking soda	Mild cleaner, antacid
NaOH	Sodium hydroxide	Lye	Drain cleaner
NaF	Sodium fluoride	n/a	Active ingredient in toothpaste

TABLE 8.2: (continued)

Formula	Name	Common name	Uses
NaOCl	Sodium hypochlorite	Bleach	Mild or strong cleaner, disinfectant

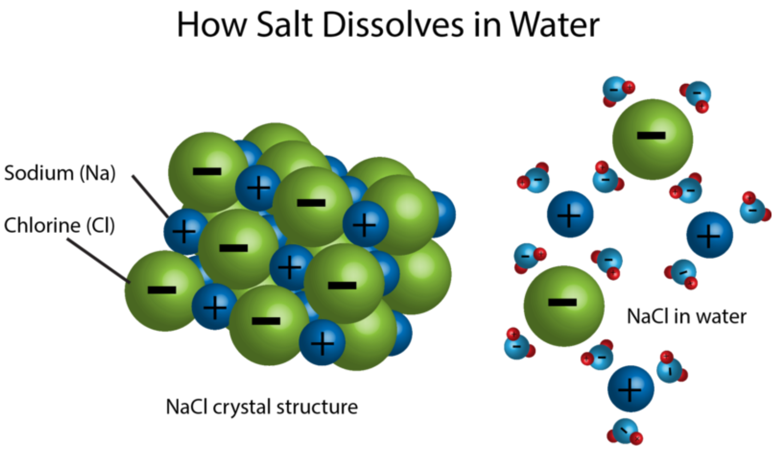


FIGURE 8.8

Dissolution of NaCl.

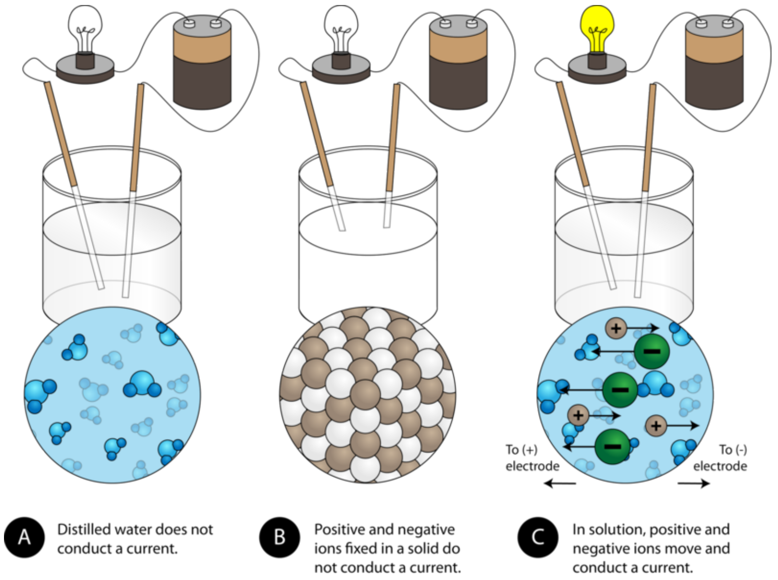


FIGURE 8.9

Conductivity of ionic solutions.

Lesson Summary

- Ionic bonds are electrostatic attractions between two oppositely charged ions. Ions can be formed and then bonded when metal atoms donate their valence electrons to nonmetal atoms.
- The ions in ionic compounds are arranged in rigid three-dimensional patterns called crystal lattices. The crystal lattice that is formed is a characteristic property of a given compound.
- We can indirectly measure the energy necessary to break apart a given lattice into its isolated ions. We call this value the lattice energy, and it gives us one way to measure the strength of the ionic bonds in that compound.
- Ionic compounds have the following properties: (1) they form crystals; (2) they have high melting/boiling points; (3) they are hard and brittle; (4) they can conduct electricity when dissolved in water.
- Dissolution is a process in which water interacts with the ions in a crystal lattice, causing the lattice to break apart.

Review Questions

1. How do the electrons from two atoms interact in an ionic bond?
2. Predict the formulas for the ionic compounds formed when each of the metals in the **Table** 8.3 reacts with each nonmetal.

TABLE 8.3: **Reactions**

	Oxygen	Sulfur	Chlorine
Calcium			
Sodium			
Aluminum			

3.
4. What is dissolution?
5. If sodium chloride is placed in water, it will completely dissociate into its ionic components, described by the dissociation equation:
6. Write a similar dissociation equation for the solid ionic compound calcium chloride.
7. Which physical properties of ionic compounds can be attributed to the crystal lattice structure?
8. How does lattice energy relate to the strength of an ionic compound?
9. True or false: The high melting points of ionic solids suggest that ionic bonds are fairly weak.
10. Using **Table** 8.1 as a reference, what trend can be recognized between lattice energy and the characteristics of the ions which comprise the compound? For example, NaF, NaCl, NaBr, NaI have lattice energies (kJ/mol) of 910, 788, 732, and 682, respectively. What is different between the anions that may be causing such differences?

Further Reading / Supplemental Links

- Animation of Sodium chloride dissolution: http://www.mhhe.com/physsci/chemistry/essentialchemistry/flash/molvie1.swf

Points to Consider

- We have generally assumed that ionic compounds are composed of metal cations and nonmetal anions. While this is common, there are ionic compounds in which no metal is involved. For example, the ammonium cation is positively charged but does not involve any metal atoms. Similarly, some polyatomic anions are not solely comprised of nonmetallic atoms. What are some examples of these anions?

8.3 Metals and Metallic Bonds

Lesson Objectives

- Describe the general properties of metals compared to other element types.
- Describe the arrangement of atoms in metallic substances.
- Describe the behavior of electrons in metals.
- Define and give examples of alloys.

Lesson Vocabulary

- **malleable**: When pure metals are able to be stamped, pressed, or rolled into thin sheets.
- **ductile**: Metal that can be stretched, bent, or twisted without breaking.
- **toughness**: The ability of a material to withstand shock and to be deformed without rupturing.
- **luster**: When pure metals tend to be shiny in appearance.
- **corrosion**: The gradual degradation of a material due to its exposure to the environment.
- **metallic bond**: The attraction of the stationary metal cations to the surrounding mobile electrons.
- **alloy**: A mixture of pure metals.
- **amalgam**: An alloy that is mostly composed of mercury.

Check Your Understanding

1. Identify the ions that make up the following compounds:
   a. NaCl
   b. $BaSO_4$
   c. K_2O
2. How many valence electrons do the neutral atoms of metals in Groups 1, 2, and 3 in the periodic table have?

Introduction

Metals represent approximately 25% of the elemental makeup of the Earth's crust. The bulk of these metals, primarily aluminum, iron, calcium, sodium, potassium, and magnesium, are typically found in combined form. The most abundant metal is aluminum, which occurs almost exclusively as the ionic mineral bauxite. The other most common metals, including iron, sodium, potassium, magnesium, and calcium, are also found primarily as the cationic portion of an ionic compound. Very few metals actually occur naturally as pure substances. The ones that do are often referred to as precious or semi-precious metals.

As pure substances, metals are tough, yet malleable. They are strong, and some of them are quite resistant to corrosion. They are also good conductors of electricity and heat. Due to these and other useful properties, pure metals have been valued for millennia. In this lesson, we are going to investigate a few properties of metals and the chemical reasons behind some of these characteristics.

Properties of Metals

Physical Properties

Most pure metals share a number of physical properties. Metals are good conductors of electricity and heat. They are also **malleable**, which means that they can be stamped, pressed, or rolled into thin sheets. For example, aluminum foil can be made into sheets that are only 13 μm thick, and gold (the most malleable pure metal) can be hammered so thin that it is practically transparent. Metals also tend to be **ductile**, which means that they can be stretched, bent, or twisted without breaking. The copper wire shown in **Figure** 8.10 is an example of this. Both of these properties are facets of **toughness**, which is a term that describes the ability of a material to withstand shock and to be deformed without rupturing.

FIGURE 8.10

This image shows a variety of different copper wires. Copper is a commonly used substance for wire because it is highly conductive and ductile but also very abundant (and therefore inexpensive).

Pure metals tend to be shiny in appearance; this property is referred to as **luster**. Due to our everyday experiences, we may think of metals as being mostly dull gray in color. However, this is due not to the pure metal but to a surface layer in which the pure metal has formed an ionic compound, usually with oxygen atoms from either air or water. Most pure metals are silver-white, but some of the heavier ones (most notably, gold) take on a yellowish hue.

Chemical Properties

We have already discussed some of the chemical properties of pure metals. They have just a few valence electrons (generally 1-3), which tend to be fairly easy to remove due to metals low ionization energy and electronegativity values. As a result, they frequently form ionic compounds by transferring their valence electrons to nonmetallic atoms, which use these extra electrons to complete their valence shells and achieve noble gas configurations.

The driving force to combine with nonmetals to create ionic compounds varies quite a bit between different metals. Some pure metals, like cesium and potassium, are so eager to react that they must be stored under oil to avoid an immediate reaction with the oxygen present in air. Others, like platinum and gold, are stable enough that they can be found in nature as pure metals rather than as the cationic portion of an ionic compound. Gradual degradation of a material due to its exposure to the environment is known as **corrosion**. Metals like gold and platinum are unusually resistant to corrosion, which makes them especially valuable for both structural and decorative purposes.

Metals have a wide range of melting points, but most are quite high. Only one metal (mercury) melts below room temperature. Others (such as gallium) are solid at room temperature but would melt at body temperature, so they can be melted simply by holding them in your hand. On the other end of the spectrum, tungsten has a melting point of 3422°C. **Figure** 8.11 shows the melting points of various elements in their most common pure form.

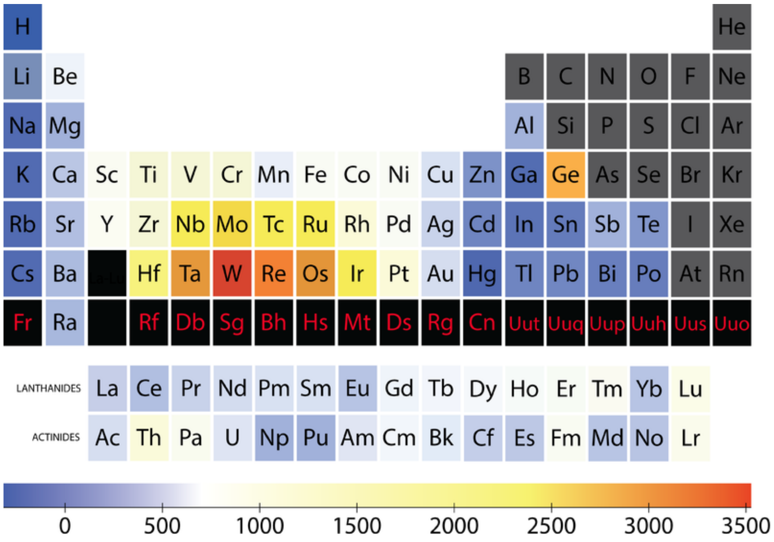


FIGURE 8.11

Melting Points of the Metallic Elements

The "Sea of Electrons"

The reason metals behave the way they do can largely be explained by the ways that metal atoms bond together to make a solid material. Pure metals are crystalline solids, but unlike ionic compounds, every point in the crystal lattice is occupied by an identical atom. The electrons in the outer energy levels of a metal are mobile and capable of drifting from one metal atom to another. This means that the metal is more properly viewed as an array of positive ions surrounded by a "sea" of mobile valence electrons (**Figure** 8.12). Electrons that are capable of moving freely throughout the empty valence orbitals of the metallic crystal are said to be delocalized. A **metallic bond** is the attraction of the stationary metal cations to the surrounding mobile electrons.

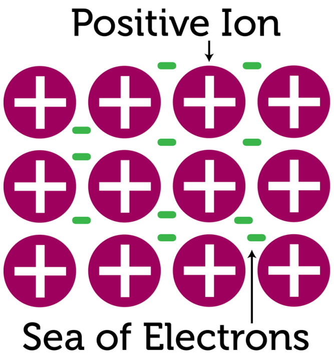


FIGURE 8.12

Electron Sea Illustration

This model for metallic bonding explains some of the physical properties of metals. Metals conduct electricity and heat very well because of their free-flowing electrons. As electrons enter one end of a piece of metal, an equal number of electrons flow outward from the other end, allowing an electrical current to pass through the material with minimal resistance. Additionally, because the electron "glue" that holds the metal atoms together is very easy to deform and reshape, bulk metals can be easily hammered, bent, and pulled without breaking apart.

Types of Metals

Precious Metals

A number of relatively rare metals are quite resistant to corrosion. These metals are sometimes referred to as precious metals due to their scarcity and their ability to remain pure over time. The exact list varies, but metals that are usually classified as precious include gold, silver, ruthenium, rhodium, palladium, osmium, iridium, and platinum. Some precious metals are shown in (**Figure** 8.13). Compared to other metals, precious metals tend to have relatively high ionization energies and electronegativity values.

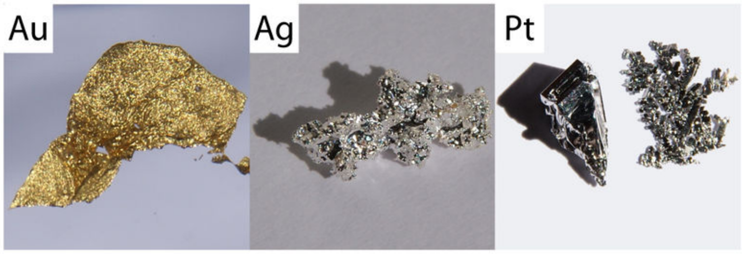


FIGURE 8.13
Precious metals

Rare Earth Metals

The rare earth metals are a set of seventeen chemical elements (the lanthanide series plus scandium and yttrium) that have particular importance for a variety of industrial processes and are used frequently in modern technology. Despite their name, rare earth metals are actually relatively abundant in the earth's crust. However, the extraction of many of these metals is quite difficult and has made their supply somewhat limited. They are highly sought after for this reason. **Figure** 8.14 shows the rare earth metals.

Alloys

In addition to being used in their pure elemental forms, metals can be melted down and combined with other metals (and sometimes small amounts of nonmetals) to form mixtures known as **alloys**. The properties of alloys are often quite different than the properties of the base elements from which they formed. For example, iron is often mixed with small amounts of carbon or other metals to create steels. By modifying the relative amounts of the added components, properties like hardness, flexibility, and corrosion resistance can be fine-tuned so that the material is suitable for a particular application. For example, elemental iron corrodes readily in air and water (see **Figure** 8.15), but stainless steel (which is still mostly iron, but contains about 10-12% chromium by mass) resists corrosion to a large extent. It is used as an exterior building material for extravagant buildings such as that shown in **Figure** below.

Alloys that are mostly composed of mercury are known as **amalgams**. Amalgams often have special properties that stem from the fact that mercury exists as a liquid at room temperature. As a result, metal amalgams are used for a

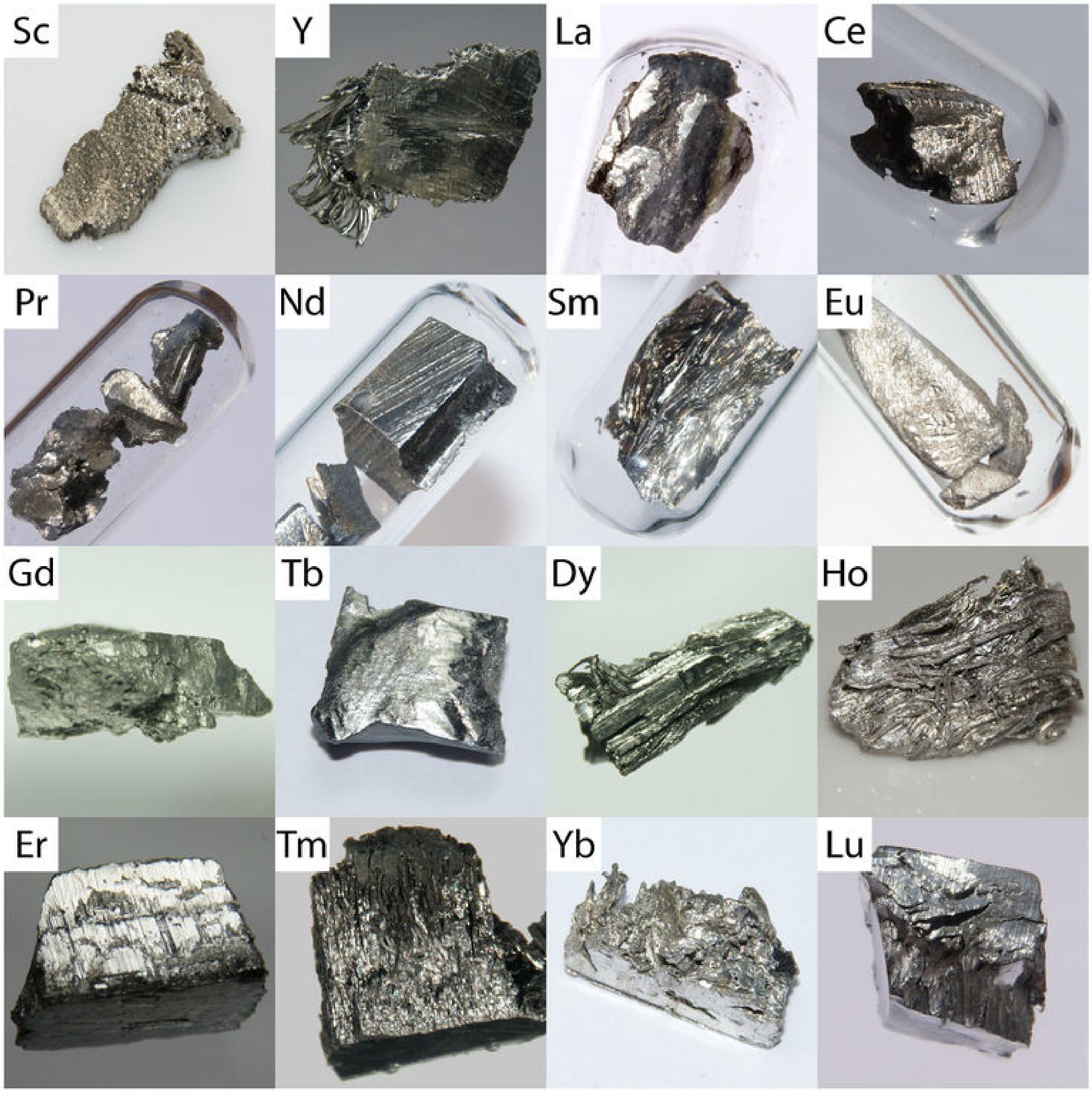


FIGURE 8.14
Rare earth metals

variety of purposes, including dentistry and the extraction of other pure metals such as gold.

Lesson Summary

- Physical properties that are common to metals include malleability, ductility, toughness, and luster.
- Chemical properties of metals include the abilities to conduct heat and electricity.

FIGURE 8.15

Corroded iron pipe.

FIGURE 8.16

Most of the exterior of the Walt Disney Concert Hall pictured here is stainless steel.

- Many of the properties of metals are due to the presence of metallic bonds, in which metal atoms are held together by a mutually shared "sea" of valence electrons.
- Metal atoms lose electrons readily to other chemical species, forming cations that can participate in ionic bonds.
- Precious metals are relatively rare and often can be found naturally as a pure metal rather than as part of an ionic compound.
- Rare earth metals are an important set of metals because of their use in a variety of modern industrial applications.
- Alloys are solid mixtures of two or more metals (sometimes with small amounts of a nonmetal, such as carbon). The properties of alloys may be quite different than the properties of the pure elements from which they are formed.

Review Questions

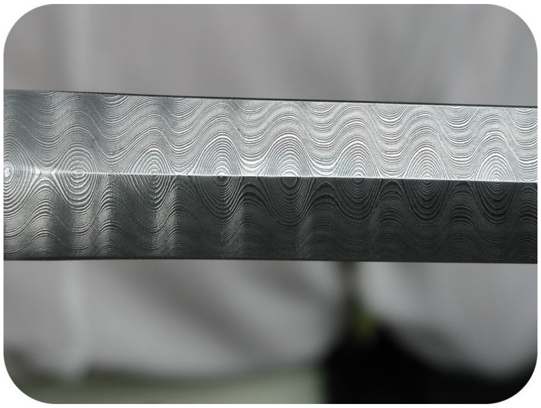
1. Define the following properties of metals
    (a) malleability
    (b) ductility
    (c) toughness
    (d) luster
2. In metal solids, the ______ electrons form a shared sea of electrons.
3. What is corrosion as it applies to metals?
4. In general, what can be said of the melting points of metals?
5. Define a metallic bond.
6. What is the relationship between the electron arrangement in metals and metals' physical properties?
7. What atomic properties distinguish "precious metals" from metals in general?
8. Why are "rare metals" so valuable?
9. How are alloys formed?

Further Reading / Supplemental Links

- Metallic Bonding Animation/Video: http://www.youtube.com/watch?v=c4udBSZfLHY
- Use of Different Types of Alloys: http://www.articlesnatch.com/Article/Uses-Of-Different-Types-Of-Alloys/599802

Points to Consider

- The following image is of a sword constructed of an alloy known as Damascus steel.



Notice the mottling pattern, reminiscent of flowing water. Damascus steel blades were a product of medieval times and were highly regarded for their toughness, resistance to shattering, and their capability to be honed and sharpened with a resilient edge. Even to this day, it is still debated as to exactly how Damascus steel was made.

8.4 References

1. Christopher Auyeung and Jodi So. CK-12 Foundation . CC BY-NC 3.0
2. Zachary Wilson. CK-12 Foundation . CC BY-NC 3.0
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CHAPTER 9

Covalent Bonding

Chapter Outline

9.1 LEWIS ELECTRON DOT STRUCTURES
9.2 MOLECULAR GEOMETRY
9.3 POLARITY IN CHEMICAL BONDS
9.4 INTERMOLECULAR FORCES
9.5 HYBRIDIZATION AND MOLECULAR ORBITALS
9.6 REFERENCES

Water and diamonds –two very different materials. Water can be found almost everywhere. It is in lakes, creeks, rivers, and oceans. We get water from the sky when it rains. Diamonds, on the other hand, are very rare. They are only found in a few locations on the earth and must be mined to become available. Major diamond mines are located in various African countries, Australia, and Russia. The United States has several underground sources of diamonds in Alaska, Colorado, Minnesota, Montana, and Wyoming, but the only "active" U.S. mine is the Crater of Diamonds mine in a state park near Murfreesboro, Arkansas. For a small fee, visitors can dig for diamonds. You won't get rich by visiting, though –only a few hundred carats of low-grade diamonds are found each year.

The two materials do have at least one thing in common. The atoms in the materials are held together by covalent bonds. These bonds consist of electrons shared between two or more atoms. Unlike ionic bonds, where electrons are either lost or gained by an atom to form charged ions, electrons in covalent compounds are shared between the two atoms, giving rise to properties that are quite different from those seen in ionic materials.

Waterfall: Beth CreMeens (Flickr:vikingsgonnapillage). www.flickr.com/photos/vikingsgonnapillage/8729855112/. CC BY 2.0. Diamond: Ruby Grace Ong. www.flic

9.1 Lewis Electron Dot Structures

Lesson Objectives

- Define and give examples of covalent bonds.
- Describe the differences between ionic and covalent bonds.
- Describe Lewis structures.
- Use Lewis structures to illustrate covalent bonds in molecules.

Lesson Vocabulary

- **covalent bond**: Forms when two or more elements share electrons.
- **Lewis structure**: One way of representing covalent bonds.
- **lone pair**: An unbonded pair of electrons.
- **double bond**: A covalent bond in which each atom shares 2 valence electrons.
- **triple bond**: A covalent bond in which each atom shares 3 valence electrons.

Check Your Understanding

Recalling Prior Knowledge

- What are valence electrons?
- How are electrons configured in s and p orbitals?
- What are electron dot diagrams?
- What is the octet rule?
- What are ions?

Introduction

Ionic substances are completely held together by ionic bonds. The full charges of the ions (for example, Na^+ and Cl^- in sodium chloride) cause electrostatic interactions that result in a stable crystal lattice. We saw in the previous chapter that most ionic compounds have high melting points, are brittle, are often soluble in water, and conduct electricity when melted or dissolved in water. Ionic compounds exist as extended, orderly arrangements of ions. As we will see, this is quite different from the structure of molecular substances, which take the form of collections of individual molecules. The atoms within a molecule are held very strongly together, but the interactions between different molecules are significantly weaker.

Ionic bonds are possible because the elements involved have either donated or accepted one or more electrons. Sodium chloride is formed when each sodium atom donates its single valence electron to a chlorine atom. As a result, both ions have a noble gas configuration, and an attraction is formed between the positive sodium ions and the negative chloride ions.

Another type of bond is also found in numerous compounds. A **covalent bond** forms when two or more elements share electrons. The electrons that form a covalent bond are not fully possessed by a single atom (as the electrons in an ion would be) but are shared between the two atoms involved in the bond. The concept of the covalent bond was first proposed in 1916 by the American chemist G.N. Lewis (1875-1946), who suggested that sharing electrons was one way that atoms could attain a complete octet of valence electrons. This idea was expanded upon by Linus Pauling (1901-1994), who eventually won the Nobel Prize in Chemistry in 1954 for his work on chemical bonding.

Single Covalent Bonds

Covalent bonding involves sharing of electrons in s and p orbitals. The simplest covalent bond is formed between two hydrogen atoms. Each hydrogen atom has a single 1s electron, and each needs two electrons for a full outer shell. The hydrogen molecule, H_2, consists of two hydrogen atoms sharing their two valence electrons. Hydrogen can also form covalent bonds with other atoms. For example, hydrogen and chlorine each need one more electron to achieve a noble gas configuration. By sharing valence electrons (each atom donates one), the stable HCl molecule is formed.

Later in this chapter, we will learn how to draw covalent bonds using orbitals, but a simplified representation of covalent bonds can be drawn using **Lewis structures**, which were developed by G.N. Lewis in 1916. These drawings are also known by various other names, including Lewis dot structures or electron dot structures, as we introduced in the previous chapter. Each dot in the structure represents one valence electron in the compound. For example, H_2 could be drawn as H:H. Each dot represents one valence electron, and the fact that they are placed between the two atoms means that they are being shared as a covalent bond. For larger molecules, it can become cumbersome to draw out all of the valence electrons, so a bonding pair of electrons can also be drawn as a straight line. Thus, H_2 can also be represented as H-H.

If we wanted to show the Lewis structure of HCl, we would draw the following:

We can see that the covalent bond consists of two electrons between the H and the Cl. The H has a full outer shell of two electrons and the chlorine has a full outer shell of eight electrons. Covalent bonds with other halogens can be written the same way.

Similar types of Lewis structures can be written for other molecules that form covalent bonds. Many compounds that contain O, N, C, S, and P are held together by covalent bonds. The number of covalent bonds an atom will form can generally be predicted by the number of electrons an atom requires to fill its valence shell. For example, oxygen has 6 electrons in its outer shell and needs two more to fill this shell, so it will only form two covalent bonds with other atoms. If we look at the water molecule (H_2O) (see **Figure** 9.1), we see that the oxygen atom makes two total bonds (one with each hydrogen atom):

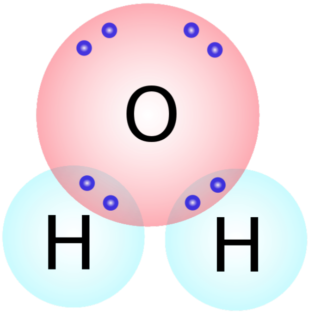
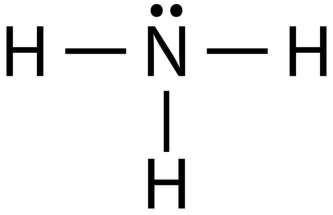


FIGURE 9.1
Electron sharing in a water molecule.

As you can see, there are two pairs of electrons not involved in covalent bonding. These unbonded pairs of electrons are known as **lone pairs** and contribute to the overall shape of the molecule. Similarly, nitrogen needs three electrons to complete its valence shell, so it tends to make three covalent bonds, with one lone pair of non-bonding electrons left over:



Again, each of the lines stands for a *pair* of bonding electrons (a single bond), and the lone pair on nitrogen is drawn as two dots.

Double and Triple Bonds

So far we have considered only single bonds, formed by the sharing of one electron from each atom. Many molecules contain **double bonds**, in which each atom shares two electrons, or **triple bonds**, in which each atom shares three electrons. These are represented by drawing two or three lines in between the bonded atoms. For example, a carbon-carbon double bond can be written as C::C or C=C. A carbon-carbon triple bond is shown as C:::C or with three lines between the two carbon atoms, as seen below in the structure of an organic molecule called acetylene:

FIGURE 9.2
Acetylene molecule

Steps for Drawing Lewis Structures

1. Identify the atoms that are participating in a covalent bond.
2. Draw each atom by using its element symbol. The number of valence electrons is shown by placing up to two dots on each side of the element symbol, with each dot representing a single valence electron.
3. Predict the number of covalent bonds each atom will make using the octet rule.

4. Draw the bonding atoms next to each other, showing a single covalent bond as either a pair of dots or a line representing a shared valence electron pair. If the molecule forms a double or triple bond, use two or three lines to represent the shared electron pairs, respectively.

Lesson Summary

- Covalent bonds are formed between atoms sharing electrons.
- Lewis structures are a simple way of representing covalent bonds. The shared valence electrons can be drawn using dots to represent individual valence electrons, or lines to represent shared electron pairs.
- A pair of valence electrons in a bonded atom that does not participate in bonding is called a lone pair. Lone pair electrons contribute to molecular shape.
- Atoms can form double or triple covalent bonds as well, in which each atom shares two valence electrons (double bond) or three valence electrons (triple bond).

Lesson Review Questions

1. How is a covalent bond formed?
2. What is the major difference between a covalent bond and an ionic bond?
3. What orbitals are used in covalent bonding?
4. What types of elements generally form covalent bonds?
5. How do double and triple covalent bonds differ from single covalent bonds?
6. Predict the number of covalent bonds the following atoms will make:
   a. N (nitrogen)
   b. S (sulfur)
   c. Br (bromine)
   d. F (fluorine)
7. Draw Lewis structures for the following molecules:
   a. HBr
   b. CO_2
   c. NCl_3
   d. PCl_5
8. Determine how many lone pairs are present in each of the molecules from the problem above.

Further Reading / Supplemental Links

- An extensive collection of materials showing the contributions made by Linus Pauling to our understanding of the chemical bond:

http://osulibrary.oregonstate.edu/specialcollections/coll/pauling/bond/

- Practice drawing Lewis Dot Structures of Covalent Compounds: http://www.wisc-online.com/objects/ViewObject.aspx?ID=GCH6404

Points to Consider

- What happens to the valence shell electrons not involved in a covalent bond?
- How do the lone pair electrons affect molecular shape?

9.2 Molecular Geometry

Lesson Objectives

- Explain the basis of VSEPR theory.
- Predict the shapes of molecules and polyatomic ions using VSEPR theory.
- Account for variations in bond angles based on the relative repulsive forces exerted by lone pairs and bonding pairs of electrons.
- Describe the relationship between molecular geometry and electron domain geometry.

Lesson Vocabulary

- **molecular geometry**: The three-dimensional arrangement of atoms in a molecule.
- **valence shell**: The outermost occupied shell of electrons in an atom.
- **valence shell electron pair repulsion (VSEPR) theory**: States that a molecule will adjust its shape so that the valence electron pairs stay as far apart from each other as possible.
- **electron domain geometry**: The number of atoms bonded to the central atom plus the number of lone pairs on the central atom.

Check Your Understanding

Recalling Prior Knowledge

- How are Lewis electron dot structures determined?
- What are bonding pairs of electrons and what are lone pairs?

Introduction

Molecular geometry is the three-dimensional arrangement of atoms in a molecule. The molecular geometry, or shape, of a molecule is an important factor that affects the physical and chemical properties of a compound. Those properties include melting and boiling points, solubility, density, and the types of chemical reactions that a compound undergoes. In this lesson, you will learn a technique to predict molecular geometry based on a molecule's Lewis electron dot structure.

VSEPR Theory

The **valence shell** is the outermost occupied shell of electrons in an atom. This shell holds the valence electrons, which are the electrons that are involved in bonding and shown in a Lewis structure. **Valence-shell electron pair repulsion theory**, or VSEPR theory, states that a molecule will adjust its shape so that the valence electron pairs stay as far apart from each other as possible. This makes sense, based on the fact that negatively charged electrons repel one another. We will systematically classify molecules according to the number of bonding pairs of electrons and the number of nonbonding or lone pairs around the central atom. For the purposes of the VSEPR model, a double or triple bond is no different in terms of repulsion than a single bond. We will begin by examining molecules in which the central atom does not have any lone pairs.

Central Atom with No Lone Pairs

In order to easily understand the types of molecules possible, we will use a simple system to identify the parts of any molecule.

A = central atom in a molecule
B = atoms surrounding the central atom

Subscripts after the B will denote the number of B atoms that are bonded to the central A atom. For example, AB_4 is a molecule with a central atom surrounded by four covalently bonded atoms. Again, it does not matter if those bonds are single, double, or triple bonds.

AB

Beryllium hydride (BeH_2) consists of a central beryllium atom with two single bonds to hydrogen atoms. Note that it violates the octet rule, because the central atom has only 4 valence electrons. This is acceptable because beryllium only has two valence electrons to begin with, so it is not possible for it to create more than two covalent bonds with hydrogen atoms.

$$\mathrm{H{-}Be{-}H}$$

According to the requirement that electron pairs maximize their distance from one another, the two bonding pairs in the BeH_2 molecules will arrange themselves on directly opposite sides of the central Be atom. The resulting geometry is a *linear* molecule, shown in a "ball and stick" model in **Figure** 9.3:

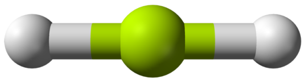
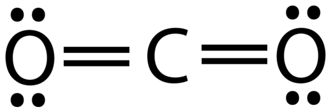


FIGURE 9.3

The H-Be-H bond angle is 180° because of its linear geometry.

Carbon dioxide is another example of a molecule which falls under the AB_2 category. Its Lewis structure consists of double bonds between the central carbon atom and each oxygen atom.



The repulsion between the two double bonds on either side of the carbon atom is no different than the repulsion between the two single bonds on either side of the beryllium in the previous example. Therefore carbon dioxide is also linear, as this achieves the maximum distance between the electron pair bonds.

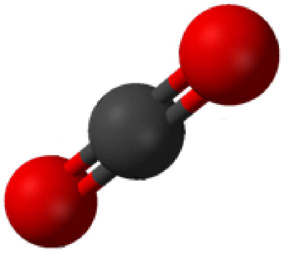
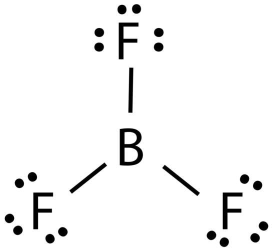


FIGURE 9.4

AB

Boron trifluoride (BF_3) consists of a central boron atom with three single bonds to fluorine atoms. The boron atom is an exception to the octet rule, and generally only needs 6 atoms to be stable in a bonded molecule.



The geometry of the BF_3 molecule is called *trigonal planar*. The fluorine atoms are positioned at the vertices of an equilateral triangle. The F-B-F angle is 120°, and all four atoms lie in the same plane.

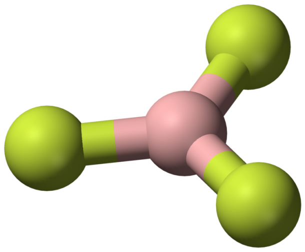
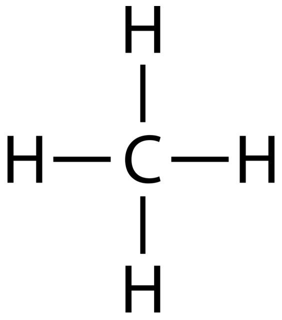


FIGURE 9.5

AB

Methane (CH_4) is an organic compound that is the primary component of natural gas. Its structure consists of a central carbon atom with four single bonds to hydrogen atoms.



$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ & & H & & \end{array}$$

In order to maximize their distance from one another, the four groups of bonding electrons do not lie in the same plane. Instead, each of the hydrogen atoms lies at the corners of a geometrical shape called a tetrahedron. The carbon atom is at the center of the tetrahedron. Each face of a tetrahedron is an equilateral triangle.

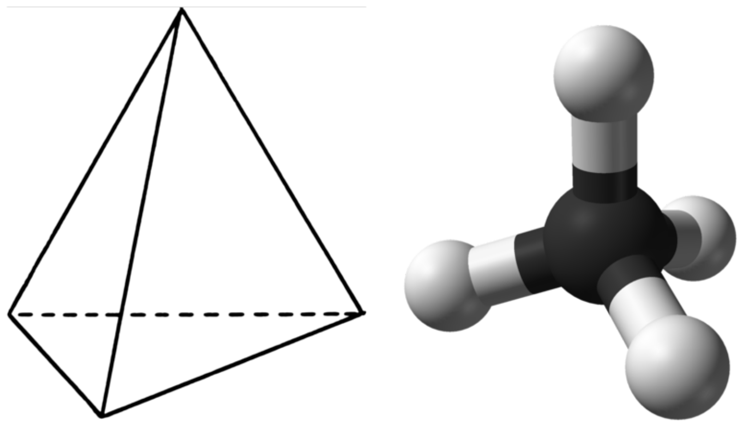


FIGURE 9.6

(*left*) Tetrahedron. (*right*) Ball and stick model of methane.

The molecular geometry of the methane molecule is referred to as *tetrahedral*. The H-C-H bond angles are 109.5°, which is larger than the 90° that they would be if the molecule was planar. This way, the bonds are as far apart as possible to minimize electron repulsion. When drawing a structural formula for a molecule such as methane, it is advantageous to be able to indicate the three-dimensional character of its shape. The structural formula below is called a *perspective drawing*. The dotted line bond should be visualized as going back into the page, while the solid triangle bond should be visualized as coming out of the page.

AB

The central phosphorus atom in a molecule of phosphorus pentachloride (PCl_5) has ten electrons surrounding it, exceeding the octet rule. This is allowed because phosphorus is a third period element and has access to d orbitals, which will be discussed later on.

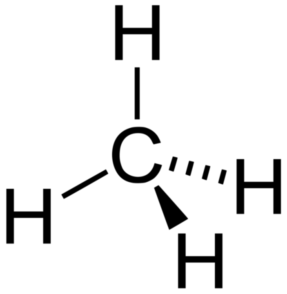
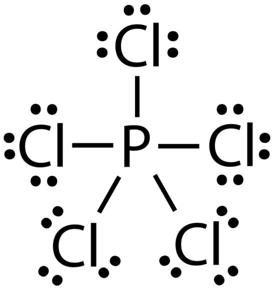


FIGURE 9.7



Unlike the other basic shapes, the five chlorine atoms in this arrangement are not equivalent with respect to their geometric relationship to the phosphorus atom. Three of the chlorine atoms lie in a plane, with Cl-P-Cl bond angles of 120°. This portion of the molecule is essentially the same as a trigonal planar arrangement. These chlorine atoms are referred to as the *equatorial* atoms because they are arranged around the center of the molecule. The other two chlorine atoms are oriented exactly perpendicular to the plane formed by the phosphorus atom and the equatorial chlorine atoms. These are called the *axial* chlorine atoms.

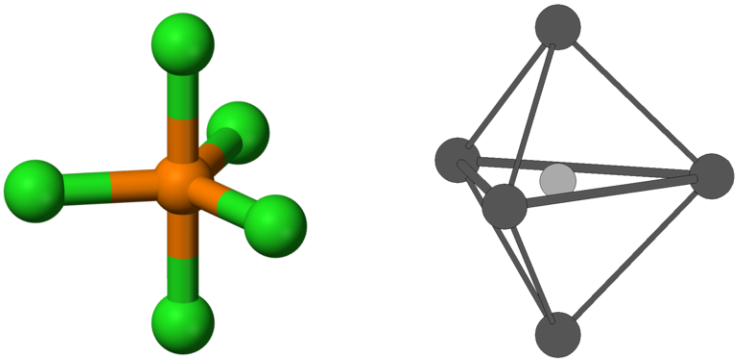


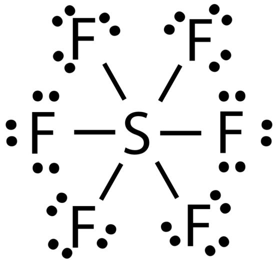
FIGURE 9.8

(*left*) Trigonal bipyramidal. (*right*) Ball and stick model of phosphorus pentachloride.

In the figure above, the axial chlorine atoms form a vertical axis with the central phosphorus atom. There is a 90° angle between P-Cl$_{axial}$ bonds and P-Cl$_{equitorial}$ bonds. The molecular geometry of PCl_5 is called *trigonal bipyramidal*. A surface covering the molecule would take the shape of two three-sided pyramids pointing in opposite directions.

AB

The sulfur atom in sulfur hexafluoride (SF_6) also exceeds the octet rule.



Unlike the trigonal bipyramidal structure, all of the fluorine atoms in SF_6 are equivalent. The molecular geometry is called *octahedral*, because a surface covering the molecule would have eight sides. All of the F-S-F angles are 90° in an octahedral molecule, with the exception of the fluorine atoms that are directly opposite one another which have a 180° bond angle.

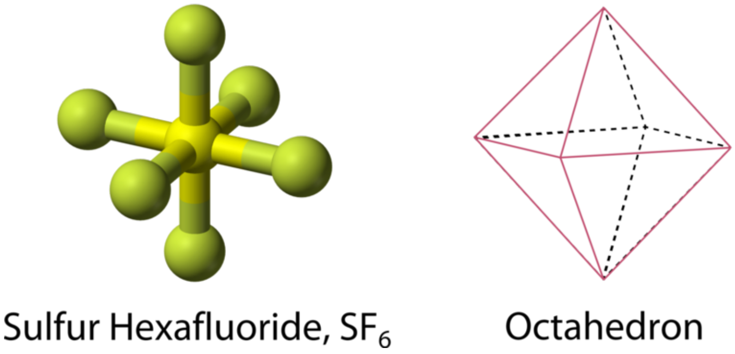


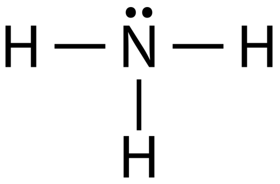
FIGURE 9.9

Central Atom with One or More Lone Pairs

The molecular geometries of molecules change when the central atom has one or more lone pairs of electrons. The number bonds to the central atom plus the number of lone pairs on the central atom gives us what is called the **electron domain geometry**. Electron domain geometries refer to the five molecular shapes learned so far: linear, trigonal planar, tetrahedral, trigonal bipyramidal, or octahedral. However, if one or more of the bonding pairs of electrons is replaced with a lone pair, the shape of the molecules is altered. This can apply to any of the geometries discussed above, but for now we will focus on the tetrahedral electron domain geometry.

Ammonia (NH

The ammonia molecule contains three single bonds and one lone pair on the central nitrogen atom.



The domain geometry for a molecule with four electron pairs is tetrahedral, as was seen with CH_4. In the ammonia molecule, one of the electron pairs is a lone pair rather than a bonding pair. The molecular geometry of NH_3 is called *trigonal pyramidal*.

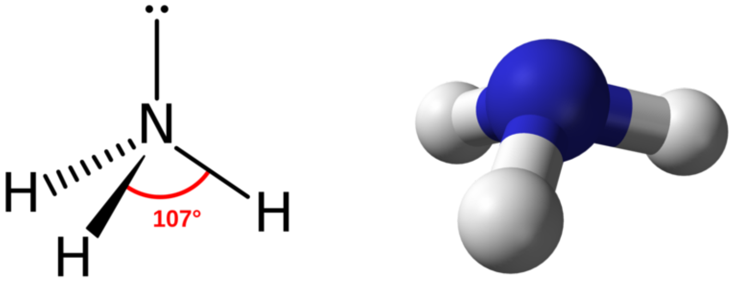


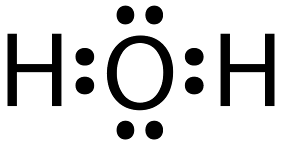
FIGURE 9.10

Ammonia, NH_3.

Recall that the bond angles in the tetrahedral CH_4 molecule are all equal to 109.5°. One might expect the H-N-H bond angles in ammonia to be 109.5° as well, but slight adjustments need to be made for the presence of lone pairs. Within the context of the VSEPR model, lone pairs of electrons are considered to be slightly more repulsive than bonding pairs of electrons, due to their closer proximity to the central atom. In other words, lone pairs "take up more space". Therefore the H-N-H angle is slightly less than 109.5°. Its actual value is approximately 107°.

Water (H

A water molecule consists of two bonding pairs and two lone pairs.



The water molecule, like the ammonia and methane molecules, has a tetrahedral domain geometry. In the water molecule, two of the electron pairs are lone pairs rather than bonding pairs. The molecular geometry of the water molecule is referred to as *bent*. The H-O-H bond angle is 104.5°, which is smaller than the bond angle in NH_3.

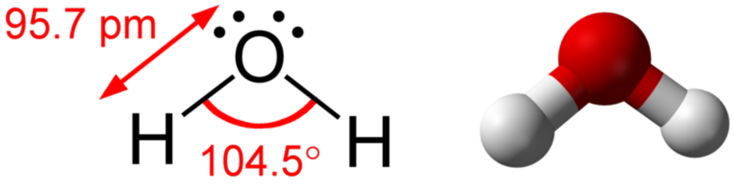


FIGURE 9.11

Water, H_2O.

Summary of VSEPR

The VSEPR model can be applied to predict the molecular geometry of a given molecular compound. There are a number of additional shapes that can be constructed starting from other electron domain geometries and replacing one or more atoms with lone pairs. We will not go over each individual case in this book, but the names for various shapes are provided in the tables below as a reference. To determine the shape of a given molecule, use the following steps:

- Draw the Lewis electron dot structure for the molecule.
- Count the total number of electron pairs around the central atom. This is referred to as the *electron domain geometry*.
- If there are no lone pairs around the central atom, refer to **Table** 9.1, to determine the molecular geometry, which is the same as the electron domain geometry.
- If there are one or more lone pairs on the central atom, the molecular geometry (the actual shape of the molecule) will not be the same as the electron domain geometry. Refer to **Table** 9.2.
- In predicting bond angles, remember that a lone pair takes up more space than a bonding pair or pairs of electrons.

TABLE 9.1: **Geometries of Molecules in Which the Central Atom Has No Lone Pairs**

Atoms Around Central Atom	Electron Domain Geometry	Molecular Geometry	Example
2	linear	linear	$BeCl_2$
3	trigonal planar	trigonal planar	BF_3
4	tetrahedral	tetrahedral	CH_4
5	trigonal bipyramidal	trigonal bipyramidal	PCl_5
6	octahedral	octahedral	SF_6

TABLE 9.2: **Geometries of Molecules in Which the Central Atom Has One or More Lone Pairs**

Atoms Plus Lone Pairs Around Central Atom	Number of Surrounding Atoms	Number of Lone Pairs	Electron Domain Geometry	Molecular Geometry	Example
3	2	1	trigonal planar	bent	O_3
4	3	1	tetrahedral	trigonal pyramidal	NH_3
4	2	2	tetrahedral	bent	H_2O
5	4	1	trigonal bipyramidal	seesaw	SF_4
5	3	2	trigonal bipyramidal	T-shaped	ClF_3
5	2	3	trigonal bipyramidal	linear	XeF_2
6	5	1	octahedral	square pyramidal	BrF_5
6	4	2	octahedral	square planar	XeF_4

Practice with basic molecule shapes at http://phet.colorado.edu/en/simulation/molecule-shapes-basics . Practice building molecules at http://phet.colorado.edu/en/simulation/build-a-molecule . Build 3D molecules at http://phet.colorado.edu/en/simulation/molecule-shapes .

Lesson Summary

- Valence shell electron pair repulsion (VSEPR) theory is a technique for predicting the molecular geometry of a molecule. A molecule's shape provides important information that can be used to understand its chemical and physical properties.
- According to VSEPR, covalent bonds and lone pairs distribute themselves around a central atom in such a way as to maximize their distance from each other.
- Electron domain geometries are based on the total number of bonds and lone pairs, while molecular geometries look only at the arrangements of atoms and bonding pairs.

Lesson Review Questions

1. What is the basic principle of VSEPR theory?
2. How many covalent bonds would there be attached to a central atom in the following configurations:
   a. tetrahedral
   b. octahedral
   c. trigonal planar
   d. linear
3. What is the difference between the electron domain geometry and the molecular geometry?
4. How do lone pairs act differently than bonding pairs in terms of electron repulsion?
5. Using the VSEPR method, predict the molecular geometries (including bond angles) for each of the following molecules:
   a. SF_2
   b. PBr_3
   c. $AlCl_3$
   d. $TeCl_6$
   e. HCN

Further Reading / Supplemental Links

Video on VSEPR theory: http://www.youtube.com/watch?v=FhVkCH9COZo

Possible shapes of molecules according to VSEPR theory: http://www.youtube.com/watch?v=i3FCHVlSZc4

Points to Consider

- How might molecular geometry affect how molecules interact with one another?

9.3 Polarity in Chemical Bonds

Lesson Objectives

- Understand the concept of polarity.
- Define electronegativity.
- Determine the polarity of a chemical bond using the electronegativity chart.
- Distinguish between nonpolar covalent, polar covalent, and ionic bonds in terms of electron sharing.

Lesson Vocabulary

- **polarity**: A property of molecules in which one or more atoms possess either a partial positive or a partial negative charge.
- **electronegativity**: The ability to attract shared electrons.
- **nonpolar covalent bond**: Exists only between two identical atoms.
- **polar covalent bond**: Exists when the electrons are still shared (the bond is covalent), but the bond is significantly polarized.

Check Your Understanding

Recalling Prior Knowledge

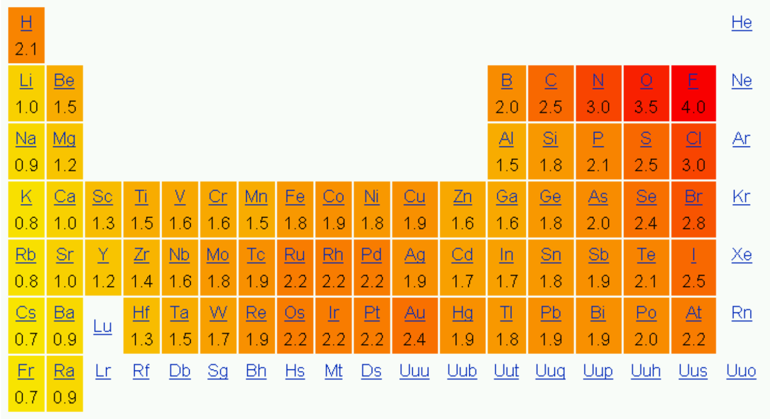
- What are covalent bonds?

Introduction

We have learned that covalently bonded molecules share valence electrons in order for atoms to fill their valence shells. However, sometimes one of the atoms has a greater attraction for electrons than another, resulting in an unequal sharing of electrons. This results in molecular **polarity**.

Electronegativity

When two atoms of different elements come together to form a bond, the atoms generally do not attract the shared electrons with the same amount of pull. The ability to attract shared electrons is a property known as **electronegativity**. The higher the electronegativity value, the more pull is exerted by that element. Electronegativity values for various elements are found in **Figure** 9.12:



H 2.1																	He
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.9	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe
Cs 0.7	Ba 0.9	Lu	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 2.0	At 2.2	Rn
Fr 0.7	Ra 0.9	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Uuu	Uub	Uut	Uuq	Uup	Uuh	Uus	Uuo

FIGURE 9.12

Electronegativities of the elements.

The general trend in electronegativity is that the value increases from left to right across a row in the periodic table and decreases down a column. The most electronegative element is fluorine, which has a value of 4.0. As discussed in the lesson *Trends in the Periodic Table*, electronegativity increases across a row as the number of protons in the nucleus increases and therefore has a stronger pull. Electronegativity decreases down a column due to an increased effect of electron shielding in larger atoms.

Polar Bonds

If there is a difference between the electronegativity values of the two atoms involved in a covalent bond, the bond is said to be polar. In this situation, the more electronegative atom has a stronger tendency to attract the shared electrons toward itself. For example, in the water molecule, oxygen has an electronegativity value of 3.5, while hydrogen has a value of 2.1. Since O has a higher electronegativity value, the electrons in each covalent bond will be pulled closer to the oxygen atom. Because the negatively charged electrons are spending more time near the oxygen atom and less time near the hydrogen atoms, each atom appears to have a partial electric charge when averaged over time. The Greek letter δ (delta) is used to designate a partial charge. As we see in the illustration, oxygen has a partial negative charge, and the hydrogens each have a partial positive change. These charges are fractional charges, less than the full +1 or -1 charge that we might see for a sodium or chloride ion.

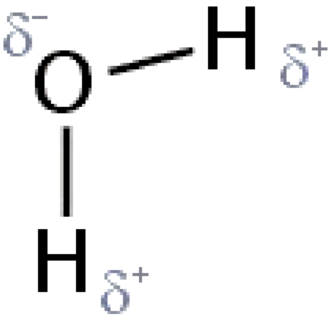


FIGURE 9.13

Partial charges in the water molecule.

A similar situation occurs in the hydrogen fluoride molecule. The difference in electronegativity between fluorine (4.0) and hydrogen (2.1) is quite high, so the shared electrons spend much more time in the vicinity of the fluorine atom. As a result, fluorine carries a partial negative charge in this molecule, whereas hydrogen carries a partial positive charge.

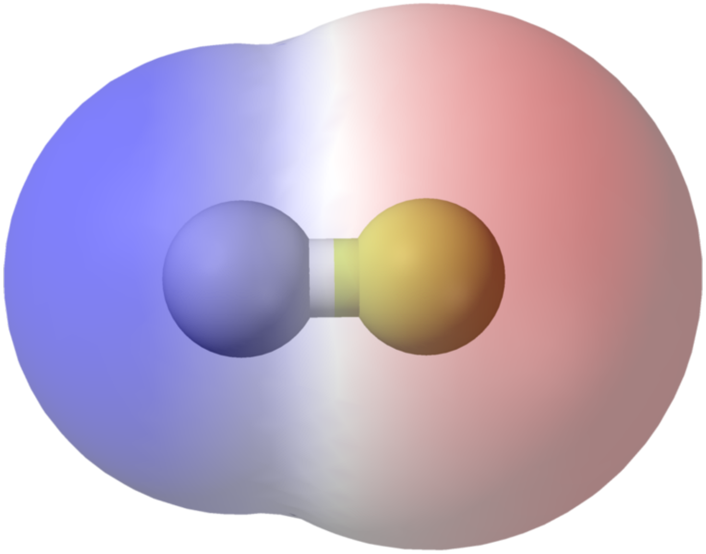


FIGURE 9.14

The hydrogen fluoride molecule. The blue region represents an area of partial positive charge, the white area is electrically neutral, and the pink area is a zone of partial negative charge.

Classifying Chemical Bonds

How do we know if a specific pair of electrons will form a covalent bond or an ionic one? Electronegativity data turns out to be a fairly useful tool to make these predictions. Although there is no clear line between a polar covalent bond and an ionic one, we can define some general guidelines:

1. Pure **nonpolar covalent bonds** exist only between two identical atoms. The H-H bond would be 100% covalent, because there is no difference in electronegativity between the two atoms.
2. If the electronegativity difference between the two atoms is 0.4 or less, the polarity of the bond is very minimal, and neither atom takes on a significant partial charge. For example, the C-H bond (an electronegativity difference of 0.4) is essentially non-polar.
3. When the difference in electronegativity is between 0.5-1.6, the electrons are still shared (the bond is covalent), but it is significantly polarized. We refer to these as **polar covalent bonds**.
4. Ionic bonds tend to form between atoms for which the electronegativity differences are 2.0 and above. In general, ionic bonds between two atoms require one metal and one nonmetal.

Lesson Summary

- Electronegativity is the tendency of an atom to draw shared electrons towards itself.
- Polar bonds contain atoms that possess either a partial positive or a partial negative charge.
- Electronegativity differences can be used to predict the extent to which a particular chemical bond is polarized.

Lesson Review Questions

Reviewing Concepts

1. What causes molecular polarity?
2. Define electronegativity.
3. Explain how electronegativity changes across a period and down a group of the periodic table.
4. Define and give an example of a polar bond.

Problems

1. Which is the most electronegative atom in the periodic table?
2. Calculate the electronegativity difference for each of the following bonds:
   a. C-N
   b. C-F
   c. C-O
   d. H-I
3. Would you expect the bond in each of the following cases to be ionic or polar? Explain your reasoning.
   a. Mg-O
   b. H-I
   c. Li-F
   d. C-N

Further Reading / Supplemental Links

- Electronegativity video: http://www.brightstorm.com/science/chemistry/the-periodic-table/electronegativity/#

- Molecular polarity video: http://www.youtube.com/watch?v=0-zVXdeX7f4

Points to Consider

- How does the polarity of a molecule affect how that molecule interacts with other molecules?

9.4 Intermolecular Forces

Lesson Objectives

- Define and give examples of intermolecular forces.
- Explain what it means for a molecule to be polar.
- Describe various types of intermolecular interactions, including ion-ion, ion-dipole, dipole-dipole, and dispersion forces.

Lesson Vocabulary

- **dipole**: Occurs when two opposite charges are separated by some distance.
- **molecular dipole**: The overall dipole in a molecule, or the geometric sum of all the individual bond dipoles in a molecule.
- **dipole-dipole force**: The force of two polar molecules interacting with one another.
- **dispersion force**: An attractive force that arises as a result of temporary dipoles induced in atoms or molecules.
- **hydrogen bond**: A bond that only occurs in molecules where hydrogen is covalently bonded to one of three elements: fluorine, oxygen, or nitrogen.

Check Your Understanding

Recalling Prior Knowledge

- What is electronegativity?
- How does electronegativity influence the charge distribution within a molecule?

Introduction

In some ways, a collection of gas molecules represents the simplest form of matter. Because the individual molecules are so far apart, they have only fleeting interactions with one another. In contrast, molecules that have clustered together to form a liquid or solid are constantly exerting forces on each other. In fact, it is only because of these attractive forces that molecular solids and liquids exist at all. In this lesson, we will look at some of the ways in which molecules and ions attract one another to form solids and liquids.

Ion-Ion Interactions

Ion-ion interactions have already been considered in a previous chapter, so we will simply do a short review. These interactions are most significant in the solid state. When dissolved in water, ions are shielded from one another by water molecules, making ion-ion interactions less prevalent.

In the solid state, ions interact by forming lattices in which oppositely charged ions arrange themselves in a regular fashion. In the **Figure** 9.15, the small purple Na ions interlock with the larger green chlorine ions in a pattern defined by the relative sizes and charges of the two ions. Because each ion has a full positive or negative charge, the forces holding two ions together are relatively strong.

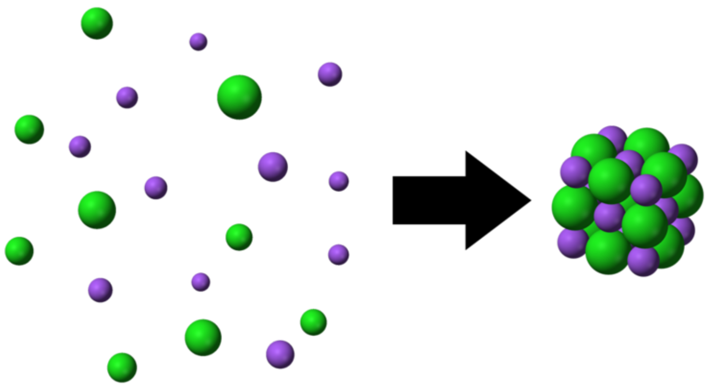


FIGURE 9.15

Ion-ion interaction to form a lattice.

More complex polyatomic ions can also participate in these types of interactions. Sodium acetate (**Figure** 9.16) is one such material.

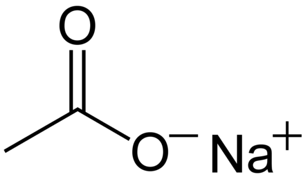


FIGURE 9.16

Sodium acetate

Dipole-Dipole Interactions

A **dipole** occurs when two opposite charges are separated by some amount of distance. We have already seen dipoles in the form of polar bonds. For example, each O-H bond in water is an example of a dipole; the partial positive charge on hydrogen is separated from the partial negative charge on oxygen by the length of the bond. A **molecular dipole** is the geometric sum of all the individual bond dipoles in a molecule. In order for a molecule to have a dipole, it must have at least one polar bond. However, not all molecules with polar bonds have an overall molecular dipole. Sometimes the dipoles within a molecule will effectively cancel each other out, giving a zero net molecular dipole. This is often seen in symmetrical molecules.

A **dipole-dipole force** can be seen when two polar molecules interact with one another. The partial positive region of one molecule will be attracted to the partial negative region of an adjacent one. Because both charges are partial (less than a full charge), these interactions are weaker than those involving ions. An example of a dipole-dipole interaction between two molecules of HCl is shown below:

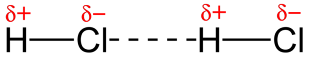


FIGURE 9.17

Dipole-dipole interactions

Ion-Dipole Interactions

An ion-dipole interaction involves the attraction between a fully charged entity and a polar molecule. Both cations and anions can participate in this type of bonding. A cation will be attracted to the partial negative portion of the polar molecule, while an anion will interact with the partial positive region.

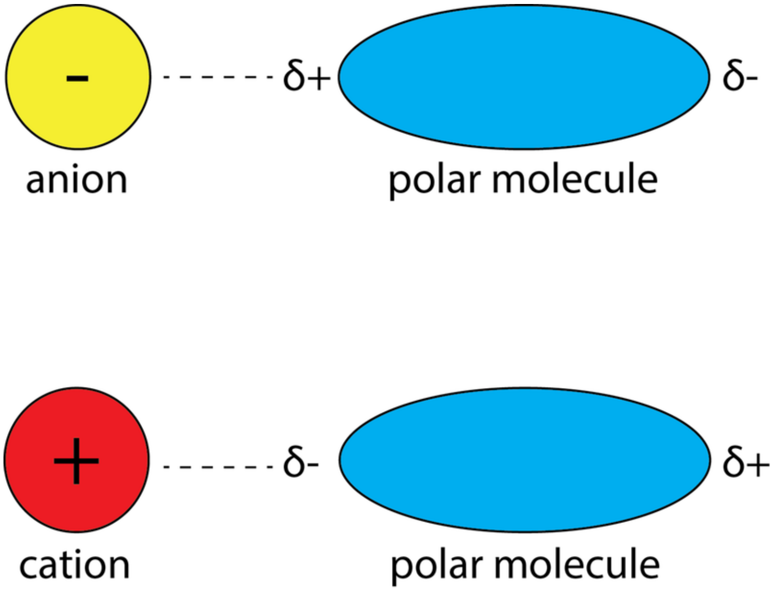


FIGURE 9.18

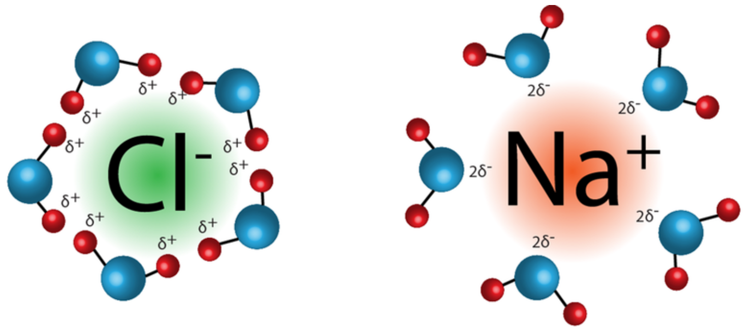
Polar molecules.

The interaction of sodium and chloride ions with water is one example of an ion-dipole interaction:

The positive sodium ions are attracted to the partial negative portion of the water molecule (the red oxygen atoms), while the negative chloride ions interact with the partial positive hydrogen portion (the blue atoms). Because one of the bonding partners has only a partial positive or negative charge, these forces are somewhat weaker than ion-ion interactions.

Dispersion Forces

Somewhat more challenging to visualize are **dispersion forces**. These interactions are defined as attractive forces that arise as a result of temporary dipoles induced in atoms or molecules. They are often referred to as London dispersion forces due to the work done by the German-American physicist Fritz London (1900-1954).



Slightly positive hydrogen are attracted to chlorine anions

Slightly negative oxygen are attracted to sodium cations

FIGURE 9.19

Interactions of ions with polar water molecules.

Two things need to be kept in mind with regard to these forces: they are relatively weak, and they do not require any permanent polarity. Induced dipoles are caused by local and temporary changes in the environment immediately around a molecule. Brief distortions in the electron cloud cause temporary dipoles to come and go, and these provide a way for even completely nonpolar molecules to attract one another. Although these may seem almost insignificant compared to the stronger forces discussed above, nonpolar substances would have no way to form solids or liquids without them. Note that all molecular substances experience dispersion forces, but for small polar molecules, dipole-dipole interactions will be the dominant attractive force.

The Hydrogen Bond

A "special case" of dipole-dipole interactions is referred to as the **hydrogen bond**. Hydrogen bonding occurs only in molecules where hydrogen is covalently bonded to one of three elements: fluorine, oxygen, or nitrogen. These three elements are so electronegative that they withdraw the majority of the electron density from the covalent bond with hydrogen, leaving the H atom very electron-deficient. Because the hydrogen atom does not have any electrons other than the ones in the covalent bond, its positively charged nucleus is almost completely exposed, allowing strong attractions to other nearby lone pairs. These lone pairs are generally on atoms with partial negative charges in adjacent molecules, although hydrogen bonds within a single molecule can also occur if the structure of the molecule is appropriate.

A particularly important example of hydrogen bonding occurs between water molecules. Because water has two O-H bonds and two lone pairs on each oxygen atom, extensive networks of hydrogen bonds can form, allowing ice and liquid water to exist.

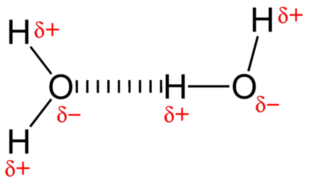


FIGURE 9.20

Quite often, the partial charges are not explicitly written when drawing hydrogen bonds, but they are always there. Illustrated below are a few more examples of hydrogen bonding in molecules.

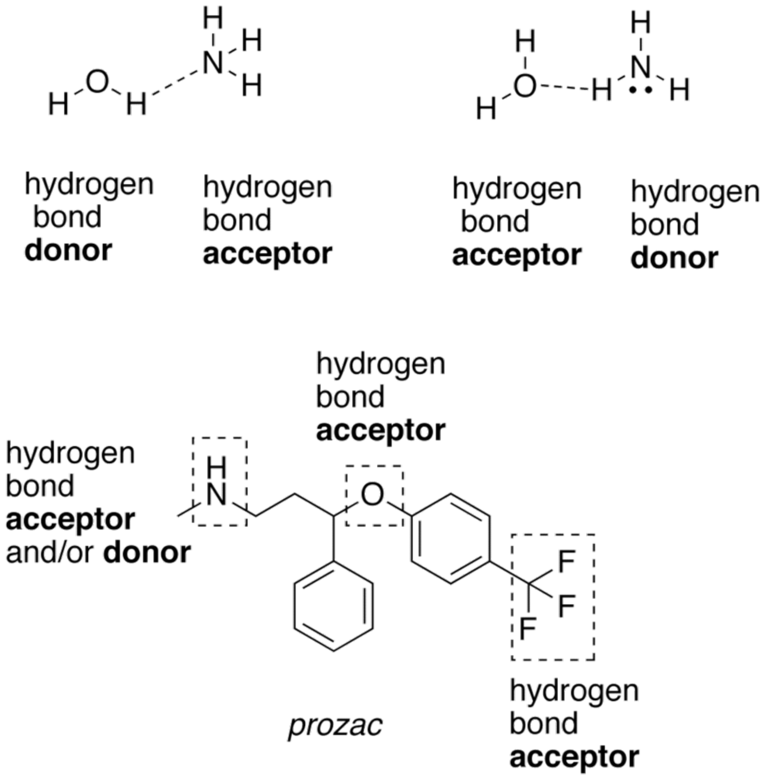


FIGURE 9.21

Lesson Summary

- A variety of interactions can occur between molecules that involve attractions between full or partial charges.
- Molecules that have a partial positive region and a partial negative region are said to possess a molecular dipole. The interactions between these dipoles are what allow molecules to condense into the liquid or solid states.
- Even completely nonpolar molecules can attract each other due to dispersion forces.
- The hydrogen bond is a special type of dipole-dipole interaction that is seen in a variety of molecular compounds.

Lesson Review Questions

Reviewing Concepts

1. Explain what gives a molecule a molecular dipole.
2. What is a dipole-dipole interaction?
3. Define the term hydrogen bond.
4. Explain what dispersion forces are.

Problems

1. What would be the strongest intermolecular force holding together collections of each of the following molecules?
    a. $CH_3CH_2CH_2CH_3$
    b. CH_3OH
    c. PCl_5
    d. O_2
2. Draw the hydrogen-bond interactions that can occur between molecules of CH_3NH_2.
3. How would molecules containing N-F bonds interact with one another?

Further Reading / Supplemental Links

- Video discussing intermolecular forces: http://meaghersclasses.podomatic.com/entry/2007-02-24T21_30_52-08_00
- Video discussing van der Waal's forces: http://www.youtube.com/watch?v=8qfzpJvsp04
- Tutorial on intermolecular forces: http://www.ausetute.com.au/intermof.html

Points to Consider

We have looked very briefly at where electrons are in covalent bonds.

- How does the location of the electron in a bond influence the three-dimensional geometry of that molecule?
- What modifications do we have to make to our understanding of orbitals in order to explain some details of covalent bonding?

9.5 Hybridization and Molecular Orbitals

Lesson Objectives

- Describe valence bond theory as it pertains to the formation of a covalent bond between atoms.
- Describe the process of electron promotion and hybridization during the formation of hybrid orbitals.
- Explain the relationship between electron domain geometry and the various types of hybrid orbitals.
- Distinguish between sigma and pi bonding.

Lesson Vocabulary

- **valence bond theory**: States that covalent bonds are formed by the overlap of partially filled atomic orbitals.
- **hybridization**: The mixing of the atomic orbitals in an atom to produce a set of hybrid orbitals.
- **hybrid orbitals**: The atomic orbitals obtained when two or more nonequivalent orbitals from the same atom combine in preparation for bond formation.
- **sigma bond (σ)**: A bond formed by the overlap of orbitals in an end-to-end fashion, with the electron density concentrated between the nuclei of the bonding atoms.
- **pi bond (π)**: A bond formed by the overlap of orbitals in a side-by-side fashion, with the electron density concentrated above and below the plane of the nuclei of the bonding atoms.
- **molecular orbitals**: Orbitals created as a result of atomic orbitals combining to make covalent bonds

Check Your Understanding

Recalling Prior Knowledge

- How are electrons arranged in atomic orbitals?
- What is the difference between the electron domain geometry of a molecule and its molecular geometry?

Earlier in this chapter, you learned how to draw Lewis electron-dot structures for molecules and predict their shapes using VSEPR theory. In this lesson, we will see how these concepts relate to the way in which electrons behave in their atomic orbitals when a covalent bond forms.

Introduction

Atoms form covalent bonds by sharing valence electrons. The valence electrons are located in atomic orbitals. However, when a bond forms, the structure of the atomic orbitals changes. In this lesson, we will see how the atomic orbitals interact to share valence electrons and form different types of covalent bonds.

Valence Bond Theory

Covalent bonds form when the electron clouds of two atoms overlap with each other. In a simple H_2 molecule, the single electron in each atom becomes attracted to the nucleus of the other atom in the molecule as the atoms come closer together. Other covalent bonds form in the same way as unpaired electrons from two atoms "match up" to form the bond. In a fluorine atom, there is an unpaired electron in one of the 2p orbitals. When a F_2 molecule forms, the 2p orbitals from each of the two atoms overlap to produce the F−F covalent bond. The overlapping orbitals do not have to be of the same type to form a covalent bond. For example, in a molecule of HF, the 1s orbital of the hydrogen atom overlaps with the 2p orbital of the fluorine atom (**Figure** 9.22):

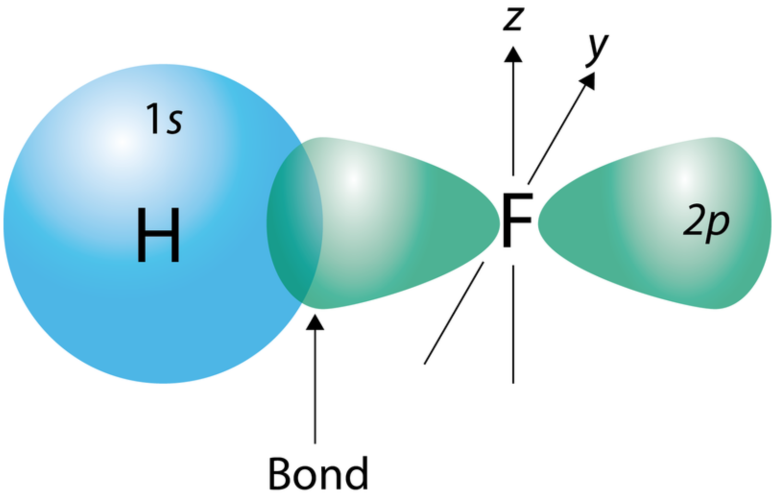


FIGURE 9.22
In a molecule of hydrogen fluoride (HF), the covalent bond occurs due to an overlap between the 1s orbital of the hydrogen atom and the 2p orbital of the fluorine atom.

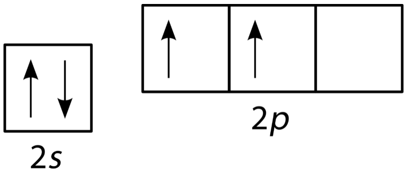
In essence, any covalent bond results from a combination of atomic orbitals. This idea forms the basis for a quantum mechanical theory called valence bond (VB) theory. **Valence bond theory** states that covalent bonds are formed by the overlap of partially filled atomic orbitals.

Hybrid Orbitals

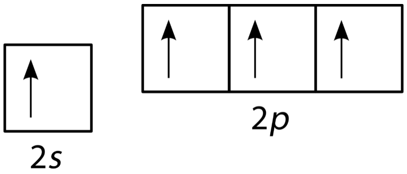
The bonding scheme described by valence bond theory must account for molecular geometries as predicted by VSEPR theory. To do that, we must introduce a concept called hybrid orbitals.

sp

Unfortunately, overlap of existing atomic orbitals (s, p, etc.) is not sufficient to explain some of the bonding and molecular geometries that are observed. Consider the carbon atom in the methane (CH_4) molecule. An isolated carbon atom has an electron configuration of $1s^22s^22p^2$, meaning that it has two unpaired electrons in its 2p orbitals, as shown below.



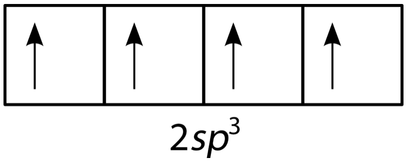
According to the description of valence bond theory so far, carbon would be expected to form only two bonds, corresponding to its two unpaired electrons. However, methane is a common and stable molecule that contains four equivalent C−H bonds. One way to account for this might be to promote one of the 2s electrons to the empty 2p orbital.



Now, four bonds are possible. The promotion of the electron "costs" a small amount of energy, but recall that the process of bond formation is accompanied by a decrease in energy. The two extra bonds that can now be formed result in a lower overall energy, and thus a greater stability, for the CH_4 molecule. Carbon normally forms four bonds in most of its compounds.

The number of bonds is now correct, but the geometry is wrong. The three p orbitals (p_x, p_y, p_z) are oriented at 90° angles relative to one another. However, as we saw in our discussion of VSEPR theory, the observed H−C−H bond angle in the tetrahedral CH_4 molecule is actually 109.5°. Therefore, the methane molecule cannot be adequately represented by simple overlap of the 2s and 2p orbitals of carbon with the 1s orbitals of each hydrogen atom.

To explain the bonding in methane, it is necessary to introduce the concept of hybridization and hybrid atomic orbitals. **Hybridization** is the mixing of the atomic orbitals in an atom to produce a set of hybrid orbitals. When hybridization occurs, it must do so as a result of the mixing of nonequivalent orbitals. For example, s and p orbitals can hybridize, but p orbitals cannot hybridize only with other p orbitals. **Hybrid orbitals** are the atomic orbitals obtained when two or more nonequivalent orbitals from the same atom combine in preparation for bond formation. In the current case of carbon, the single 2s orbital hybridizes with the three 2p orbitals to form a set of four hybrid orbitals, called sp^3 hybrids.



The sp^3 hybrids are all equivalent to one another. Spatially, the hybrid orbitals point towards the four corners of a tetrahedron (**Figure** 9.23):

The large lobe from each of the sp^3 hybrid orbitals then overlaps with normal unhybridized 1s orbitals on each hydrogen atom to form the tetrahedral methane molecule.

Another example of sp^3 hybridization occurs in the ammonia (NH_3) molecule. The electron domain geometry of ammonia is also tetrahedral, meaning that there are four groups of electrons around the central nitrogen atom. Unlike methane, however, one of those electron groups is a lone pair. The resulting molecular geometry is trigonal pyramidal. Just as in the carbon atom, the hybridization process starts as a promotion of a 2s electron to a 2p orbital, followed by hybridization to form a set of four sp^3 hybrids. In this case, one of the hybrid orbitals already contains a pair of electrons, leaving only three half-filled orbitals available to form covalent bonds with three hydrogen atoms.

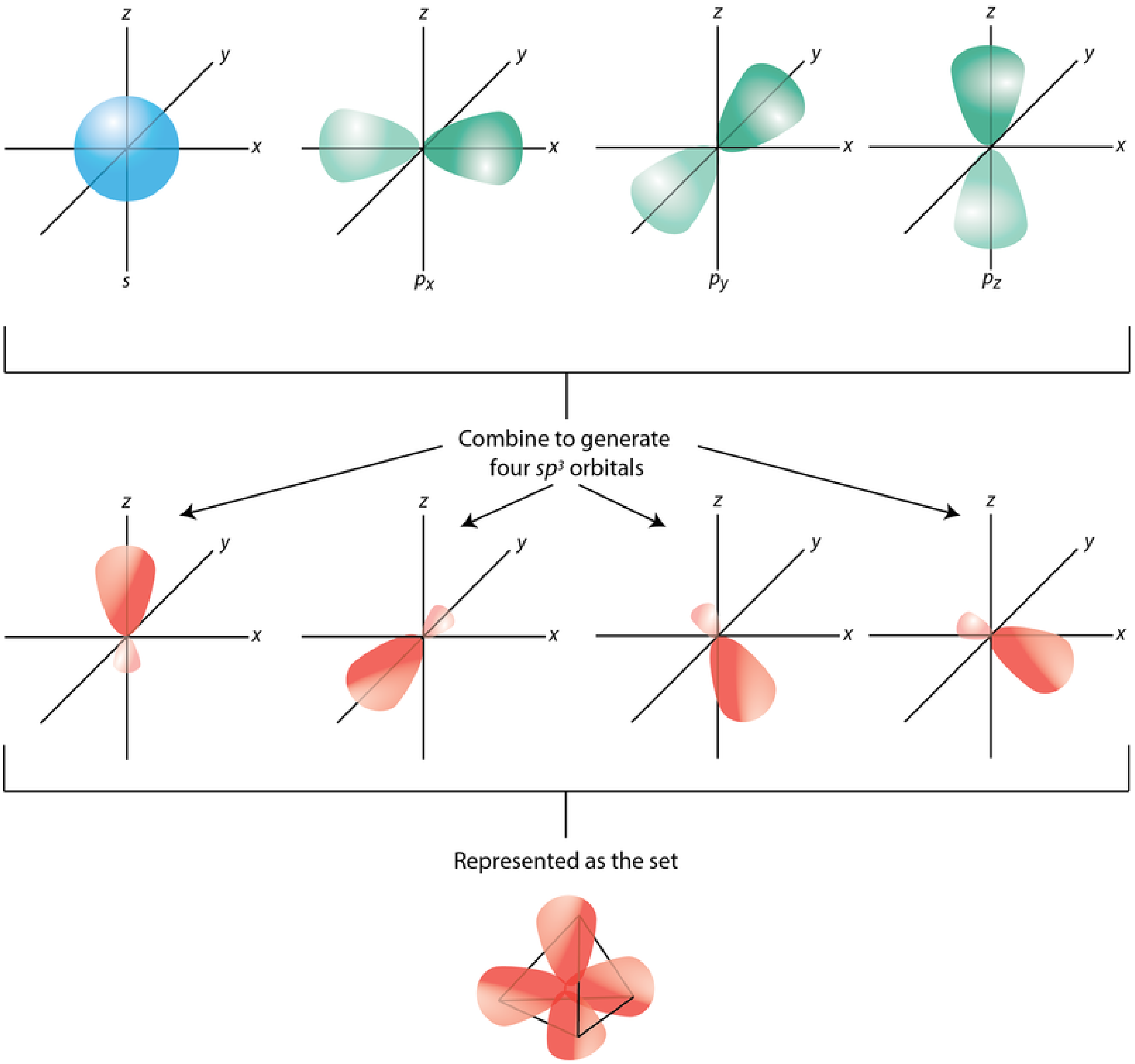


FIGURE 9.23

The process of sp^3 hybridization is the mixing of an s orbital with a set of three p orbitals to form a set of four sp^3 hybrid orbitals. Each large lobe of the hybrid orbitals points to one corner of a tetrahedron.

The methane and ammonia examples illustrate the connection between orbital hybridization and the VSEPR model. The electron domain geometry predicted by VSEPR leads directly to the type of hybrid orbitals that must be formed to accommodate that geometry. Both methane and ammonia have tetrahedral electron domain geometries and thus both undergo sp^3 hybridization.

Likewise, the bent-shaped water molecule (H_2O) also involves the formation of sp^3 hybrids on the oxygen atom. In this case, however, there are two hybrid orbitals which have lone pairs and two which bond to the hydrogen atoms. Because the electron domain geometry for H_2O is tetrahedral, the hybridization is sp^3.

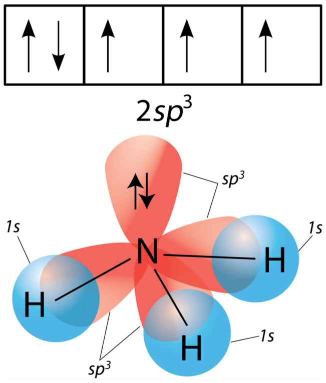
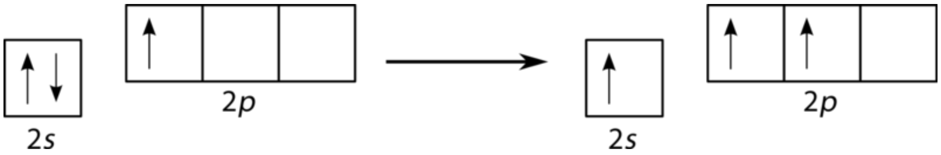


FIGURE 9.24

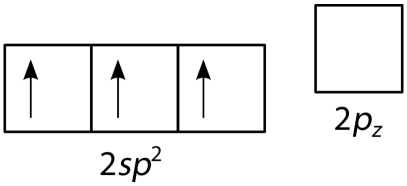
The trigonal pyramidal ammonia molecule also results from sp^3 hybridization of the central (nitrogen) atom. Of the four groups of electrons surrounding the nitrogen atom, three form single covalent bonds to hydrogen atoms, while one group is a lone pair.

sp

Boron trifluoride (BF_3) is predicted to have a trigonal planar geometry by VSEPR. First, a paired 2s electron is promoted to an empty 2p orbital.



This is followed by hybridization of the three occupied orbitals to form a set of three sp^2 hybrids, leaving the $2p_z$ orbital unhybridized. The choice of which p orbital to leave unhybridized is arbitrary, but $2p_z$ is conventionally chosen in the case of sp^2 hybrids.

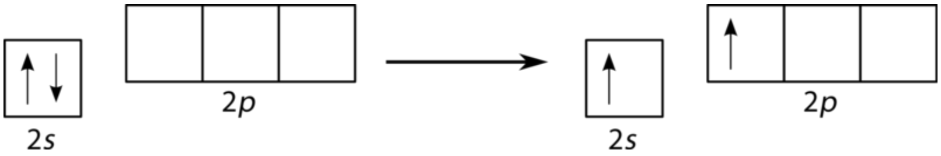


The geometry of the sp^2 hybrid orbitals is trigonal planar, with the large lobe of each orbital pointing towards one corner of an equilateral triangle (**Figure** 9.25). The angle between any two of the hybrid orbital lobes is 120°. Each can bond with a $2p$ orbital from a fluorine atom to form the trigonal planar BF_3 molecule.

Other molecules with a trigonal planar electron domain geometry also form sp^2 hybrid orbitals. For example, the electron domain geometry of ozone (O_3) is trigonal planar, although the presence of a lone pair on the central oxygen atom makes the molecular geometry bent. The hybridization of the central O atom of ozone is sp^2.

sp Hybridization

A beryllium hydride (BeH_2) molecule is predicted to be linear by VSEPR. The beryllium atom contains only paired electrons, so it must also undergo hybridization. One of the 2s electrons is first promoted to an empty 2p orbital.



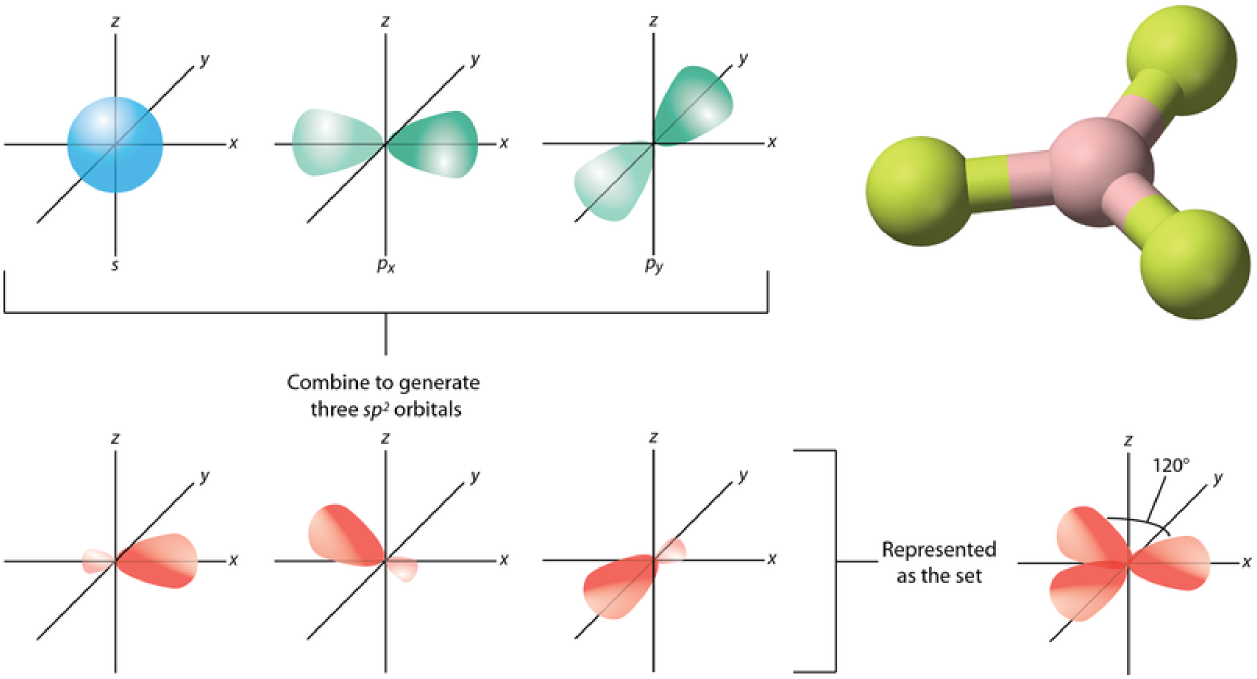
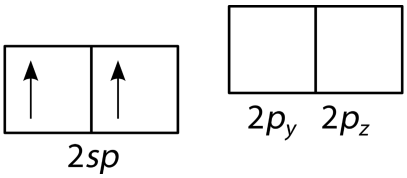


FIGURE 9.25

The process of sp^2 hybridization involves the mixing of one s orbital with a set of two p orbitals (p$_x$ and p$_y$) to form a set of three sp$_2$ hybrid orbitals. Each large lobe of the hybrid orbitals points to one corner of a triangle.

The occupied orbitals are then hybridized, and the result is a pair of sp hybrid orbitals. The two remaining p orbitals (arbitrarily chosen to be p$_y$ and p$_z$) do not hybridize and remain unoccupied.



The geometry of the sp hybrid orbitals is linear, with the large lobes of the two orbitals pointing in opposite directions along one axis, arbitrarily defined as the x-axis (**Figure** 9.26). Each can bond with a 1s orbital from a hydrogen atom to form the linear BeH_2 molecule.

Other molecules whose electron domain geometry is linear and for whom hybridization is necessary also form sp hybrid orbitals. Examples include CO_2 and C_2H_2, which will be discussed further in the next section on hybridization and multiple bonds.

It should be noted that molecules with trigonal bipyramidal or octahedral electron geometries form different types of hybrids that also involve the participation of one or more d orbitals. However, we will not consider these types of hybrid orbitals here.

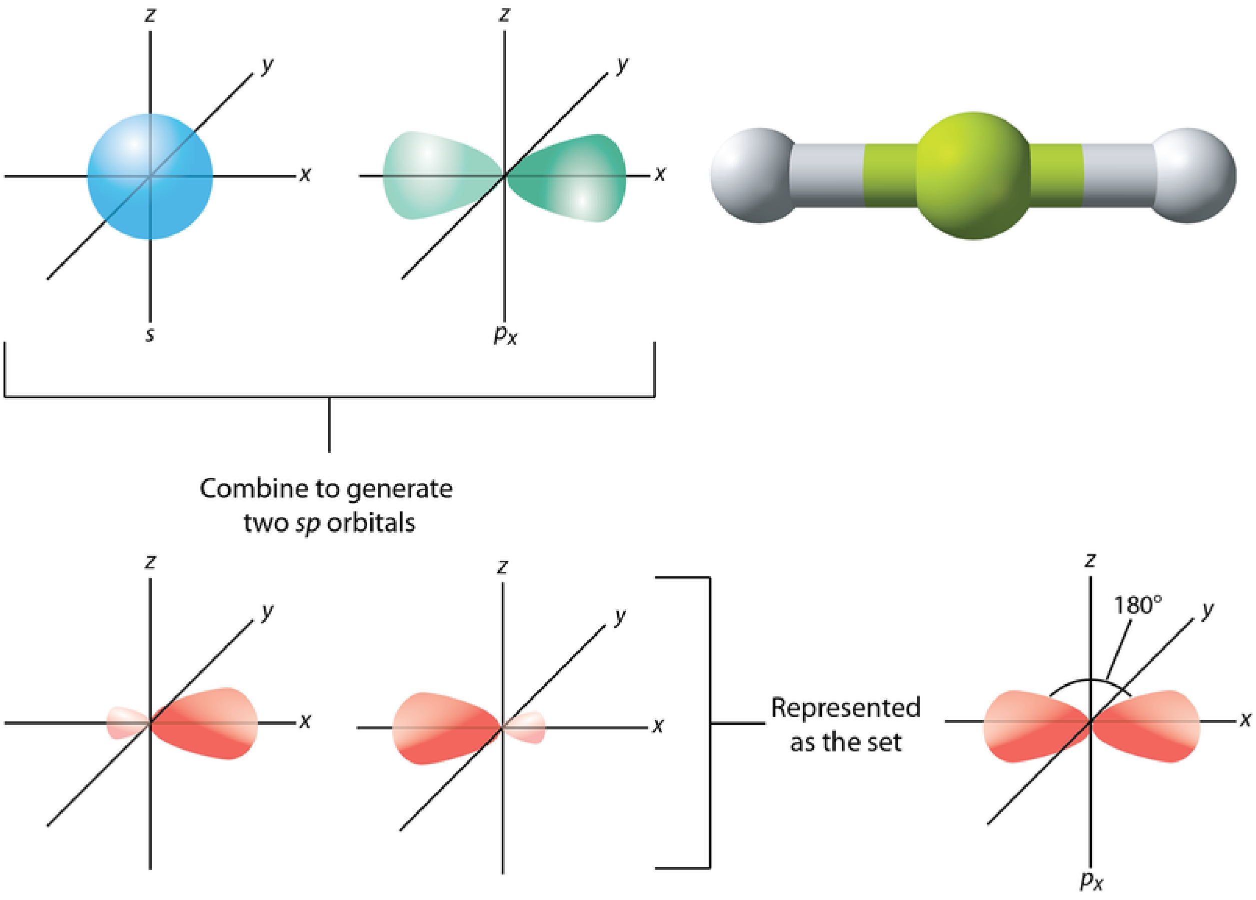


FIGURE 9.26

The process of sp hybridization involves the mixing of an s orbital with a single p orbital (conventionally the p_x orbital), to form a set of two sp hybrids. The two lobes of the sp hybrids point in opposite directions to produce a linear molecule.

Hybridization in Molecules with Double or Triple Bonds

The hybridization model helps explain molecules with double or triple bonds. Consider the ethene molecule (C_2H_4), which contains a double covalent bond between the two carbon atoms and single bonds between the carbon atoms and the hydrogen atoms. The entire molecule is planar.

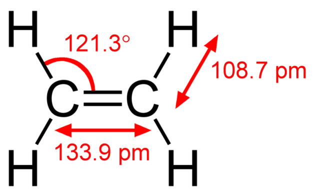
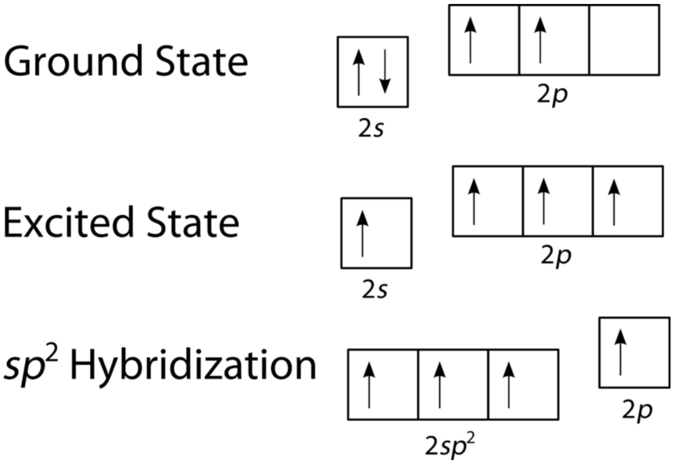


FIGURE 9.27

As can be seen in **Figure** 9.27, the electron domain geometry around each carbon atom is trigonal planar, which corresponds to sp^2 hybridization. Previously, we saw carbon undergo sp^3 hybridization in a CH_4 molecule, so how does it work in this case? As seen below, the electron promotion is the same, but the hybridization occurs only between the single s orbital and two of the three p orbitals. This generates a set of three sp^2 hybrids along with an unhybridized $2p_z$ orbital. Each orbital contains one electron and is capable of forming a covalent bond.



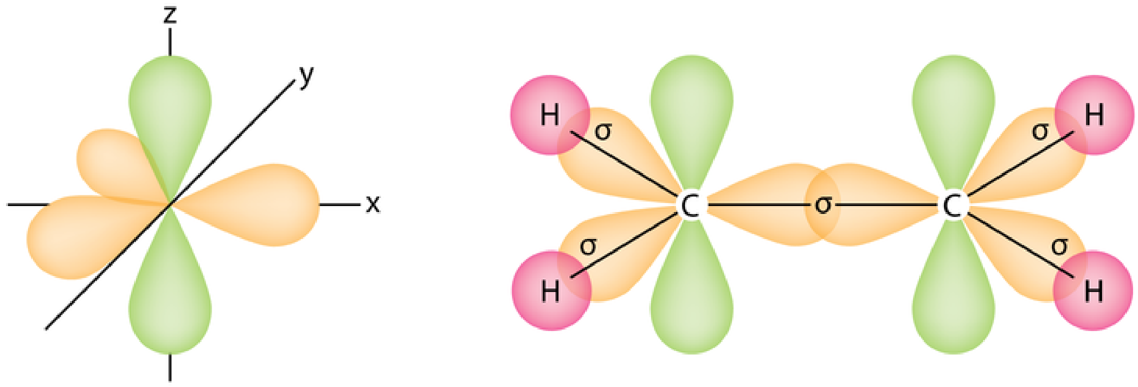
The three sp^2 hybrid orbitals lie in one plane, while the unhybridized $2p_z$ orbital is oriented perpendicular to that plane. The bonding in C_2H_4 is explained as follows. One of the three sp^2 hybrids forms a bond by overlapping with the identical hybrid orbital on the other carbon atom. The remaining two hybrid orbitals from bonds by overlapping with the 1s orbital of a hydrogen atom. Finally, the $2p_z$ orbitals on each carbon atom form another bond by overlapping with one another sideways.

It is necessary to distinguish between the two types of covalent bonds in a C_2H_4 molecule. A **sigma bond (σ bond)** is a bond formed by the overlap of orbitals in an end-to-end fashion, with the electron density concentrated between the nuclei of the bonding atoms. A **pi bond (π bond)** is a bond formed by the overlap of orbitals in a side-by-side fashion, with the electron density concentrated above and below the plane of the nuclei of the bonding atoms. **Figure** 9.28 shows the two types of bonding in C_2H_4. The sp^2 hybrid orbitals are orange and the p_z orbital is green. Three sigma bonds are formed by each carbon atom with its hybrid orbitals. The pi bond is the "second" bond of the double bond between the carbon atoms and is shown as an elongated blue lobe that extends both above and below the plane of the molecule, which contains the six atoms and all of the sigma bonds.

In a conventional Lewis electron-dot structure, a double bond is shown as two lines between the atoms, as in C=C. It is important to realize, however, that the two bonds are different; one is a sigma bond, while the other is a pi bond.

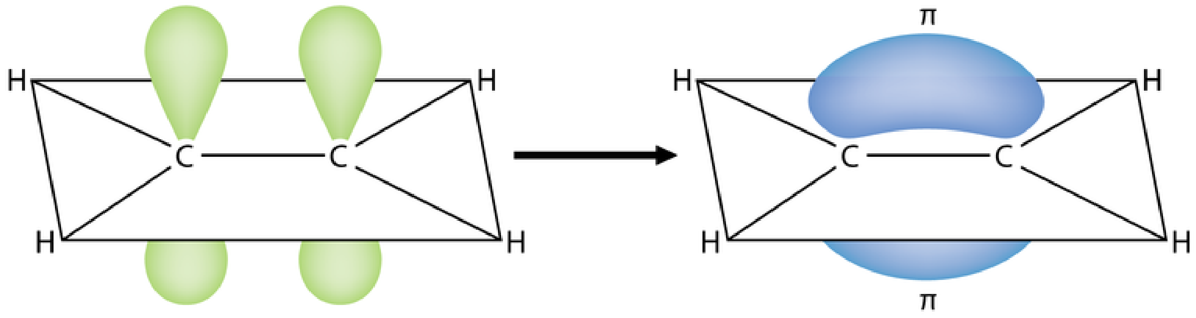
Ethyne (C_2H_2) is a linear molecule with a triple bond between the two carbon atoms. Since each carbon atom is bonded to two other atoms and has no lone pairs, the hybridization of each carbon is sp.

Again, the promotion of an electron in the carbon atom occurs in the same way. However, the hybridization now involves only the 2s orbital and the $2p_x$ orbital, leaving the $2p_y$ and the $2p_z$ orbitals unhybridized.



The set of orbitals $sp^2 + p$

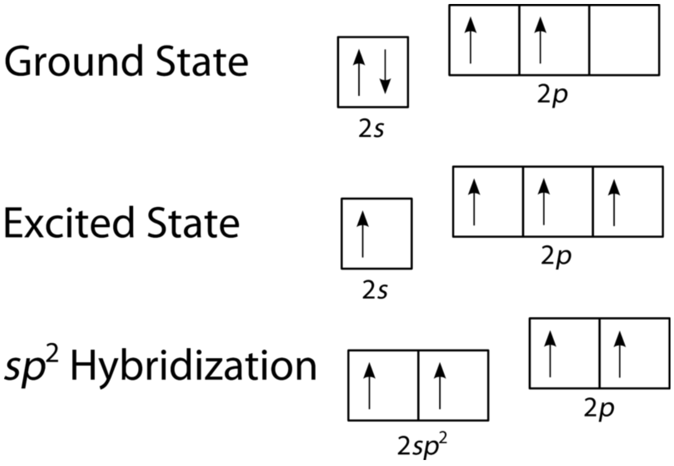
Sigma (σ) bond



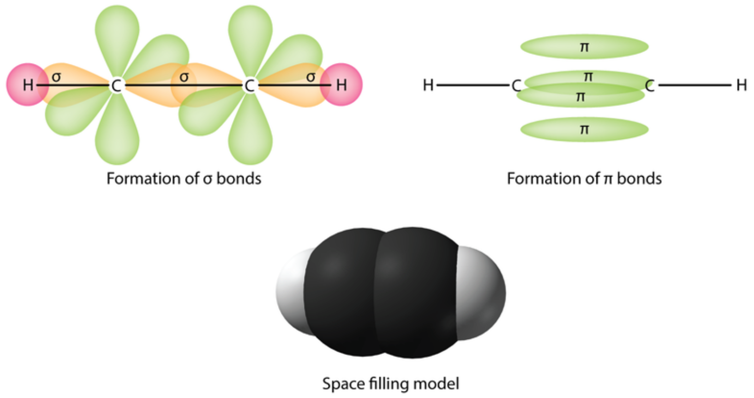
Overlap of p orbitals leading to pi (π) bond

FIGURE 9.28

The C_2H_4 molecule contains five sigma bonds and one pi bond. Sigma bonds are formed by a direct overlap of bonding orbitals, while a pi bond is formed by a side-to-side overlap of unhybridized p orbitals.



The sigma bond between the two carbon atoms is formed from sp hybrid orbitals, and the remaining hybrid orbitals form sigma bonds to the two hydrogen atoms. Both the p_y and the p_z orbitals on each carbon atom form pi bonds with each other. As with ethene, these side-to-side overlaps are not directly on the line between the two bonded atoms. Additionally, these two pi bonds are perpendicular to one another (**Figure** 9.29); one pi bond is above and below the line of the molecule, while the other is in front of and behind the page.



Formation of σ bonds

Formation of π bonds

Space filling model

FIGURE 9.29

The C_2H_2 molecule contains a triple bond between the two carbon atoms, one of which is a sigma bond, and two of which are pi bonds. The pi bonds come from overlap between the p_y and the p_z orbitals on each carbon.

In general, single bonds between atoms are always sigma bonds. Double bonds are comprised of one sigma and one pi bond. Triple bonds are comprised of one sigma bond and two pi bonds.

Molecular Orbitals

In most of the above illustrations, bonds are depicted as two overlapping atomic orbitals that still retain their original shapes. However, a more accurate way to show the electron density after the bond has formed is shown in **Figures** below and below. When atomic orbitals combine to make covalent bonds, the results are new orbitals known as **molecular orbitals**. Molecular orbital theory plays an important role in our understanding of various molecular properties.

Lesson Summary

- Valence bond theory describes the formation of covalent bonds in terms of the overlap of singly occupied atomic orbitals.
- The hybridization of nonequivalent atomic orbitals is necessary to correctly predict the bonding and molecular geometries of many molecules. The types of hybrid orbitals that form on the central atom are dictated by the electron domain geometry.
- Sigma bonds are formed by the end-to-end overlap of bonding orbitals. Pi bonds are formed by the side-to-side overlap of p orbitals. Single bonds are normally sigma bonds. A double or triple bond consists of one sigma bond and either one or two pi bonds.
- Atomic orbitals from different atoms overlap to form molecular orbitals.

Lesson Review Questions

1. Why do atoms "promote" electrons to higher orbitals in order to form bonds?

2. Describe the type of hybrid orbitals formed corresponding to each of the following electron domain geometries:
   a. tetrahedral
   b. trigonal planar
   c. linear
3. In sp^3 hybridization, how many hybrid orbitals are there? How do the hybrid orbitals compare to one another?
4. What is the hybridization state of Si in SiH_4?
5. What hybrid orbitals are used by the nitrogen atoms in $H_2N\text{-}NH_2$?
6. What types of bonds make up single, double, and triple bonds?
7. What hybrid orbitals are used by the carbon atoms in each of the following:
   a. $H_3C\text{-}CH{=}CH_2$
   b. CO_2
8. Describe the covalent bonds in each of the molecules from the question above.

Further Reading / Supplemental Links

- Discussion of hybrid orbitals:

http://www.uwosh.edu/faculty_staff/gutow/Orbitals/N/What_are_hybrid_orbitals.shtml

- Animation of orbital hybridizations:

http://www.bluffton.edu/~bergerd/classes/CEM222/Handouts/spanimation.html

Points to Consider

- How does molecular geometry influence reactivity?

9.6 References

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10. (”left”) User:Booyabazooka/Wikimedia Commons; (”right”) Ben Mills (User:Benjah-bmm27/Wikimedia Commons). (”left’’) http://commons.wikimedia.org/wiki/File:Ammonia_lone_electron_pair.svg; (’’right”) http://commons.wikimedia.org/wiki/File:Ammonia-3D-balls-A.png . Public Domain
11. (User:Benjah-bmm27/Wikimedia Commons). (”left’’) http://commons.wikimedia.org/wiki/File:Water-dimensions-from-Greenwood%26Earnshaw-2D.png; (”right”) http://commons.wikimedia.org/wiki/File:Water-3D-balls-A.png . Public Domain
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14. Ben Mills (User:Benjah-bmm27/Wikimedia Commons). http://commons.wikimedia.org/wiki/File:Hydrogen-fluoride-elpot-transparent-3D-balls.png . Public Domain
15. Ben Mills (User:Benjah-bmm27/Wikimedia Commons). http://commons.wikimedia.org/wiki/File:Lattice-enthalpy-NaCl-3D-ionic.png . Public Domain
16. Ben Mills (User:Benjah-bmm27/Wikimedia Commons). http://commons.wikimedia.org/wiki/File:Sodium-acetate-2D-skeletal.png . Public Domain
17. Ben Mills (User:Benjah-bmm27/Wikimedia Commons). http://commons.wikimedia.org/wiki/File:Dipole-dipole-interaction-in-HCl-2D.png . Public Domain
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19. Christopher Auyeung and Jodi So. CK-12 Foundation . CC BY-NC 3.0
20. Ben Mills (User:Benjah-bmm27/Wikimedia Commons). http://commons.wikimedia.org/wiki/File:Hydrogen-bonding-in-water-2D.png . Public Domain
21. User:Mcpazzo/Wikimedia Commons. http://commons.wikimedia.org/wiki/File:WikipediaHDonorAcceptor.png . Public Domain
22. Jodi So. CK-12 Foundation . CC BY-NC 3.0

23. Jodi So. CK-12 Foundation . CC BY-NC 3.0
24. Jodi So. CK-12 Foundation . CC BY-NC 3.0
25. Jodi So, using 3D molecule by Ben Mills (User:Benjah-bmm27/Wikimedia Commons). CK-12 Foundation; 3D molecule: http://commons.wikimedia.org/wiki/File:Boron-trifluoride-3D-balls.png . CC BY-NC 3.0 (3D molecule available under public domain)
26. Jodi So, using 3D molecule by Ben Mills (User:Benjah-bmm27/Wikimedia Commons). CK-12 Foundation ; 3D molecule: http://commons.wikimedia.org/wiki/File:Beryllium-hydride-molecule-IR-3D-balls.png . CC BY-NC 3.0 (3D molecule available under public domain)
27. Ben Mills (User:Benjah-bmm27/Wikimedia Commons). http://commons.wikimedia.org/wiki/File:Ethylene-CRC-MW-dimensions-2D.png . Public Domain
28. Zachary Wilson. CK-12 Foundation . CC BY-NC 3.0
29. Zachary Wilson, using 3D model by Ben Mills (User:Benjah-bmm27/Wikimedia Commons). CK-12 Foundation; 3D molecule: http://commons.wikimedia.org/wiki/File:Acetylene-CRC-IR-3D-vdW.png . CC BY-NC 3.0 (3D model available under public domain)

CHAPTER 10 The Mole

Chapter Outline

10.1 THE MOLE CONCEPT

10.2 MASS, VOLUME, AND THE MOLE

10.3 CHEMICAL FORMULAS

10.4 REFERENCES

Humans have long been interested in how much of something they have. Ancient commerce was often conducted by trading goods for a certain weight of gold or silver. Both religious and civil statutes forbade the use of false weights in conducting business. In chemistry, we routinely weigh materials to determine how much of a chemical we are adding to a reaction. The amount of product is often weighed to determine reaction yield. Chemical solutions are prepared by weighing a specified amount of material and dissolving it in a defined volume of solvent. Weight and volume are two different ways to measure how much of a substance is present. In this chapter, we will explore how to express amounts of materials in a way that indicates the number of atoms or molecules contained in a given sample.

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10.1 The Mole Concept

Lesson Objectives

- Describe three methods of measuring matter.
- Define Avogadro's number.
- Define mole.
- Perform calculations to convert between the number of moles and the number of particles in a sample.
- Calculate the molar mass of a substance.

Lesson Vocabulary

- **mole**: The name given to a group of 6.022×10^{23} items.
- **Avogadro's number**: 6.022×10^{23}.
- **representative particle**: The smallest unit of a substance that retains its chemical identity.
- **molar mass**: The mass of one mole of representative particles of a substance.

Check Your Understanding

- What units are used to describe the atomic mass (or weight) of an element?

Introduction

As you have learned, matter comprises most everything around us. The atoms and molecules that make up this matter are so tiny that you cannot see them with the naked eye. Imagine you had a bag of apples. You could measure, rather easily, the weight of the apples, the volume of the apples, and the number of apples in your bag. But what if you wanted to know the number of atoms that were in those apples? How could you possibly count something you cannot even see? In this lesson you will learn about the mole concept, which enables scientist to quantify things as tiny as atoms.

Determining the Amount of Material

Determining by Weight

One common method of seeing how much material is present is to weigh it. This practice goes back many centuries. The Code of Hammurabi (established around 1760 B.C.) spelled out methods for assuring fair weights in business and trade dealings. Many societies had harsh penalties for using false weights. Today we have state and federal agencies that make sure the scales used for business are accurate.

Shopping in a grocery store provides many opportunities for purchases by weight. Most fresh meat and fresh vegetables are marketed by weight, as are flour, sugar, and many other packaged goods.

Determining by Volume

Volume is another way of measuring material. Gases cannot be easily weighed, but their volume can be determined quickly and accurately. Liquid chemicals as well as foods and beverages are also sold by volume. Gasoline for our cars and trucks is sold by the gallon. At the grocery store, we can buy a gallon of milk or a two-liter bottle of soda pop.

Determining by Counting

The third way to indicate how much of something is present is to count the objects. At the grocery store, we could buy a dozen eggs, six donuts, or two loaves of bread. We might buy movie tickets or t-shirts, based on price per item. The weight or volume for many of items could be determined, but counting is generally faster for small numbers of objects and does not require any additional measurement tools.

Converting between Different Measurements

Sometimes one method of measurement is easiest but does not provide us with the information that we need. For example, say you had a huge sack of pennies and wanted to know how much it was worth. You could count them, but it might be much faster to weigh the sack. Say you find out that you have 4.801 pounds (2177.5 grams) of pennies. If you know that each penny weighs 2.5 grams (on average), then you could divide 2177.5 by 2.5, and you would know that you have about 871 pennies, or $8.71. Such conversions become even more important when dealing with much more miniscule objects, such as atoms or molecules. Because the numbers involved when talking about amounts of atoms are so large, a new unit was developed to make discussing such amounts easier. This unit is referred to as the mole.

The Mole

As we will see in the chapter on gases, the Italian scientist Amadeo Avogadro (1776-1856) proposed that the volume of a gas is directly proportional to the number of atoms or molecules in a given sample. Due to the vast quantities of atoms and molecules in an easily observable sample of any material, chemists needed a name that can stand for a very large number of items. A **mole** (abbreviated "mol") is the name given to a group of 6.022×10^{23} items. This value is named **Avogadro's number** as a tribute to his influential work.

The word "mole" is analogous to the word "dozen", in that it is a name that stands for a number. A dozen donuts is simply another way of saying 12 donuts. Similarly, a mole of donuts would be another way of saying 6.022×10^{23} donuts. Obviously, this would be an excessive amount of donuts. However, it becomes a more useful quantity when talking about objects like molecules. One mole of water molecules is equivalent to 6.022×10^{23} molecules of water. This amount of liquid water has a volume of a little over one tablespoon, which is a very normal amount to be dealing with.

Technically speaking, the mole is defined as the amount of carbon atoms in exactly 12 grams of carbon-12 (the isotope of carbon that contains 6 protons and 6 neutrons). This value cannot be determined by literally counting atoms, but it has been calculated in a variety of ways. When written out to 8 significant figures, the currently

FIGURE 10.1

Amadeo Avogadro (1776-1856)

accepted value is 6.0221413×10^{23}. However, because we don't usually deal with other measurements that are this precise, the rounded value of 6.022×10^{23} is sufficient for any situations that you are likely to encounter.

The mole is such an important parameter in chemistry that Mole Day was established in the U.S. on October 23, where it is celebrated from 6:02 AM to 6:02 PM. The day was originally established to generate interest in chemistry.

The scale of Avogadro's number is nearly incomprehensible in terms of everyday objects. This can be illustrated with examples like the following problem, in which we use the dimensional analysis technique from the chapter *Measurement* to convert between units.

Example 10.1

If you were given one million dollars every second, how long would it take to accumulate a mole of dollars?

Answer:

$$1 \text{ mol of dollars} \times \left(\frac{6.022\times10^{23} \text{ dollars}}{1 \text{ mol of dollars}}\right)\left(\frac{1 \text{ sec}}{1{,}000{,}000 \text{ dollars}}\right)\left(\frac{1 \text{ min}}{60 \text{ sec}}\right)\left(\frac{1 \text{ hour}}{60 \text{ min}}\right)\left(\frac{1 \text{ day}}{24 \text{ hours}}\right)\left(\frac{1 \text{ year}}{365 \text{ days}}\right) = 1.91 \times 10^{10} \text{ years}$$

Even at this very fast rate, it would take over 19 billion years to obtain a mole of dollars. To put this into perspective, the universe is believed to be about 14 billion years old, and our Sun will run out of fuel and burn out about 6 billion years from now.

Representative Particles

When we talk about one mole of a particular chemical substance, it is important to know exactly how much material is being referenced. For example, the phrase "a mole of water molecules" is often shortened to "a mole of water." When we talk about moles of a molecular substance, it is assumed that we are referring to moles of molecules. Similarly, the phrase "five moles of carbon dioxide" would refer to five moles of CO_2 molecules. In these cases, the molecule is sometimes called a **representative particle**, which is simply the smallest unit of a substance that retains its chemical identity.

What about when we are discussing non-molecular substances? Recall that an ionic compound does not exist as discrete molecules, but rather as an extended three-dimensional network of ions called a crystal lattice. The empirical formula of an ionic compound tells us the ratio of the ions in the crystal. In these cases, one mole of the substance is assumed to mean one mole of each ion in the empirical formula. For example, one mole of sodium oxide (Na_2O) refers to two moles of sodium ions (Na^+) and one mole of oxide ions (O^{2-}). The empirical formula gives you the representative particle for ionic substances. Unlike molecules, these representative particles do not exist as isolated units (sodium oxide does not exist as small clusters of three atoms each).

In the case of pure metals, the representative particle is simply the atom. One mole of zinc refers to a mole of Zn atoms.

Example 10.2

Calculate the number of moles of iron atoms that are present in 2 moles of Fe_2O_3.

$2 \text{ mol } Fe_2O_3 \times (\frac{2 \text{ mol Fe}}{1 \text{ mol } Fe_2O_3}) = 4 \text{ mol Fe}$

Example 10.3

Calculate the number of atoms that must be present in 3.05 moles of Pb.

$3.05 \text{ mol Pb} \times (\frac{6.022 \times 10^{23} \text{ atoms Pb}}{1 \text{ mol Pb}}) = 1.84 \times 10^{24} \text{ atoms Pb}$

Molar Mass

Because we are not able to count individual atoms, it is important to have a way to convert between amounts, which are expressed in moles, and a unit of quantity that we can more easily measure, such as mass. We begin by looking at the periodic table, which tells us the relative masses of various elements.

Molar Masses of the Elements

As you learned previously, the average atomic masses found on the periodic table are in atomic mass units (amu). For example, one atom of the most abundant isotope of hydrogen has a mass of approximately 1 amu, and one atom of helium has a mass of about 4 amu. Atomic masses are relative masses; they are based on the definition that one amu is equal to $1/12^{th}$ of the mass of a single atom of carbon-12. Therefore, one atom of carbon-12 has a mass of 12 amu, which is three times heavier than an atom of helium. This ratio would hold for any number of carbon and helium atoms. One hundred carbon-12 atoms would have three times the mass of one hundred helium atoms. By extension, 12.00 g of carbon-12 would contain the same number of atoms as 4.00 g of helium.

The relative scale of atomic masses in amu is also a relative scale of masses in grams. We said before that the mole is officially equal to the number of carbon atoms in exactly 12 g of carbon-12. In other words, one carbon-12 atom has a mass of exactly 12 amu, and one mole of carbon atoms has a mass of exactly 12 grams. This relationship is true for all substances. If one atom of helium has a mass of 4.00 amu, one mole of helium atoms has a mass of 4.00 g. One molecule of water has a mass of 18.0 amu, so one mole of water molecules has a mass of 18.0 grams. **Molar mass** is defined as the mass of one mole of representative particles of a substance. It is expressed in units of grams per mole (g/mol).

The values on the periodic table can be read either as average atomic masses or as molar masses. For example, the mass associated with chlorine is 35.45, even though no atoms of chlorine actually have a mass of 35.45 amu. However, in naturally occurring samples of chlorine atoms, about 75% will be chlorine-35 atoms (which have a mass of 35.0 amu), and about 25% will be chlorine-37 atoms (which have a mass of 37.0 amu). Since any usable quantity of chlorine contains a very, very large number of atoms, one mole of chlorine atoms will contain a mixture of these two isotopes in this ratio, resulting in a sample with a mass of 35.45 grams. Therefore chlorine has a molar mass of 35.45 g/mol.

Molar Masses of Compounds

The molecular formula of carbon dioxide is CO_2. One molecule of carbon dioxide consists of 1 atom of carbon and 2 atoms of oxygen. We can calculate the molar mass of carbon dioxide by adding together the molar masses of each atom present in the compound.

12.01 g/mol + 2(16.00 g/mol) = 44.01 g/mol

One mole of carbon dioxide molecules would have a mass of 44.01 grams. What about for an ionic compound? The molar mass of sodium sulfide (Na_2S) can be calculated as follows:

2(22.99 g/mol) + 32.06 g/mol = 78.04 g/mol

Because Na_2S is the empirical formula for this substance, the representative particle consists of two sodium atoms and one sulfur atom.

Example 10.4

What is the molar mass of hydrogen peroxide (H_2O_2).

Answer:

H - 2 × 1.0 g/mol = 2.0 g/mol

O - 2 × 16.0 g/mol = 32.0 g/mol

H_2O_2 = 34.0 g/mol

Example 10.5

How many moles of carbon are present in a 10.00 gram sample?

Answer:

$10.00 \text{ g C} \times \left(\frac{6.022 \times 10^{23} \text{ atoms C}}{1 \text{ mol C}}\right) = 6.022 \times 10^{24} \text{ atoms C}$

Lesson Summary

- One mole of any chemical substance contains 6.022 x 10^{23} representative particles.
- The masses on the periodic table can be read as average atomic masses or as molar masses.
- Molar mass is the mass of one mole of any given substance.

Lesson Review Questions

1. Imagine that you have 1 mole of coins, each of which is 1.5 mm thick. If they were placed in a single stack, how tall would the stack be (in km)? If the closest distance between the earth and the moon is 356,400 km, would the coins reach the moon? (Hint: Use the technique of dimensional analysis.)
2. Calculate the number of moles of N that must be present in 3 moles of NH_3.
3. Calculate the number of moles of oxygen that must be present in 2 moles of $C_6H_{12}O_6$.
4. How many moles of gold are present in a sample containing 1.81 x 10^{24} gold atoms?
5. How many atoms are in 0.065 moles of Hg?
6. Calculate the number of Br^- ions in 0.0038 moles of $CaBr_2$.
7. Calculate the molar mass of $K_2Cr_2O_7$.
8. Calculate the molar mass of dinitrogen tetroxide (N_2O_4).

Further Reading / Supplemental Links

- Avogadro biography: http://www.bulldog.u-net.com/avogadro/avoga.html

- The mole –its history and use: http://www.visionlearning.com/library/module_viewer.php?mid=53
- Mole Day: http://chemistry.about.com/od/historyofchemistry/a/mole-day.htm
- National Mole Day Foundation: http://www.moleday.org/

Points to Consider

- How can we use this information to determine the number of atoms or molecules in a given amount of a material?

10.2 Mass, Volume, and the Mole

Lesson Objectives

- Be able to convert between mass and moles of a substance.
- Explain how Avogadro's hypothesis relates to volumes of gases at standard temperature and pressure.
- Convert between moles and volume of a gas at STP.
- Calculate the mass of a gas at STP when given its volume.
- Make conversions between mass, number of particles, and gas volumes.

Lesson Vocabulary

- **standard temperature and pressure (STP)**: A pressure of one atmosphere and a temperature of 0°C.

Check Your Understanding

- What is the value of Avogadro's number, and what does it represent?

Introduction

As we discussed in the previous lesson, there are many different ways to measure how much of something you have. Usually, there is a particular unit of measurement that is easiest to use, depending on what you are trying to quantify. In this lesson you will learn the significance of using moles in converting between measurements and in understanding how much of something you have.

Mass and Moles

When we need materials for a chemical reaction, counting out a certain number of atoms or molecules is obviously impractical, so we weigh out a certain mass of each substance instead. As we will see in a later chapter, chemical equations tell us the molar ratios in which chemicals react with one another. This information can be used to determine how much of one chemical is needed to fully react with a set amount of another substance.

Example 10.6

In a certain reaction, we want to use two moles of silver nitrate, $AgNO_3$. We need to know how many grams of silver nitrate will be needed. First, we determine the molecular weight of the chemical:

Ag: 1 x 107.9 g/mol = 107.9 g/mol

N: 1 x 14.0 g/mol = 14.0 g/mol

O: 3 x 16.0 g/mol = 48.0 g/mol

$AgNO_3$ - 169.9 g/mol

Because 169.9 grams of $AgNO_3$ is equivalent to one mole of $AgNO_3$, we can use that as a conversion factor. We start with the amount that we need (2.0 moles), and convert to the desired units (grams of $AgNO_3$):

$$2.0 \text{ moles } AgNO_3 \times \frac{169.9 \text{ grams } AgNO_3}{1 \text{ mole } AgNO_3} = 339.8 \text{ grams } AgNO_3$$

The units of moles cancel, and we are left with grams.

Example 10.7

In another reaction, we determine that we need 0.45 moles of NaBr. We check our chemical supplies and find we have 37.2 grams NaBr on hand. Do we have enough for this reaction?

Na: 1 x 23.0 g/mol = 23.0 g/mol

Br: 1 x 79.9 g/mol = 79.9 g/mol

NaBr - 102.9 g/mol

$$0.45 \text{ moles NaBr} \times \frac{102.9 \text{ grams NaBr}}{1 \text{ mole NaBr}} = 46.3 \text{ grams NaBr}$$

We need 0.45 moles, which our calculation tells us is equivalent to 46.3 grams. We only have 37.2 grams available, so we do not have enough for this experiment.

Example 10.8

We run an experiment that gives us 65.4 grams of Rb_2O as a product. How many moles did we obtain?

First, we need to calculate the molar mass of the compound:

Rb: 2 x 85.5 g/mol = 171.0 g/mol

O: 1 x 16.0 g/mol = 16.0 g/mol

Rb_2O - 187.0 g/mol

$$65.4 \text{ g } Rb_2O \times \frac{1 \text{ mol } Rb_2O}{187.0 \text{ g } Rb_2O} = 0.350 \text{ mol } Rb_2O$$

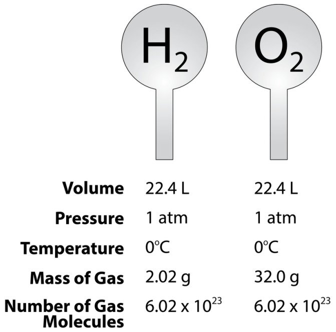
We obtained 0.350 moles of Rb_2O. Note that the conversion factor of molar mass (187.0 grams Rb_2O = 1 mole Rb_2O) was written "upside-down," with the grams on the bottom and the moles on top. This is so that the unwanted units (grams) cancel, leaving only the desired units (moles) in our final answer. Whenever we have this type of conversion factor, the choice of which quantity to put in the numerator and denominator depends on the units that we wish to cancel.

Volume and Moles

Avogadro's Hypothesis

Avogadro proposed that equal volumes of gases at the same temperature and pressure contain the same number of particles, and therefore the same combining ratios. This means that at a given temperature and pressure, one mole of any gas will take up the same volume, regardless of its identity. This is very different than the case for solids and liquids. For example, a mole of water takes up significantly more space than a mole of gold, which is quite dense.

Because different gases have different molar masses, the mass contained in a set volume of gas *will* depend on the identity of the gas. For example, at a certain temperature and pressure, one liter of hydrogen gas has a mass of 0.0899 grams, while a liter of oxygen gas has a mass of 1.43 grams. This ratio is approximately equal to 1:16, which is the ratio of the molar masses for these two elements. The table below shows the amount of mass contained in a given volume of various gases.



	H_2	O_2
Volume	22.4 L	22.4 L
Pressure	1 atm	1 atm
Temperature	0°C	0°C
Mass of Gas	2.02 g	32.0 g
Number of Gas Molecules	6.02×10^{23}	6.02×10^{23}

FIGURE 10.2

Relative masses of various gases.

The implications of Avogadro's work were extensive and helped in developing the kinetic theory of gases in the last half of the 19^{th} century. They also were useful as practical guidelines for how to run reactions with gases. For example, water has a formula of H_2O, which means that for each mole of oxygen atoms, there are two moles of hydrogen atoms. A complete reaction can occur with no leftover hydrogen or oxygen only if the volume of hydrogen used is twice the volume of oxygen used. Because the volume of a gas is easier to measure than its mass, this is a useful experimental tool.

Example 10.9

Let's say you have three balloons. One is filled with hydrogen gas, one with oxygen gas, and one with nitrogen gas. The molar masses of these gases are 2 g/mol for H_2, 32 g/mol for O_2, and 28 g/mol for N_2. If all three balloons are the same volume, which contains the most mass, and which contains the least?

Answer:

Based on their molar masses, hydrogen is the lightest molecule, and oxygen is the heaviest. Because all three volumes are the same, each balloon contains the same number of gas molecules. Therefore, the hydrogen balloon will have the lowest mass, and the oxygen balloon will have the highest.

Calculations Involving Gases

Because the volume of a gas is dependent on the pressure and temperature, scientists found it useful to collect data at fixed pressures and temperatures so that they could be compared between different gases. A pressure of one atmosphere and a temperature of 0°C is known as **standard temperature and pressure (STP)**. Under these conditions, one mole of any gas takes up a volume of 22.4 liters. This information allows us to convert between liters and moles for gases at STP.

Example 10.10

At STP, we have 46.2 liters of helium. How many moles of helium do we have?

$(46.2 \text{ L He})(\frac{1 \text{ mol He}}{22.4 \text{ L He}}) = 2.06 \text{ mol He}$

Example 10.11

What volume does 4.96 moles of O_2 occupy at STP?

$(4.96 \text{ mol } O_2)(\frac{22.4 \text{ L } O_2}{1 \text{ mol } O_2}) = 111 \text{ L } O_2$

If we know the volume of a gas at STP, we can combine this information with its molar mass to determine how much mass is present in the sample.

Example 10.12

What is the mass of 86.7 liters of N_2 at STP?

The molar mass of N_2 is 28.0 grams/mole, and because one mole of a gas at STP takes up 22.4 L of space, we can perform the following calculation.

$(86.7 \text{ L } N_2)(\frac{1 \text{ mol } N_2}{22.4 \text{ L } N_2})(\frac{28.0 \text{ g } N_2}{1 \text{ mol } N_2}) = 108 \text{ g } N_2$

The conversion factors are arranged so that all units cancel except for grams, which are the units of our final answer.

When studying chemical reactions, we frequently need to convert back and forth between mass, volume, moles, and number of particles. This will be expanded upon in our chapter on stoichiometry. **Figure** 10.3 summarizes the relationships that we have studies so far between these different quantities.

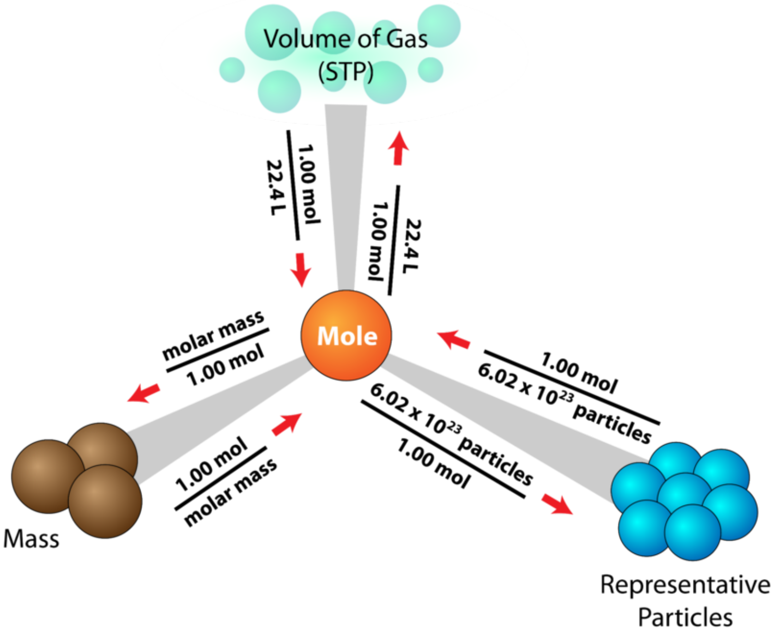


FIGURE 10.3

Mole relations for mass, volume, and particles.

Lesson Summary

- Molar masses can be used to determine the mass of a given quantity of material.
- At standard temperature and pressure (1 atmosphere of pressure and 0°C), one mole of a gas occupies 22.4 liters.
- The mass of a sample can be calculated for a given volume of a known gas at STP using Avogadro's number.

Review Questions

1. Calculate the number of moles in 56.3 grams of $CaCO_3$.

2. What is the mass (in grams) of 3.2 moles of glucose ($C_6H_{12}O_6$)?
3. You are running an experiment that needs three moles of $NaHCO_3$, and you only have 150 grams of material. Calculate the number of moles you have, and determine if this is enough to run the experiment.
4. A balloon contains 96 grams of CO_2 gas at STP. How many moles are present?
5. How many atoms are there in 12.2 grams of Zn?
6. A container holds 68.5 liters of HBr gas. What is the mass of HBr in the container?

Further Reading / Supplemental Links

- Mole-mass calculations: http://www.ausetute.com.au/massmole.html
- Molar mass calculations: http://misterguch.brinkster.net/molarmass.html
- Gas calculations: http://www.sciencegeek.net/Chemistry/taters/Unit5MolarVolume.htm

Points to Consider

- How can you use information about the composition of a substance to determine its chemical formula?

10.3 Chemical Formulas

Lesson Objectives

- Use a chemical formula or mass data to calculate the percent composition of a compound.
- Use the percent composition of a compound to calculate the mass of an element in a given sample.
- Be able to calculate the empirical formula for a compound when given percent composition data.
- Be able to calculate the molecular formula for a compound when you know its molar mass and its empirical formula.

Lesson Vocabulary

- **percent composition**: The percent by mass of each element in a compound.
- **empirical formula**: An elemental formula showing the lowest whole-number ratio of the elements in a compound.
- **molecular formula**: A formula showing how many atoms of each element are present in one molecule of a molecular compound.

Check Your Understanding

- How can you calculate the amount of a substance in moles from its mass and its molar mass?

Introduction

Packaged foods that you eat typically have nutritional information provided on the label. The label of a popular brand of peanut butter (**Figure** 10.4) reveals that one serving size is considered to be 32 g. The label also gives the masses of various types of compounds that are present in each serving. One serving contains 7 g of protein, 15 g of fat, and 3 g of sugar. This information can be used to determine the composition of the peanut butter on a percent by mass basis. For example, to calculate the percent of protein in the peanut butter, we could perform the following calculation:

$$\frac{7 \text{ g protein}}{32 \text{ g}} \times 100\% = 22\% \text{ protein}$$

In a similar way, chemists often need to know what elements are present in a compound and in what percentages. The **percent composition** is the percent by mass of each element in a compound. It is calculated in a way that is similar to what we just saw for the peanut butter.

Nutrition Facts

Serv. Size 2 tbsp (32g)
Servings about 16

Calories 180
Fat Cal. 130

*Percent Daily Values (DV) are based on a 2,000 calorie diet.

Amount Per Serving	% DV*	Amount Per Serving	% DV*
Total Fat 15g	23%	**Total Carbohydrate** 8g	3%
Saturated Fat 2g	10%	Dietary Fiber 2g	8%
Trans Fat 0g		Sugars 3g	
Cholesterol 0mg	0%	**Protein** 7g	
Sodium 140mg	6%		

Vitamin A 0% • Vitamin C 0% • Calcium 2% • Iron 4%

INGREDIENTS: PEANUTS, SUGAR, HYDROGENATED VEGETABLE OIL (RAPESEED, COTTONSEED, OYBEAN), SALT, MOLASSES.

FIGURE 10.4

Foods like peanut butter provide nutritional information on the label in the form of masses of different types of compounds present per serving.

Percent Composition and Mass

Determining Percent Composition from Mass Data

We can calculate percent composition based on the following formula:

$$\% \text{ by mass} = \frac{\text{mass of element}}{\text{mass of compound}} \times 100\%$$

The example below shows how the percent composition of a compound can be calculated based on mass data:

Example 10.13

A certain newly synthesized compound is known to contain the elements zinc and oxygen. When a 20.00 g sample of the compound is decomposed, 16.07 g of pure zinc remains. Determine the percent composition of the compound.

Answer:

If the compound contained only zinc and oxygen, and 16.07 grams was due to the zinc, we can subtract to determine the mass of oxygen in the original sample:

Mass of oxygen = 20.00 g –16.07 g = 3.93 g O

Then, we divide the individual masses of each element by the total mass of the sample to determine the percent (by mass) of each element in the compound:

$$\% \text{ Zn} = \frac{16.07 \text{ g Zn}}{20.00 \text{ g}} \times 100\% = 80.35\% \text{ Zn}$$
$$\% \text{ O} = \frac{3.93 \text{ g O}}{20.00 \text{ g}} \times 100\% = 19.65\% \text{ O}$$

The calculations make sense because the sum of the two percentages adds up to 100%. By mass, the compound is mostly zinc.

Determining Masses from Percent Composition Data

We can also perform the reverse calculation, determining the mass of an element in a given sample, if we know the total mass of the sample and its percent composition.

Example 10.14

You have a 10.0 g sample of a metal alloy that contains only aluminum and zinc. If the sample is 36% aluminum by mass, what masses of Al and Zn are present?

Answer:

We are told that the sample is 36% aluminum by mass. Because the only other component is zinc, it must make up the remaining 64% of the mass. We can multiply each of these percentages by 10.0 grams to find the masses of each element.

10.0 g sample × 0.36 = 3.6 g Al

10.0 g sample × 0.64 = 6.4 g Zn

Empirical Formulas

Recall that an **empirical formula** is one that shows the lowest whole-number ratio of the elements in a compound. Because the structure of ionic compounds is an extended three-dimensional network of positive and negative ions, only empirical formulas are used to describe ionic compounds. However, we can also consider the empirical formula of a molecular compound. Ethene is a small hydrocarbon compound with the formula C_2H_4 (**Figure** 10.5). While C_2H_4 is its molecular formula and represents its true molecular structure, it has an empirical formula of CH_2. The simplest ratio of carbon to hydrogen in ethene is 1:2. In each molecule of ethene, there is 1 carbon atom for every 2 atoms of hydrogen. Similarly, we can also say that in one mole of ethene, there is 1 mole of carbon for every 2 moles of hydrogen. The subscripts in a formula represent the molar ratio of the elements in that compound.

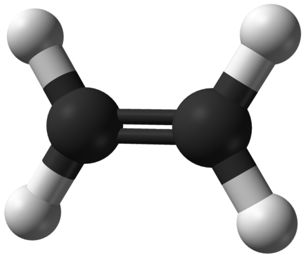


FIGURE 10.5

Ball-and-stick model of ethene, C_2H_4.

Determining Percent Composition from a Chemical Formula

The percent composition of a compound can also be determined from its chemical formula. The subscripts in the formula are first used to calculate the mass of each element found in one mole of the compound. That value is then divided by the molar mass of the compound and multiplied by 100%.

$$\% \text{ by mass} = \frac{\text{mass of element in 1 mol of compound}}{\text{molar mass of compound}} \times 100\%$$

The percent composition of a given compound is always the same as long as the compound is pure.

Example 10.15

Dichlorine heptoxide (Cl_2O_7) is a highly reactive compound used in some synthesis reactions. Calculate the percent composition of dichlorine heptoxide.

Answer:

Determine the mass of each element in one mole of the compound, and find the total molar mass of the compound:

- mass of Cl in 1 mol Cl_2O_7 = 2 x molar mass of Cl = 70.90 g
- mass of O in 1 mol Cl_2O_7 = 7 x molar mass of O = 112.00 g
- molar mass of Cl_2O_7 = 70.90 g/mol + 112.00 g/mol = 182.90 g/mol

Now, calculate the percent by mass of each element by dividing the mass of that element in 1 mole of the compound by the molar mass of the compound and multiplying by 100%.

$$\% \text{ Cl} = \frac{70.90 \text{ g Cl}}{182.90 \text{ g}} \times 100\% = 38.76\% \text{ Cl}$$
$$\% \text{ O} = \frac{112.00 \text{ g O}}{182.90 \text{ g}} \times 100\% = 61.24\% \text{ O}$$

As expected, the percentages add up to 100%.

Determining Empirical Formulas from Percent Composition

A procedure called elemental analysis allows us to determine the empirical formula of an unknown compound. Percent composition data can be directly obtained with this technique, and these values can be used to find the molar ratios of the elements, which gives us the empirical formula. The steps to be taken are outlined below.

1. Assume a 100 g sample of the compound so that the given percentages can be directly converted into grams.
2. Use each element's molar mass to convert the grams of each element to moles.
3. In order to find a whole-number ratio, divide the moles of each element by the smallest value obtained in step 2.
4. If all the values at this point are whole numbers (or very close), each number is equal to the subscript of the corresponding element in the empirical formula.
5. In some cases, one or more of the values calculated in step 3 will not be whole numbers. Multiply each of them by the smallest number that will convert all values into whole numbers (or very close to whole numbers). Note that all values must be multiplied by the same number so that the relative ratios are not changed. These values can then be used to write the empirical formula.

Example 10.16

A compound of iron and oxygen is analyzed and found to contain 69.94% iron and 30.06% oxygen by mass. Find the empirical formula of the compound.

Answer:

Follow the steps outlined in the text.

1. Assume a 100 g sample. In 100 grams of the compound, there would be 69.94 g Fe and 30.06 g O.
2. Convert to moles.

$$69.94 \text{ g Fe} \times \frac{1 \text{ mol Fe}}{55.85 \text{ g Fe}} = 1.252 \text{ mol Fe}$$
$$30.06 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 1.879 \text{ mol O}$$

3. Divide both values by the smallest of the results.

$$\frac{1.252 \text{ mol Fe}}{1.252} = 1 \text{ mol Fe}$$
$$\frac{1.879 \text{ mol O}}{1.252} = 1.501 \text{ mol O}$$

4. Since the moles of O is still not a whole number, both numbers can be multiplied by 2. The results are now close enough to be rounded to the nearest whole number.

$$1 \text{ mol Fe} \times 2 = 2 \text{ mol Fe}$$
$$1.501 \text{ mol O} \times 2 = 3 \text{ mol O}$$

The empirical formula of the compound is Fe_2O_3.

Molecular Formulas

Molecular formulas tell us how many atoms of each element are present in one molecule of a molecular compound. In many cases, the molecular formula is the same as the empirical formula. For example, the molecular formula of methane is CH_4, and because 1:4 is the smallest whole-number ratio that can be written for this compound, that is also its empirical formula. Sometimes, however, the molecular formula is a simple whole-number multiple of the empirical formula. Acetic acid is an organic acid that gives vinegar its distinctive taste and smell. Its molecular formula is $C_2H_4O_2$. Glucose is a simple sugar that cells use as their primary source of energy. Its molecular formula is $C_6H_{12}O_6$. The structures of both molecules are shown in **Figure** 10.6. They are very different compounds, yet both have the same empirical formula, CH_2O.

The following **Table** 10.1 shows a few other compounds with their empirical and molecular formulas:

TABLE 10.1: Empirical and Molecular Formulas

Compound	Empirical Formula	Molecular Formula
water	H_2O	H_2O
hydrogen peroxide	HO	H_2O_2
methane	CH_4	CH_4
butane	C_2H_5	C_4H_{10}

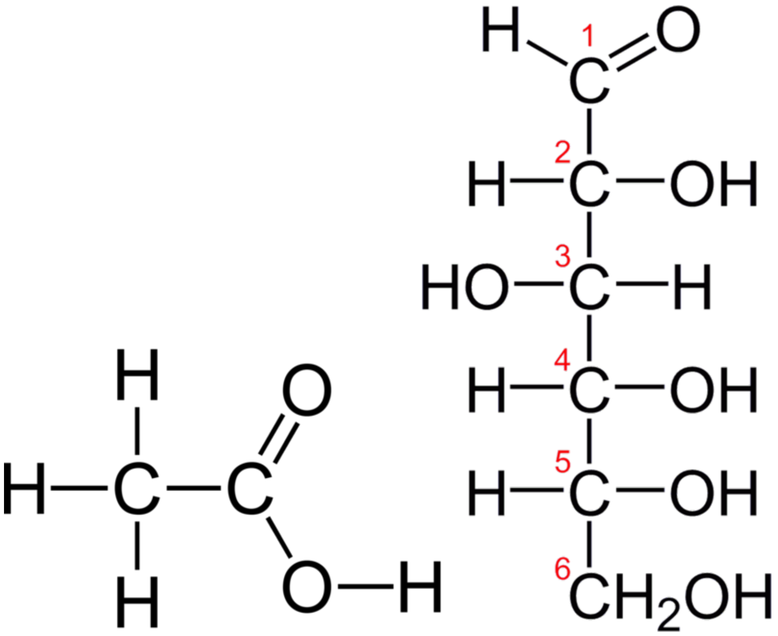


FIGURE 10.6

Acetic acid (*left*) has a molecular formula of $C_2H_4O_2$, while glucose (*right*) has a molecular formula of $C_6H_{12}O_6$. Both have the empirical formula CH_2O.

Empirical formulas can be determined from the percent composition of a compound. In order to determine its molecular formula, it is necessary to also know the molar mass of the compound. Chemists have various methods to determine the molar mass of an unknown compound. In order to go from the empirical formula to the molecular formula, follow these steps:

1. Calculate the empirical formula mass (EFM), which is simply the molar mass represented by the empirical formula.
2. Divide the molar mass of the compound by the empirical formula mass. The result should be a whole number or very close to a whole number.
3. Multiply all of the subscripts in the empirical formula by the whole number found in step 2. The result is the molecular formula.

Example 10.17

The empirical formula of a compound that contains boron and hydrogen is BH_3. Its molar mass is 27.7 g/mol. Determine the molecular formula of the compound.

Answer:

Follow the steps outlined above.

1. The empirical formula mass (EFM) = 13.84 g/mol

1. $\frac{\text{molar mass}}{\text{EFM}} = \frac{27.7}{13.84} = 2$

1. $BH_3 \times 2 = B_2H_6$

The molecular formula of the compound is B_2H_6. The molar mass of the molecular formula matches the molar mass of the compound.

You can watch a video lecture about molecular and empirical formulas at http://www.khanacademy.org/science/chemistry/chemical-reactions-stoichiometry/v/molecular-and-empirical-formulas .

You can watch a video lecture about determining molecular and empirical formulas from percent composition at http://www.khanacademy.org/science/physics/thermodynamics/v/molecular-and-empirical-forumlas-from-percent-composition .

Lesson Summary

- The percent composition of a compound is the percent by mass of each of the elements in the compound. It can be calculated from mass data or from the chemical formula.
- Percent composition data can be used to determine a compound's empirical formula, which is the molar ratio between the elements in the compound.
- The empirical formula and the molar mass of a substance can be used to determine its molecular formula, which is the number of each kind of atom in a single molecule of the compound.

Lesson Review Questions

1. Calculate the percent carbon in C_2H_6.
2. Calculate the percent nitrogen in $CH_3CH_2CH_2NH_2$.
3. A sample of a given compound contains 13.18 g of carbon and 3.32 g of hydrogen. What is the percent composition of this compound?
4. 5.00 g of aluminum is reacted with 7.00 g of fluorine to form a compound. When the compound is isolated, its mass is found to be 10.31 g, with 1.69 g of aluminum (and no fluorine) left unreacted. Determine the percent composition of the compound.
5. Calculate the percent by mass of each element present in sodium sulfate (Na_2SO_4).
6. Vitamin C contains carbon (40.9%), hydrogen (4.6%), and oxygen (54.5%). Calculate the empirical formula for vitamin C. The molecular mass is about 180. Determine the molecular formula for vitamin C.
7. Calculate the empirical formula of each compound from the percentages listed:
    a. 63.65% N, 36.35% O
    b. 81.68% C, 18.32% H
8. A compound was analyzed and found to contain 13.5 g Ca, 10.8 g O, and 0.675 g H. What is the empirical formula of the compound?
9. Calculate the percent composition of the following compounds:
    a. magnesium fluoride, MgF_2
    b. silver nitrate, $AgNO_3$
10. A compound with the empirical formula CH has a molar mass of 78 g/mol. Determine its molecular formula.
11. A compound is found to consist of 43.64% phosphorus and 56.36% oxygen. The molar mass of the compound is 284 g/mol. Find the molecular formula of the compound.

Further Reading/Supplementary Links

- Dalton and relative weights: http://dl.clackamas.edu/ch104-03/relative.htm
- Calculating formulas and composition: http://library.thinkquest.org/10429/low/chemcomp/chemcomp.htm
- Finding empirical formulas given percent composition: http://www.chemteam.info/Mole/Emp-formula-given-percent-comp.html

Points to Consider

In the next chapter we will be able to use this information to determine how much material we need for a chemical reaction and how much product we can produce as a result of a reaction.

10.4 References

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CHAPTER 11 Chemical Reactions

Chapter Outline

11.1 CHEMICAL EQUATIONS
11.2 TYPES OF CHEMICAL REACTIONS
11.3 REFERENCES

For millennia, humans have been fascinated with the composition of things and the workings of the chemical world. Over time we have come to understand that all matter is comprised of indivisible particles called atoms. Our understanding of how matter works has been a long pursuit. It started with figuring out how to make things burn. Humans have been fascinated with chemical reactions that burn, explode, produce loud bangs, and have brilliant colors. Early alchemists learned that throwing certain salts on a fire would produce different "magical" colors. Chinese alchemists created human kind's first explosion with the invention of gunpowder. This chemical recipe was eventually shared across the medieval globe. Historically, humans have been fascinated with coaxing nature into doing things, like burning. This fascination, coupled with our ability to observe, record, and share, has led us to our current understanding of matter. Our understanding of chemical reactions and the equations that describe them are based on many years of trial and error. The image above is an example of this. It is a star shell bursting over the night sky. The technology of pyrotechnics, like composition of the propellant, the explosive charge, the colors, and the shapes of the burst, is a result of hundreds of years of intensive study of chemical reactions and chemical equations. We are going to study chemical reactions and chemical equations in this chapter.

Jon Sullivan. commons.wikimedia.org/wiki/File:Firework.jpg. Public Domain.

11.1 Chemical Equations

Lesson Objectives

- Give examples of historically significant chemical recipes and equations.
- Briefly describe the major milestones that took place in developing the chemical recipe of gunpowder.
- Understand mass relations between reactants and products for a given chemical process.
- Be able to use stoichiometric coefficients in chemical equations.
- Be able to balance chemical equations.

Lesson Vocabulary

- **stoichiometric coefficient**: The letters a, b, c, and d where A and B are reactants, and C and D are products. The stoichiometric coefficients indicate the relative amounts of reactants and products.
- **balanced chemical equation**: An equation where the number of atoms of each element on the reactant side is equal to the number of atoms on the product side.

Check Your Understanding

1. Which of the following are physical changes and which are chemical changes?
   a. melting of ice
   b. a burning candle
   c. melting of candle wax
   d. sublimation of dry ice to CO_2 gas.

Introduction

Ever since the 9^{th} century, humans have been fascinated with the nature of explosions. Whether to scare away evil spirits, to light up the night sky in celebration, or to be used in warfare, our understanding of gunpowder is based on our understanding of chemical recipes. Our ability to modify, share, and replicate them has allowed us to develop new recipes and to refine existing ones. Chemical reactions can be described in terms of chemical equations. They are the foundation of our modern day chemical recipes.

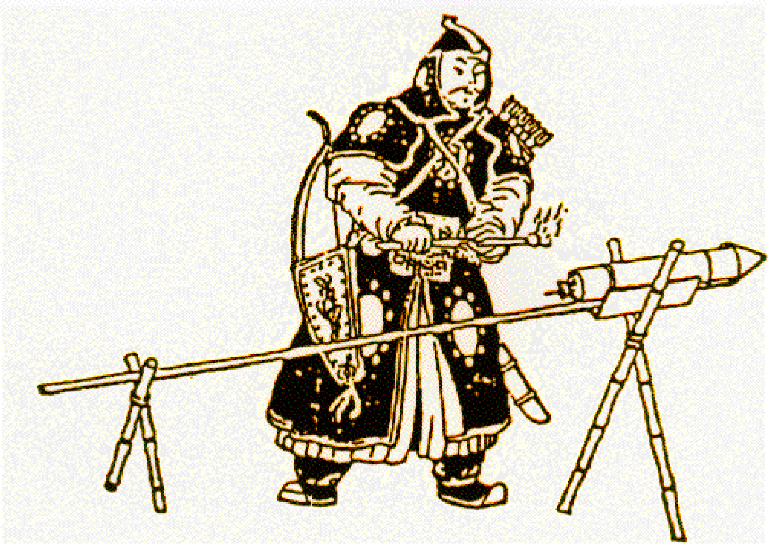
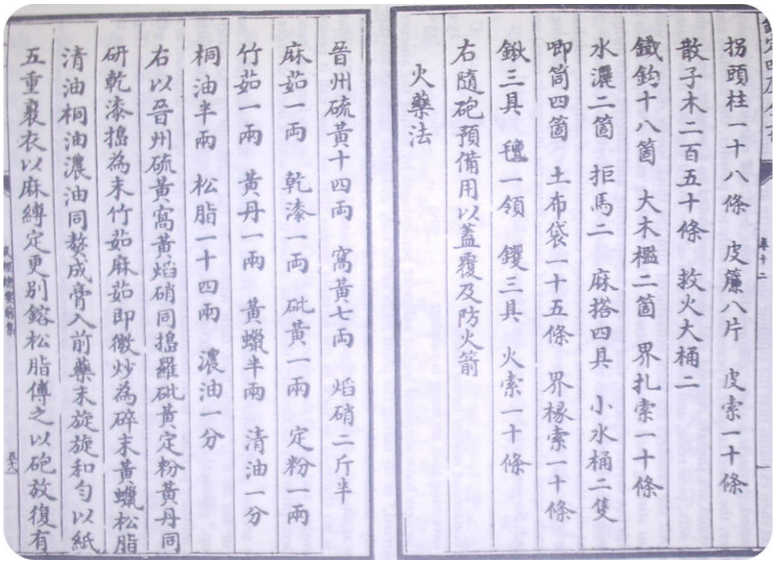


FIGURE 11.1

Origins of Chemical Recipes: Gunpowder

The first people to discover gunpowder were 9th century Chinese alchemists. This discovery was made by accident while they were creating various chemical mixtures in pursuit of an elixir that would make them immortal. The first formulation of gunpowder was a thick toffee made from honey, saltpeter (a mixture composed primarily of potassium nitrate), and sulfur. They hoped that eating it would help them live forever. In reality, it burst into flames and burnt down their homes.

Over time, Chinese alchemists refined the recipe and began to develop early pyrotechnic technology to help scare away evil spirits. A more fully developed, and more explosive, formula called for 75 percent potassium nitrate, 15 percent charcoal, and 10 percent sulfur.



拐頭柱一十八條　皮簾八片　皮索一十條
散子木二百五十條　救火大桶二
鐵鉤十八箇　大木檻二箇　界扎索一十條
水濃二箇　拒馬二　麻搭四具　小水桶二隻
唧筒四箇　土布袋一十五條　界橛索一十條
鍬三具　氈一領　钁三具　火索一十條
右隨砲預備用以蓋覆及防火箭

火藥法

晉州硫黃十四兩　窩黃七兩　焰硝二斤半
麻茹一兩　乾漆一兩　砒黃一兩　定粉一兩
竹茹一兩　黃丹一兩　黃蠟半兩　清油一分
桐油半兩　松脂一十四兩　濃油一分
右以晉州硫黃窩黃焰硝同擣羅砒黃定粉黃丹同
研乾漆擣為末竹茹麻茹即微炒為碎末黃蠟松脂
清油桐油濃油同熬成膏入前藥末旋旋和匀以紙
五重裹衣以麻縛定更別鎔松脂傅之以砲放復有

FIGURE 11.2

Medieval Europe

This recipe made its way to Europe in medieval times. A Franciscan friar named Roger Bacon was particularly fascinated by the properties of gunpowder. He discovered that a key factor in the energetics of the mixture was the purity of the saltpeter. Bacon was responsible for developing early crystallization techniques to purify the mixture. He also discovered that the more tightly packed the powder, the larger the explosion.

Bacon feared that bad things could happen if the mixture ended up in the wrong hands. He encoded the recipe in an anagram, which read (when translated from the original Latin) *"And so thou wilt call up thunder and destruction if thou know the art."* The secret recipe, however, did not stay secret for long.

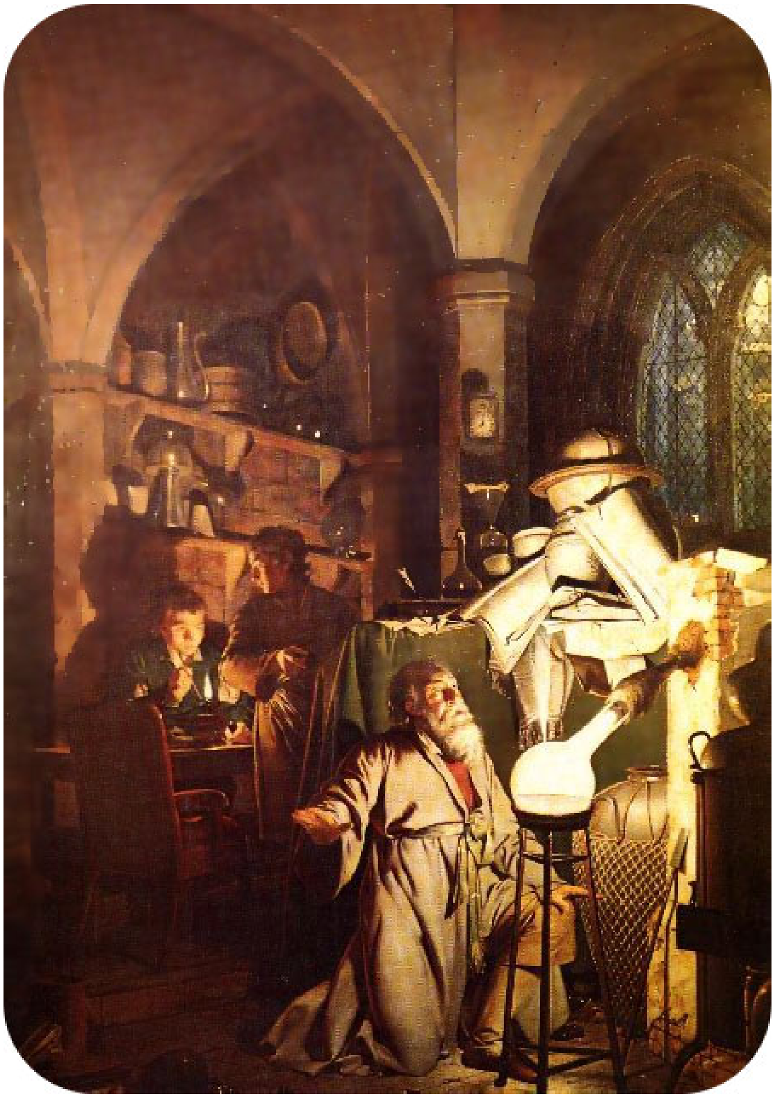


FIGURE 11.3

Pyrotechnics, or fireworks, used in events recorded in 14^{th} century Italy show that the recipe was no longer a secret. During the 15^{th} and 16^{th} centuries, the Italians continued refining the art of pyrotechnics. Then, in 1830, a major leap forward in gunpowder technology occurred. It was discovered that replacing potassium nitrate with potassium chlorate resulted in a more energetic mixture, and so the recipe was revised once again.

The modern day formulation of gun powder is called black powder. It is still commonly used today. Its formulation is still quite similar to what was used in 9^{th} century China. Black powder is considered a low explosive. It is a mixture that burns quickly, but the resulting shock wave travels at subsonic speeds. The speed at which it burns is

FIGURE 11.4

dependent on the accessibility of oxygen atoms to the carbon source. In contrast, high explosives like nitroglycerin detonate instead of burning, creating shock waves that are supersonic (faster than the speed of sound).

The Chemical Equation

Chemical equations describe the changes in composition that take place during a chemical reaction. Along with the identities of the starting reactants and the final products, chemical equations show the ratios in which these substances are consumed and produced. The reaction of iron with oxygen to form iron(III) oxide is shown in the **Figure** 11.5:

FIGURE 11.5
The sparks from a steel grinder are molten iron. The iron reacts with oxygen to form iron(III) oxide.

We can describe this reaction with a chemical equation:

$4Fe_{(s)} + 3O_{2(g)} \rightarrow 2Fe_2O_{3(s)}$

This equation is said to be balanced, because the amount of each element expressed on the reactants side is equal to the amounts expressed on the products side. This is shown more explicitly in the following **Table** 11.1:

TABLE 11.1: **4Fe**

	Reactants	Products
Fe	4	4
O	6	6

Often times, the processes described by chemical equations do not represent a single reaction. For example, the following equation shows the starting materials and the products for photosynthesis:

$6CO_{2(g)} + 6H_2O_{(l)} \overset{light}{\rightarrow} C_6H_{12}O_{6(s)} + 6O_{2(g)}$

This process does not occur in a single step. A sequence of many individual reactions is required to make glucose and oxygen gas out of carbon dioxide and water. Chemical equations can be used to represent individual reactions or the net change that occurs after multiple sequential chemical processes.

The Balanced Chemical Equation

We can describe chemical reactions in terms of generic expressions like the following equation:

$aA + bB \rightarrow cC + dD$

where A and B are reactants, and C and D are products. The letters a, b, c, and d represent **stoichiometric coefficients**, or the relative amount of each substance that is involved in the reaction. In this particular reaction, there are two reactants and two products, but others might have more or less. For example, the equation describing the rusting of iron had two reactants (Fe and O_2) and one product (Fe_2O_3).

In a **balanced chemical equation**, the number of atoms of each element on the reactant side is equal to the number of atoms on the product side. This is necessary for all chemical equations, due to the law of conservation of mass. Atoms are neither created nor destroyed during a chemical reaction, only rearranged. Here are some examples of general expressions that will be applied to specific reactions in the next section.

Example 11.1

Substance A reacts with substance B to form substance AB. Write the balanced chemical equation for this process.

Answer:

Write the general expression.

$A + B \rightarrow AB$

Balance (it already is).

TABLE 11.2: **A + B → AB**

	Reactants	Products
A	1	1
B	1	1

Example 11.2

Substance A reacts with substance B_2 to form substance AB. Write the balanced chemical equation for this process.

Answer:

Write the general expression.

$A + B_2 \rightarrow AB$

Balance.

$2A + B_2 \rightarrow 2AB$

TABLE 11.3: Example 11.2

	Reactants	Products
A	2	2
B	2	2

Example 11.3

Substance A_2 reacts with substance B_2 to form substance AB_3. Write the balanced chemical equation for this process.

Answer:

Write the general expression.

$A_2 + B_2 \rightarrow AB_3$

Balance.

TABLE 11.4: A

	Reactants	Products
A	2	2
B	6	6

Balancing Chemical Equations for Real Reactions

Now that we have studied the general process for describing and balancing chemical equations, we are going to apply this approach to examples that include actual chemicals. As we present the following reactions, we are going to focus only on the changes in composition from reactants to products. In later chapters, we will look at other reaction properties, such as states of matter, temperature, and the energy lost or gained by a given reaction. In the following lesson, we will look at ways to classify different types of reactions. This knowledge will allow us to make reasonable predictions about the products that might be generated from a given set of reactants.

Tips for Balancing Equations

Before we get started with balancing chemical equations, here are some simple tips to consider:

1. If there are polyatomic ions that exist unchanged on both sides of the equation, it is often simpler to treat them

as single units than to break them down into their individual elements.

2. It is often easier to leave elements that occur in their pure elemental form (on either side of the equation) for last.
3. If a reactant or product has a coefficient of 1, this number is not explicitly written.
4. In a correctly balanced equation, all coefficients must be whole numbers. However, the use of fractions can be helpful as a way of finding the correct coefficients. If all atoms in an equation are balanced but some have fractional coefficients, multiply all coefficients in the entire equation (including those not explicitly written!) by the lowest common denominator to get the final balanced equation.

Example 11.4

Liquid mercury is heated in the presence of oxygen to produce mercury(II) oxide. Write the balanced chemical equation for this process.

Answer:

Start by writing the general expression.

$\mathrm{Hg}(l)+\mathrm{O}_2(g)\rightarrow\mathrm{HgO}(s)$

Then, alter the coefficients to balance each element.

TABLE 11.5: **2Hg(l)+O**

	Reactants	Products
Hg	2	2
O	2	2

Notice that in this example, the formula for oxygen is the diatomic form O_2. Many pure nonmetallic elements are unstable as individual atoms and combine readily to make diatomic molecules. Hydrogen (H_2), nitrogen (N_2), oxygen (O_2), and the halogens (F_2, Cl_2, Br_2, and I_2) exist as diatomic molecules when in their pure elemental forms.

Example 11.5

Hydrogen gas and fluorine gas react to form hydrogen fluoride gas. Write the balanced chemical equation for this process.

Answer:

Start by writing the general expression.

$\mathrm{H}_2(g)+\mathrm{F}_2(g)\rightarrow\mathrm{HF}(g)$

Then balance each element.

TABLE 11.6: **H**

	Reactants	Products
H	2	2
F	2	2

Again, pure hydrogen and fluorine exist as diatomic gases.

Example 11.6

Ammonium nitrate decomposes to form nitrogen gas, water, and oxygen gas. Write the balanced chemical equation for this process.

Answer:

Write the general expression.

$NH_4NO_3(s) \rightarrow N_2(g) + H_2O(l) + O_2(g)$

Balance.

Because this equation involves more than two elements, it is slightly less straightforward to balance. Since nitrogen and oxygen both occur in their pure elemental forms, we start by balancing hydrogen:

$NH_4NO_3(s) \rightarrow N_2(g) + 2H_2O(l) + O_2(g)$

Hydrogen and nitrogen are now balanced, but oxygen is not. This can be fixed by changing the coefficient on its pure elemental form:

$NH_4NO_3(s) \rightarrow N_2(g) + 2H_2O(l) + \frac{1}{2}O_2(g)$

The atoms are now balanced, but to avoid having fractional coefficients, we must multiply all coefficients in the equation by 2:

$2NH_4NO_3(s) \rightarrow 2N_2(g) + 4H_2O(l) + O_2(g)$

We can confirm that this equation is balanced by writing the following **Table** 11.7:

TABLE 11.7: **2NH**

	Reactants	Products
N	4	4
H	8	8
O	6	6

Example 11.7

Lead(II) nitrate reacts with sodium chloride to form lead(II) chloride and sodium nitrate. Write the balanced chemical equation for this process.

Answer:

Write the general expression.

$Pb(NO_3)_2 + NaCl \rightarrow PbCl_2 + NaNO_3$

Balance.

TABLE 11.8: **Pb(NO**

	Reactants	Products
Pb	1	1
NO_3	2	2
Na	2	2
Cl	2	2

By keeping the polyatomic nitrate ion intact as a single unit, balancing this equation becomes somewhat simpler. This was done because the ion exists unchanged on both sides of the equation. Note that this is in contrast to the previous example, in which the nitrate ion decomposed to form other substances.

Lesson Summary

- The composition of gunpowder gradually changed as alchemists and scientists experimented with ways to make it even more explosive.
- Chemical reactions are described using chemical equations.
- Stoichiometric coefficients are used in chemical equations to indicate the amounts of reactants and products.
- Because of the law of conservation of mass (matter can neither be created nor destroyed through chemical reactions), chemical equations must have equal amounts of each specific atom on both sides of the equation.

Review Questions

1. Early Chinese alchemists discovered an early form of gunpowder. What was the composition of this substance?
2. What later developments were made to the gunpowder recipe that improved its pyrotechnic properties?
3. Make an argument for why the burning of a candle is consistent with the law of conservation of matter/mass.
4. Think of an experiment that you could conduct to demonstrate that mass is conserved for a given chemical change.
5. Balance the following chemical equations:
    a. $C + O_2 \rightarrow CO$
    b. $CO + O_2 \rightarrow CO_2$
    c. $H_2 + Br_2 \rightarrow HBr$
    d. $K + H_2O \rightarrow KOH + H_2$
    e. $O_3 \rightarrow O_2$
    f. $N_2 + H_2 \rightarrow NH_3$
    g. $Zn + AgCl \rightarrow ZnCl_2 + Ag$
    h. $Cl_2 + NaI \rightarrow NaCl + I_2$
    i. $P_4O_{10} + H_2O \rightarrow H_3PO_4$
    j. $Be_2C + H_2O \rightarrow Be(OH)_2 + CH_4$
    k. $S + HNO_3 \rightarrow H_2SO_4 + NO_2 + H_2O$
    l. $NH_3 + CuO \rightarrow Cu + N_2 + H_2O$
    m. $HCl + CaCO_3 \rightarrow CaCl_2 + H_2O + CO_2$

Further Reading / Supplemental Links

- Youtube Video of Kaboom! The Sizzling Story of Explosions: http://www.youtube.com/watch?v=CShA52EKY80
- Gunpowder in Ancient China: http://www.historyforkids.org/learn/war/gunpowder.htm
- Practice Balancing Chemical Equations:
    - http://education.jlab.org/elementbalancing/index.html
    - http://www.files.chem.vt.edu/RVGS/ACT/notes/scripts/bal_eq1.html

  - http://gregthatcher.org/Chemistry/BalanceEquation/S
- Chemical Equation Balances: http://www.personal.psu.edu/jzl157/balance.htm

Points to Consider

- What is the relationship between chemical equations and chemical reactions?
- In this chapter, an argument was made that the human fascination with fire and explosions ultimately contributed to our current understanding of chemical equations. Can you think of other aspects of nature for which further exploration has contributed to our current understanding of chemistry?

11.2 Types of Chemical Reactions

Lesson Objectives

- Be able to classify a chemical reaction as a combination, decomposition, single replacement, double replacement, or combustion reaction.
- Be able to predict the products when given a set of reactants for a given chemical process.
- Explain the concept of solubility and the process of precipitation.
- Use solubility information to predict whether or not a given substance is soluble in water.
- Use the general solubility rules to predict chemical behavior.
- Be able to write molecular, ionic, and net ionic equations for a given chemical process.

Lesson Vocabulary

- **combination reaction**: A reaction where two or more chemical species combine to produce a single new compound.
- **decomposition reaction**: A reaction where a single chemical species breaks down to produce two or more new chemical species.
- **single replacement reaction**: Occurs when one chemical species (often a single element) replaces a portion of another compound to produce two new products.
- **double replacement reaction**: Occurs when the cations from the original two ionic compounds trade anions to make two new ionic compounds.
- **molecular equation**: An equation that shows all ionic components as neutral compounds, but the ones that are dissolved in water are denoted with "(aq)."
- **ionic equation**: A chemical equation in which the various reaction components are represented as they actually exist in the reaction, for example, as individual ions.
- **spectator ion**: Ions that are present in solution but do not participate in the overall reaction.
- **net ionic equation**: The simplified ionic equation in which all of the spectator ions are cancelled out.
- **combustion**: Occurs when a hydrocarbon reacts in the presence of oxygen to produce water and carbon dioxide.

Check Your Understanding

Study the **Figure** 11.6, which depicts the mass change that occurs when steel wool burns in air.

1. What happens to the mass of the steel wool as the reaction proceeds?
2. Given that mass must be conserved in chemical reactions (it cannot come from nowhere), what might be your explanation for the change in the mass of the steel wool?
3. How might mass changes such as this help us identify and categorize a given chemical process?

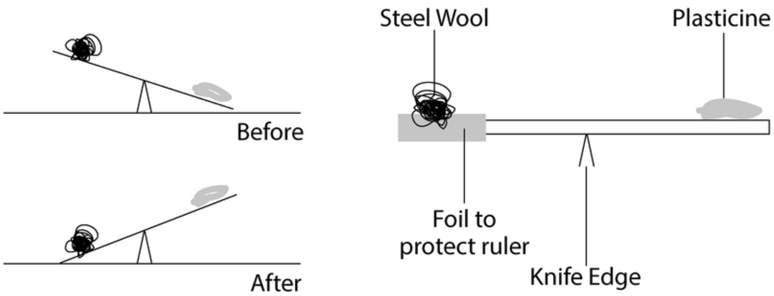


FIGURE 11.6

Mass changes for steel wool burning in air

Introduction

MEDIA

Click image to the left for more content.

The video above at http://www.youtube.com/watch?v=_Y1alDuXm6A (1:12) shows the decomposition of mercury(II) oxide into liquid mercury and oxygen gas. This reaction was an important one in the history of chemistry, because it helped early chemists to understand the relationship between reactants and products.

In the last lesson, we began investigating how a chemical equation can represent a given chemical reaction. In this lesson, we are going to study the ways in which chemical reactions are classified. There are literally thousands of chemical reactions that take place every day in our lives. Some reactions take place in the atmosphere, such as the combustion of fossil fuels. Others occur in solution, like the reactions responsible for photosynthesis or the reactions that break down our food to give us energy. Chemical reactions can take place in a variety of environments. Reactions happen on the sea floor, in our cells, and in the upper atmosphere. As we look at chemical reactions, we notice some commonalities and trends. When we studied the elements, we saw characteristics that allowed us to categorize them by family. There are also various ways to categorize chemical reactions. Some reactions produce heat, while others consume it. Some reactions are spontaneous, while others are not. Some reactions happen in nanoseconds, while others happen over longer spans of time. Some produce electricity, some emit light, and some release gaseous products. The products of chemical reactions tell us a lot about the chemistry of the process. In the above figure, we see mercury(II) oxide decomposing into elemental mercury and oxygen gas. Decomposition was one of the first reaction types to be identified by chemists. Decomposition is one type of reaction you'll learn about in this lesson.

Combination Reactions

The first type of reaction that we will investigate is the **combination reaction**, which is sometimes also referred to as a synthesis reaction. In combination reactions, two or more chemical species combine to produce a single new compound. A generic combination reaction might have the following form:

$A + B \rightarrow C$

Substances in all states of matter can participate in combination reactions. For example, oxygen in the air can react with iron to produce rust. Rusting is a common occurrence, especially in regions of the world where precipitation is relatively high. Although rust tends to be a mixture of compounds, its primary component is iron(III) oxide (Fe_2O_3). Rusting is generally a very slow process, but when the iron has a very high surface area, as in the case of steel wool, it can happen at a much faster rate, as shown in the following video:

http://www.youtube.com/watch?v=5MDH92VxPEQ

MEDIA

Click image to the left for more content.

The balanced chemical equation for this process is shown below:

$4\text{Fe}(s)+3\text{O}_2(g) \rightarrow 2\text{Fe}_2\text{O}_3(s)$

Decomposition Reactions

A decomposition reaction is the exact opposite of a combination reaction. In decomposition reactions, a single chemical species breaks down to produce two or more new chemical species. A generic decomposition reaction might take the following form:

$C \rightarrow A+B$

Again, substances in all states of matter commonly participate in decomposition reactions. For example, hydrogen peroxide will decompose over time to produce water and oxygen gas according to the following equation:

$2\text{H}_2\text{O}_2(l) \rightarrow 2\text{H}_2\text{O}(l)+\text{O}_2(g)$

Another common type of decomposition reaction involves the process of electrolysis, in which an electrical current is passed through a substance to break apart a compound. One example of a decomposition reaction requiring the use of electrolysis is the decomposition of molten sodium chloride, as shown by the following equation:

$2\text{NaCl}(s) \rightarrow 2\text{Na}(s)+\text{Cl}_2(g)$

Single Replacement Reactions

A **single replacement reaction** (sometimes called a single displacement reaction) occurs when one chemical species (often a single element) replaces a portion of another compound to produce two new products. The general form of a single replacement reaction is shown below:

$AB+C \rightarrow AC+B$

Two common types of single replacement reactions involve pure metals reaction with aqueous solutions of either an acid or an ionic compound. When a reactive metal is placed in an acid solution, the following reaction is likely to occur:

Metal + acid → ionic solution + hydrogen gas

An example of this would be the reaction between zinc and hydrochloric acid, which produces zinc chloride and hydrogen gas. Here is an image of this reaction:

FIGURE 11.7

Zinc metal reacting with a solution of hydrochloric acid

The balanced chemical equation for this single replacement reaction is shown below:

$\text{Zn}(s) + 2\text{HCl}(aq) \rightarrow \text{ZnCl}_2(aq) + \text{H}_2(g)$

Another type of single replacement reaction involves a solid metal replacing the metal cation in an ionic compound that has been dissolved in water. If the solid metal is more reactive than the dissolved metal cations, the following type of reaction can occur:

Metal + ionic solution → different metal + different ionic solution

A common example of this reaction is when iron is replaced by the more reactive zinc metal. The balanced chemical equation for this process is shown below.

$\text{Zn}(s) + \text{FeSO}_4(aq) \rightarrow \text{Fe}(s) + \text{ZnSO}_4(aq)$

Double Replacement Reactions

Double replacement reactions typically include two water-soluble salts that react with one another in solution. The general form of a double replacement reaction would look something like the following:

$AB + CD \rightarrow AD + CB$

In **double replacement reactions**, the cations from the original two ionic compounds trade anions to make two new ionic compounds. In general, at least one of the new compounds must precipitate (form an insoluble solid) for us to conclude that a reaction has occurred. An example of such a process is shown below with the double replacement reaction between solutions of potassium iodide and lead(II) nitrate.

At the molecular level, our model for the way in which a precipitate forms can be described in an animation:

FIGURE 11.8

A double replacement reaction is used to form lead(II) iodide. The reactants shown here are colorless solutions of potassium iodide and potassium nitrate. When combined, these produce a yellow precipitate of lead(II) iodide.

http://www.crescent.edu.sg/crezlab/webpages/PptReaction_PbI2.htm

Representing Ionic Reactions as Chemical Equations

For reactions that involve ions dissolved in water, there are several different ways to express the overall process as a chemical equation. For example, the overall **molecular equation** shows all ionic components as neutral compounds, but the ones that are dissolved in water are denoted with "(aq)." Note that the ionic substances do not exist as molecules, but we write them out as though they were. In the following example, two water-soluble compounds trade partners to produce one dissolved ionic compound and one solid precipitate:

$$AB(aq) + CD(aq) \rightarrow AD(aq) + CB(s)$$

In reality, the aqueous substances do not exist as molecules or ionic crystal lattices. Instead, the individual ions are dissolved and distributed throughout the solution. If the reaction above were written as an **ionic equation**, it would look something like the following:

$$A^+(aq) + B^-(aq) + C^+(aq) + D^-(aq) \rightarrow A^+(aq) + D^-(aq) + CB(s)$$

In this example, the various reaction components are presented in a form that is closer to the way they actually exist during the reaction. The aqueous components are separated into ions, and the precipitate is found as a combined solid. We are assuming in this example that A and C form cations with a charge of 1+, while B and D form anions with a charge of 1-. In real examples, we would look at which group each element is found in on the periodic table to determine its likely charge.

Notice that in the ionic equation, A^+ and D^- were unchanged over the course of the reaction; they exist as aqueous ions on both the reactant and product sides. In other words, these species did not experience any net change. Ions that are present in solution but do not participate in the overall reaction are known as **spectator ions**. The ionic equation can be simplified to the **net ionic equation** by canceling out all the spectator ions.

$$\cancel{A^+(aq)} + B^-(aq) + C^+(aq) + \cancel{D^-(aq)} \rightarrow \cancel{A^+(aq)} + \cancel{D^-(aq)} + CB(s)$$
$$B^-(aq) + C^+(aq) \rightarrow CB(s)$$

Let's look at these three types of equations again using a real example. If we were to mix aqueous solutions of potassium iodide and lead(II) nitrate, lead(II) iodide would precipitate as a solid, and potassium nitrate would remain dissolved. This can be represented by any of the three following equations:

Molecular Equation

$2\text{KI}(aq) + \text{Pb}(\text{NO}_3)_2(aq) \rightarrow 2\text{KNO}_3(aq) + \text{PbI}_2(s)$

Ionic Equation

$2\text{K}^+(aq) + 2\text{I}^-(aq) + \text{Pb}^{2+}(aq) + 2\text{NO}_3^-(aq) \rightarrow 2\text{K}^+(aq) + 2\text{NO}_3^-(aq) + \text{PbI}_2(s)$

Net Ionic Equation

$\text{Pb}^{2+}(aq) + 2\text{I}^-(aq) \rightarrow \text{PbI}_2(s)$

Predicting Solubility of Ionic Compounds

How do we determine which ions are likely to form an insoluble precipitate and which will remain dissolved in water? By combining various ionic solutions, chemists have come up with some general guidelines for whether a given cation-anion pairing is likely to be soluble or insoluble in water. It should be noted that such an approach is an oversimplification. Each compound has its own solubility value, so two "soluble" compounds might have very different abilities to dissolve in water. Additionally, even "insoluble" salts can dissolve in water to a very limited extent. We will take a more quantitative approach to solubility in the chapter on solutions. However, qualitative rules like the ones in the **Table** 11.9 are useful for predicting whether a precipitate is likely to form when combining moderate amounts of specific cations and anions.

TABLE 11.9: Solubility Properties to Predict Products of Chemical Reactions

Type of Particle	Soluble	Insoluble
Common Cations	Alkali metal cation (Li^+, Na^+, K^+, Rb^+, or Cs^+) or the $\text{NH}_4{}^+$ cation	
Common Anions	$\text{ClO}_4{}^-$ and $\text{NO}_3{}^-$ compounds	
Halides	Most Cl^-, Br^-, and I^- compounds	Compounds that include the Ag^+, Pb^{2+}, or $\text{Hg}_2{}^{2+}$ cations
Sulfates	Most $\text{SO}_4{}^{2-}$ compounds	PbSO_4, Ag_2SO_4, Hg_2SO_4, CaSO_4, SrSO_4, and BaSO_4
Sulfides	Compounds with $\text{NH}_4{}^+$ or a metal from group IA or IIA as cation	Most S^{2-} compounds
Hydroxides	Compounds with $\text{NH}_4{}^+$, Ba^{2+}, or a metal from group IA as cation	Most OH^- compounds
Carbonates, phosphates, and sulfites	Compounds with $\text{NH}_4{}^+$ or a metal from group IA as cation	Most $\text{CO}_3{}^{2-}$ and $\text{PO}_4{}^{3-}$, and $\text{SO}_3{}^{2-}$ compounds

Combustion

Combustion occurs when a hydrocarbon reacts in the presence of oxygen to produce water and carbon dioxide. These reactions are very exothermic, which means that they produce a large amount of heat. Combustion reactions are quite common in our everyday lives, such as the burning of gasoline to fuel a car. The chemical equation for a combustion reaction has the following generic form:

$C_xH_y + O_2 \rightarrow H_2O + CO_2$

FIGURE 11.9

Combustion reaction of a marshmallow (sucrose) and wood (cellulose).

The process of cellular respiration can be thought of as a highly controlled version of a combustion reaction. We do not literally burn hydrocarbons in our body, but the overall reactants and products are the same. Hydrocarbons, such as sucrose ($C_{12}H_{22}O_{11}$), are combined with oxygen in a series of enzymatic steps to product water, carbon dioxide, and energy, which is stored in the form of reactive molecules. The unbalanced chemical equation for this overall process is shown below:

$C_{12}H_{22}O_{11} + O_2 \rightarrow CO_2 + H_2O$

Lesson Summary

- Combination reactions occur when two or more reactants combine to produce a single compound.
- Decomposition reactions involve one compound decomposing into two or more products.
- Single replacement reactions occur when one reactant replaces part of another compound to form new substances.
- A common type of double replacement reaction occurs when two ionic reactants exchange anions, making two new ionic compounds. The precipitation of a solid is a common result for this type of reaction.
- Combustion reactions involve the reaction of a hydrocarbon with oxygen gas to produce water and carbon dioxide.

Review Questions

1. Categorize the following chemical reactions as single replacement, double replacement, combustion, combination, or decomposition.
   a. Equimolar (having the same number of moles) solutions of silver nitrate and potassium chloride are mixed to produce solid silver chloride and aqueous potassium nitrate.
   b. Magnesium metal is added to hydrochloric acid to produce hydrogen gas and aqueous magnesium chloride.
   c. Ethanol is burned in air to produce water and carbon dioxide gas.
   d. Water is electrolyzed to produce hydrogen and oxygen gas.
   e. Hydrogen gas and oxygen gas are ignited to produce water.
2. Write the balanced chemical equation for the following combination and decomposition reactions.
   a. Magnesium carbonate is heated strongly to produce magnesium oxide and carbon dioxide gas.
   b. Hydrogen peroxide decomposes to produce water and oxygen gas.
   c. Solid potassium chlorate is heated in the presence of manganese dioxide as a catalyst to produce potassium chloride and oxygen gas. (Catalysts speed up reactions but are not expressed in the overall balanced equation)
   d. Molten aluminum oxide is electrolyzed using inert (non-reactive) electrodes to produce aluminum metal and oxygen gas.
3. Write the balanced chemical equations for the following replacement reactions:
   a. Zinc metal is added to a solution of iron(II) sulfate.
   b. Equimolar solutions of lead(II) nitrate and sodium chloride are mixed to produce solid lead(II) chloride and aqueous sodium nitrate.
   c. Solutions of potassium phosphate and zinc nitrate are mixed.
4. Write the balanced chemical equations for the following combustion reactions.
   a. Propane (C_3H_8) is ignited in air to produce water and carbon dioxide gas.
   b. Methanol(CH_4O) is ignited in air to produce water and carbon dioxide gas.
   c. Ethanol (C_2H_5OH) is burned in air.
5. Write the molecular equation, ionic equation, and net ionic equation for each of the following double replacement reactions.
   a. Silver nitrate reacts with potassium iodide to produce potassium nitrate and silver iodide.
   b. Silver nitrate reacts with iron(III) chloride to produce iron(III) nitrate and silver chloride.
   c. Lead(II) nitrate reacts with potassium iodide to produce potassium nitrate and lead(II) iodide.
   d. Iron(III) chloride reacts with lead(II) nitrate to produce lead(II) chloride and iron(III) nitrate.
   e. Calcium chloride reacts with sodium hydroxide to produce calcium hydroxide and sodium chloride.
6. Would it be possible to have a double precipitate formed for a double replacement process? Can you write an equation where a double precipitate forms?
7. What is meant when we describe a compound as (*aq*) or (*s*)? Explain the similarities and differences between these terms.
8. Write the balanced chemical equation for the combination reaction in which hydrogen and oxygen gases react explosively to produce water. (Remember that hydrogen and oxygen exist as diatomic gases in their most common elemental form.)
9. Write the balanced chemical equation for the reaction that occurs when a piece of aluminum metal is placed in a solution of silver nitrate.
10. Using the solubility rules given above, predict whether or not the following compounds are soluble or insoluble in water.

a. Potassium nitrate
b. Lead(II) chloride
c. Barium sulfate
d. Aluminum sulfide
e. Calcium carbonate

Further Reading / Supplemental Links

- Chemical reaction library: http://jchemed.chem.wisc.edu/JCESoft/CCA/CCA3/STILLS/VOLTAGE/VOLTAGE3/64JPG48/3.JPG
- Solubility concepts video: http://www.khanacademy.org/science/chemistry/states-of-matter/v/solubility
- How to use a solubility chart: http://www.sophia.org/solubility-table/solubility-table-tutorial

Points to Consider

1. In an earlier section, we discussed the origins of the chemical recipe for gunpowder, one of the earliest chemical formulas to be described. The recipe for gun powder is 75 percent potassium nitrate, 15 percent charcoal, and 10 percent sulfur. How might one measure out these amounts in a predictable and reliable way?
2. So far, we have discussed the characteristics of a variety of reactions. However, we have spent little time discussing how we might measure and calculate amounts of reactants and products. The steel wool reaction is as follows: $4Fe_{(s)} + 3O_{2(g)} \rightarrow 2Fe_2O_{3(s)}$. How might you measure the amounts of each reactant used and the product that forms?
3. In the chemical reactions that we have already studied, we have assumed that all reactants are transformed into products (the reaction "goes to completion"). Are there reactions that do not go to completion? How do you know whether you will have reactants left over?
4. What are some factors that control whether or not a chemical reaction takes place?

11.3 References

1. Courtesy of NASA. http://commons.wikimedia.org/wiki/File:Chinese_rocket.gif . Public Domain
2. User:PericlesofAthens/Wikimedia Commons. http://commons.wikimedia.org/wiki/File:Chinese_Gunpowder_Formula.JPG . Public Domain
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CHAPTER 12 Stoichiometry

Chapter Outline

12.1 MOLE RATIOS
12.2 STOICHIOMETRIC CALCULATIONS
12.3 LIMITING REACTANT AND PERCENT YIELD
12.4 REFERENCES

In the last chapter, we saw how gunpowder stimulated interest in understanding the composition of matter. The mixture of sulfur, charcoal and saltpeter (potassium nitrate) was refined until an optimal (maximally explosive) mixture was obtained. The effectiveness of the mixture was also affected by the purity of the ingredients. The ability to refine and reproduce such mixtures was dependent on an understanding of relative mass and ratios between the different mixture components. Alchemists and early scientists understood appropriate ratios for ingredients in a mixture, but determining the ratios of elements that are required to produce a given compound was sometimes a more difficult task. In fact, a systematic understanding of relative masses present in compounds and chemical reactions has only been developed over the last 300 years. Our modern periodic table is based on this knowledge. Using our current understanding of molar mass, we can now relate the amount of a substance (numbers of atoms or molecules) to its mass.

In this chapter, we want use these ideas to explore quantitative issues in chemical reactions. Specifically, we are going to study how the relations between mass, moles, and numbers of particles can be applied to chemical reactions. This topic is referred to as stoichiometry, a term derived from the Greek words *stoicheion* (element) and *metron* (to measure). Understanding the chemical world in terms of stoichiometry allows us to describe and predict the ratios in which reactants combine to generate products in a given chemical process. An understanding of stoichiometry was an important step in developing the capacity to manipulate, create, and replicate new chemical formulations. This knowledge is required for any practical fields in which new chemical substances are created, including pharmaceuticals, diagnostic medicine, agricultural chemistry, and even cosmetics.

User:Millenium187/Wikimedia Commons. commons.wikimedia.org/wiki/File:Brno_Underground_−_Cabbage_Square_−_Alchemical_kitchen_I.JPG. Public Domain.

12.1 Mole Ratios

Lesson Objectives

- Be able to calculate the number of moles, molecules, or atoms in a sample.
- Be able to describe mole ratios for reactants and products of a given chemical reaction.
- Understand stoichiometry and stoichiometric coefficients.
- Be able to calculate the moles of reactants needed or products generated for a reaction based on its balanced chemical equation.

Lesson Vocabulary

- **mole ratio**: When the relative amounts of two reaction components are expressed as a ratio.
- **stoichiometry**: Calculations involving the relative amounts of various reactants and products that participate in a chemical reaction.

Check Your Understanding

1. Calculate molar masses for the following compounds:
   a. H_2O
   b. NH_3
   c. CH_4
2. Calculate the mass (in grams) of the following samples:
   a. 2.6 moles of water.
   b. 1.4 x 10^{23} atoms of sulfur.

Introduction

When making a batch of chocolate chip cookies, a baker must pay careful attention to the amounts of ingredients he uses. The flour, sugar, butter, and chocolate chips must be measured and used in the correct ratios in order for the cookies to bake well. If the baker only has a certain amount of flour, only a certain amount of cookies can be made. Similarly, in chemical reactions, the resulting product is based on the initial moles of reactants present. In this lesson, you will learn how to calculate and account for the amounts of reactants and products in a given chemical reaction.

Mole Ratios: Equating Changes in Amount

We previously saw that mass is conserved for any chemical reaction. Atoms present during the beginning of a chemical reaction must be present at the end as well, even though they may be arranged in different ways. Consider the reaction between iron and oxygen to produce iron(III) oxide:

$$4\text{Fe(s)} + 3\text{O}_2\text{(g)} \rightarrow 2\text{Fe}_2\text{O}_3\text{(s)}$$

According to this equation 4 moles of iron will react with 3 moles of oxygen gas (O_2) to produce 2 moles of iron(III) oxide, Fe_2O_3, as a product. Of course, we do not need exactly 4 moles of iron or 3 moles of oxygen for this reaction to occur. Rather, this equation tells us the ratio in which these reactants combine to make a particular product.

When we express the relative amounts of two reaction components as a ratio, we refer to this as a **mole ratio** or a stoichiometric ratio. Mole ratios can be made between two reactants, two products, or one of each. For example, the following mole ratios can be obtained by looking at the balanced equation shown above:

$$\frac{4 \text{ mol Fe}}{3 \text{ mol O}_2} \ or \ \frac{3 \text{ mol O}_2}{4 \text{ mol Fe}}$$

$$\frac{4 \text{ mol Fe}}{2 \text{ mol Fe}_2\text{O}_3} \ or \ \frac{2 \text{ mol Fe}_2\text{O}_3}{4 \text{ mol Fe}}$$

$$\frac{3 \text{ mol O}_2}{2 \text{ mol Fe}_2\text{O}_3} \ or \ \frac{3 \text{ mol O}_2}{2 \text{ mol Fe}_2\text{O}_3}$$

Stoichiometry refers to the calculations involving mole ratios to determine the relative amounts of reactants needed to produce a given amount of product. Consider the reaction of sodium chloride with silver nitrate:

$$\text{AgNO}_{3(aq)} + \text{NaCl}_{(aq)} \rightarrow \text{AgCl}_{(s)} + \text{NaNO}_{3(aq)}$$

Silver chloride is an important compound that is commonly used in the production of photographic film. It also has many other uses, such as an antidote for mercury poisoning, a component of pottery glazes, and a reference standard for electrochemistry setups. It can be produced according to the reaction shown above. Now we will practice use of mole ratios and stoichiometry to determine the amounts of products and reactants necessary in our reaction.

Example 12.1

How many moles of each reactant are needed to produce 0.5 mol of silver chloride?

Answer:

For this problem, we need to relate moles of each reactant to moles of the product silver chloride. The mole ratio of silver nitrate to silver chloride is constructed as follows:

$$0.5 \text{ mol AgCl} \times \underbrace{\left(\frac{1 \text{ mol AgNO}_3}{1 \text{ mol AgCl}}\right)}_{\text{Mole Ratio}} = 0.5 \text{ mol AgNO}_3$$

As shown above, we would need 0.5 mol of silver nitrate to produce 0.5 mol of silver chloride.

We could also express the moles of silver chloride in terms of sodium chloride, our other reactant. Here is how we would do this:

$$0.5 \text{ mol } AgNO_3 \text{x} \underbrace{\left(\frac{1 \text{ mol NaCl}}{1 \text{ mol } AgNO_3}\right)}_{\text{Mole Ratio}} = 0.5 \text{ mol NaCl}$$

Therefore, we would also need 0.5 mol of sodium chloride in order to produce 0.5 mol of silver chloride. Notice that in each case, we use the mole ratio to relate moles of reactants to moles of products.

Not all reactions have 1:1 ratios between reactants and products. For instance, the reaction between lead(II) nitrate and sodium chloride produces the precipitate lead(II) chloride and aqueous sodium nitrate:

$Pb(NO_3)_{2(aq)} + 2NaCl_{(aq)} \rightarrow PbCl_{2(s)} + 2\ NaNO_{3(aq)}$

FIGURE 12.1

Lead(II) chloride is commonly used in the production of decorative glass, called aurene. It also has many other uses. For example, it is used in the production of paints and in industrial processes that remove unwanted metals.

Example 12.2

If we wanted to make 0.5 mol of lead(II) chloride, how many moles of each reactant would be needed?

Answer:

First, we will relate moles of the reactant sodium chloride to the desired product. The mole ratio between these two substances can be used as a conversion factor as follows:

$0.5 \text{ mol } PbCl_2 \times (\frac{2 \text{ mol NaCl}}{1 \text{ mol } PbCl_2}) = 1 \text{ mol NaCl}$

In order to produce 0.5 mol of lead(II) chloride, we would need 1 mol of sodium chloride. The necessary amount of the other reactant can be calculated in the same way:

$0.5 \text{ mol } PbCl_2 \times (\frac{1 \text{ mol } Pb(NO_3)_2}{1 \text{ mol } PbCl_2}) = 0.5 \text{ mol } Pb(NO_3)_2$

We can use mole ratios to determine the amounts of reactants needed to produce a given amount of product. As we will see in the next lesson, we can also convert these amounts into masses using our understanding of molar mass.

Lesson Summary

- Mole ratios can be derived from a balanced chemical equation. These ratios can then be used to determine the amounts of each substance involved in a given chemical reaction.
- Stoichiometry refers to calculations involving the relative amounts of various reactants and products that participate in a chemical reaction.

Lesson Review Questions

1. Aluminum reacts with oxygen to produce aluminum oxide as follows: $4Al + 3O_2 \rightarrow 2Al_2O_3$
    (a) If you use 2.3 moles of Al, how many moles of Al_2O_3 can you make?
    (b) If you want 3.9 moles of Al_2O_3, how many moles of O_2 are needed?
2. In the presence of sulfuric acid, metallic iron forms iron(III) sulfate: $2Fe + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 3H_2$
    (a) How many moles of hydrogen will be produced when you use 1.7 moles of iron?
    (b) How much sulfuric acid is needed to produce 2.8 moles of iron(III) sulfate?
3. Write the mole ratios for reactants in terms of products for the following equation: $2\ Mg + O_2 \rightarrow 2\ MgO$
4. How many moles of each reactant are needed to produce 2.5 mol of aluminum oxide by the following reaction? $4\ Al + 3\ O_2 \rightarrow 2\ Al_2O_3$
5. How many moles of each reactant would be necessary to produce 2.6 mol of barium sulfate by the following reaction? $BaCl_2 + Na_2SO_4 \rightarrow BaSO_4 + 2NaCl$

Further Reading/Supplementary Links

- Practice using mole ratios: http://www.wisc-online.com/Objects/ViewObject.aspx?ID=GCH7304
- Review of what stoichiometry is: http://www.chem4kids.com/files/react_stoichio.html

Points to Consider

- If you know how many moles of product a reaction yielded, can you find the mass of reactants used in the initial reaction?

12.2 Stoichiometric Calculations

Lesson Objectives

- Based on the balanced chemical equation, be able to calculate the masses of reactants or products generated in a given reaction.
- Based on the balanced chemical equation, be able to calculate the moles of reactants or products generated in a given reaction.
- Understand how to convert between masses and moles in a chemical reaction using mole ratios and molar masses.

Check Your Understanding

Recalling Prior Knowledge

1. How much hydrogen is needed to form 3.1 moles of tin according to the following reaction?

$SnO_2 + 2\ H_2 \rightarrow Sn + 2H_2O$

Mole Ratios, Molar Masses, and Chemical Equations

How can we measure out a known amount of a reactant, since actually counting atoms and molecules is not a practical approach? How can we tell what amount of product was generated in a reaction? In most cases, the mass of a reactant or product is a relatively easy quantity to measure. Recall that the molar mass of a given chemical species can be determined by referencing the periodic table. If we know the identity of the substance we wish to measure, molar mass can be used as a conversion factor between mass and amount (in moles). For any given chemical reaction, we can describe the following relationships in the **Figure** 12.2:

Example 12.3

$AgNO_{3(aq)} + NaCl_{(aq)} \rightarrow AgCl_{(s)} + NaNO_{3(aq)}$

How many grams of each reactant are needed to produce 0.500 mol of silver chloride?

Answer:

First, we need to relate the mass of silver nitrate to the amount in moles of the product silver chloride. This can be accomplished by using a series of conversion factors in which all units cancel except for those of the desired answer (grams of silver nitrate). To do this, we will need the mole ratio between these two reaction components and the molar mass of silver nitrate. Then, we can perform the following calculation:

$0.500\,\text{mol AgCl} \times \left(\frac{1\,\text{mol AgNO}_3}{1\,\text{mol AgCl}}\right)\left(\frac{169.87\,\text{g AgNO}_3}{1\,\text{mol AgNO}_3}\right) = 84.9\,\text{g AgNO}_3$

In order to produce 0.500 moles of AgCl, we would need to start with 84.9 g of silver nitrate. A similar calculation can be performed to determine the necessary mass of sodium chloride.

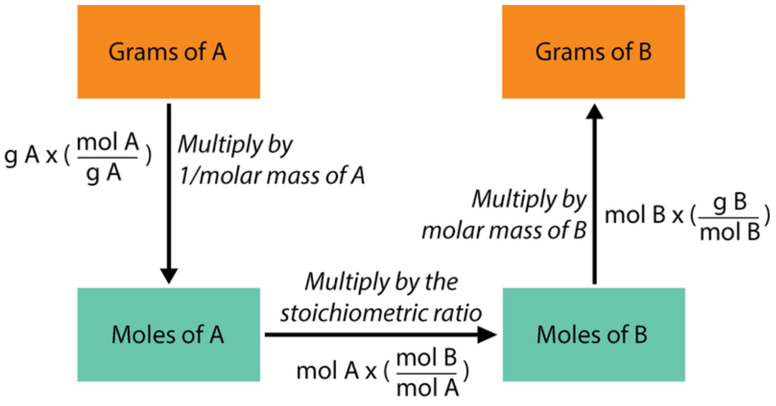

FIGURE 12.2

The above image depicts how moles, mass, and mole ratios are related for a given chemical equation.

$$0.500\,\text{mol AgCl} \times \left(\frac{1\,\text{mol NaCl}}{1\,\text{mol AgCl}}\right)\left(\frac{58.44\,\text{g NaCl}}{1\,\text{mol NaCl}}\right) = 29.2\,\text{g NaCl}$$

Mass Reactants↔Moles Reactants↔Moles Products↔Mass Products

In the chemistry lab, we frequently need to calculate the relationship between two reactants or products in a chemical reaction. For example, we may know the mass of one reactant and want to know how much of a given product will be generated if the reactant is fully consumed. We may also wish to know how much of a second reactant is required to fully react with the first reactant. These types of questions can be answered by using molar masses and mole ratios as conversion factors. We will illustrate this process with an example.

Example 12.4

How many grams of lead(II) chloride would be produced if 1.67 g of lead(II) nitrate is allowed to react completely in the presence of a sodium chloride solution? How many grams of sodium chloride would be consumed in the process?

$$\text{Pb(NO}_3)_{2(aq)} + 2\ \text{NaCl}_{(aq)} \rightarrow \text{PbCl}_{2(s)} + 2\ \text{NaNO}_{3(aq)}$$

Answer:

First, we need to relate grams of lead(II) chloride to grams of lead(II) nitrate. We can set up the following expression, using the molar masses of each component and their mole ratio, obtained from the balanced equation:

$$1.67\ \text{Pb(NO}_3)_2 \times \left(\frac{1\ \text{mol Pb(NO}_3)_2}{331.2\ \text{g Pb(NO}_3)_2}\right)\left(\frac{1\ \text{mol PbCl}_2}{1\ \text{mol Pb(NO}_3)_2}\right)\left(\frac{278.11\ \text{g PbCl}_2}{1\ \text{mol PbCl}_2}\right)=1.40\ \text{g PbCl}_2$$

Therefore, 1.40 g of lead(II) chloride would be produced if 1.67 g of lead(II) nitrate is fully consumed. The amount of NaCl that would be used in this process can be calculated as follows:

$$1.67\ \text{Pb(NO}_3)_2 \times \left(\frac{1\ \text{mol Pb(NO}_3)_2}{331.2\ \text{g Pb(NO}_3)_2}\right)\left(\frac{2\ \text{mol NaCl}}{1\ \text{mol Pb(NO}_3)_2}\right)\left(\frac{58.44\ \text{g NaCl}}{1\ \text{mol NaCl}}\right) = 0.589\ \text{g NaCl}$$

In order to fully consume 1.67 g of lead(II) nitrate, we would need at least 0.589 g of NaCl.

Lesson Summary

- Using molar masses and mole ratios, we can find the relationships between the masses of various reaction components for a given reaction.

Review Questions

1. Aluminum reacts with oxygen to produce aluminum oxide according to the following equation: $4Al + 3O_2 \rightarrow 2Al_2O_3$
   (a) How many grams of O_2 are needed to produce 5 moles of Al_2O_3?
   (b) How many grams of Al_2O_3 are produced from the reaction of 5 moles of Al?
   (c) How many grams of of Al are needed to produce 86.0 grams of Al_2O_3?
2. How many grams of each reactant are needed to produce 0.500 mol of barium sulfate according the following equation? $BaCl_2 + Na_2SO_4 \rightarrow BaSO_4 + 2NaCl$
3. How many grams of each reactant are needed to produce 28.6 grams copper (II) sulfide by the following reaction? $Cu + SO_2 \rightarrow CuS + O_2$

Further Reading / Supplemental Links

1. Stoichiometry Calculator: http://mmsphyschem.com/stoichiometry.htm
2. Practice Balancing Chemical Equations:
   a. http://education.jlab.org/elementbalancing/index.html
   b. http://www.files.chem.vt.edu/RVGS/ACT/notes/scripts/bal_eq1.html
   c. http://gregthatcher.org/Chemistry/BalanceEquation/S
3. Chemical equation balances: http://www.personal.psu.edu/jzl157/balance.htm

Points to Consider

- Our study of masses and amounts, as described by a given chemical equation, has assumed that mass is conserved for all chemical processes. How might you determine experimentally that this is the case for a given chemical reaction?
- So far, we have assumed that all of the reactants are utilized in the formation of products during each reaction. Can you think of a case in which one or more reactants would not be completely consumed?

12.3 Limiting Reactant and Percent Yield

Lesson Objectives

- Define limiting reagent, theoretical yield, and percent yield.
- Calculate theoretical yield for a given chemical process.
- Be able to determine which reactant is the limiting reactant, calculate the amount of product formed, and determine the percent yield.
- Use reaction tables to describe mass and mole changes for a given chemical reaction.

Lesson Vocabulary

- **actual yield**: The amount of product that is actually produced.
- **theoretical yield**: The maximum amount of product that can be generated from the given amounts of reactants.
- **percent yield**: Tells us what percentage of the possible amount of product (the theoretical yield) was actually obtained (the actual yield).
- **excess reactant (excess reagent)**: When there is more reactant available than is required to react with the other available reactants. Some amount of reactant will be leftover at the end of the reaction.
- **limiting reactant (limiting reagent)**: The reactant that is completely consumed in a reaction.

Check Your Understanding

Write the balanced chemical equations for the following reactions:

1. Methane (CH_4) reacts with oxygen in the air to produce water and carbon dioxide.
2. Solutions of barium chloride and sodium sulfate react to form a precipitate of barium sulfate and an aqueous solution of sodium chloride.
3. Carbon monoxide reacts with oxygen to produce carbon dioxide.

Introduction

In the last lesson, we learned how to perform stoichiometry calculations, which relate masses and moles of reactants and products for a given chemical process. In this lesson, we are going to compare theoretical yield (the maximum amount that could be produced in a reaction) to actual yield (the amount that is actually produced). We will also investigate what happens when one reactant runs out before the other reactants are fully consumed. Finally, we will study how to express changes in masses and moles for a given chemical process using the reaction table method.

Reaction Yield

Actual vs. Theoretical Yield

The yield of a chemical reaction is the amount of certain product that is produced from given amounts of each reactant. The **actual yield** is the amount of product that is actually produced. This value is generally not exactly equal to the **theoretical yield**, which represents the maximum amount that could be generated from the given amounts of reactants. For example, say we performed the copper cycle as described in the introduction by starting with 1.00 grams of copper. Theoretically, the final reaction should give us back 1.00 grams of copper; this is our theoretical yield. However, we may find that only 0.86 grams of Cu is produced; this would be our actual yield. When we perform stoichiometric calculations, we are attempting to determine the theoretical yield based on the amounts of reactants available. Actual yields can only be determined by performing the experiment and measuring the final mass of product.

Percent Yield

A common way to express the yield of a reaction is as a percentage. The **percent yield** of a reaction tells us what percentage of the possible amount of product (the theoretical yield) was actually obtained (the actual yield). Percent yield can be calculated using the following expression:

$\text{Percent Yield} = \frac{\text{Actual Yield}}{\text{Theoretical Yield}} \times 100\%$

Example 12.6

You calculate that 1.00 grams of copper should be produced (theoretical yield) from a given chemical process. After you run the experiment, you find that 0.860 grams of copper is obtained. Calculate the percent yield for this process.

Answer:

$$\begin{aligned}\text{Percent Yield} &= \frac{0.860 \text{ g Cu}}{1.00 \text{ g Cu}} \times 100\% \\ &= 86\%\end{aligned}$$

The Reaction Table Method

A reaction table can be used to keep track of the masses and moles of each reaction component over the course of a chemical reaction. For the generic reaction shown below, we can set up the following **Table** 12.1:

aA + bB → cC + dD

TABLE 12.1: Reaction Table

	A	B	C	D
Molar Mass				
Initial Mass				
Initial Moles				
Change in Moles	-ax	-bx	+cx	+dx
Final Moles				
Final Mass				

Note: The change in the number of moles for each reactant and product must be consistent with the mole ratios in the balanced chemical equation. This is designated by the factor of "x" in the Change in Moles row of the reaction table. Also recall that as a chemical reaction takes place, the reactants are being used up (indicating a negative change in moles) and the products are being created (indicating a positive change in moles).

Steps to Solving Chemical Reaction Problems

1. Write the balanced reaction.
2. Draw a reaction table.
3. Fill in the known values.
4. Calculate the missing values.

This process is easiest to explain in the form of an example problem.

Example 12.7

Magnesium metal is heated in the presence of oxygen gas to produce magnesium oxide.

$$2\text{Mg(s)} + \text{O}_2\text{(g)} \rightarrow 2\text{MgO(s)}$$

If 1.00 grams of Mg react completely with excess oxygen, how many grams of magnesium oxide will be produced? How many grams of oxygen will be used?

Answer:

First, write the balanced reaction, and then draw a blank reaction table. The changes in moles of each component can be written in terms of a variable x, which we will solve for. The relative number of moles added to or subtracted from each amount is based on the coefficients from the balanced equation.

$$2\text{Mg(s)} + \text{O}_2\text{(g)} \rightarrow 2\text{MgO(s)}$$

TABLE 12.2: **Magnesium Table Set Up**

	Mg	O_2	MgO
Molar Mass			
Initial Mass			
Initial Moles			
Change in Moles	-2x	-x	+2x
Final Moles			
Final Mass			

Now, fill in the known values. We are told that the initial mass of magnesium is 1.00 grams. We are also told that our magnesium sample reacts completely, so the final mass of magnesium (and the final moles) will be 0. We do not know exactly how much oxygen gas is present, but it is an **excess reactant** (sometimes called an excess reagent), which means that there is more than enough oxygen to react with the other available reactants. We can simply write "excess" in both the initial and final masses/moles for this reactant. Unless told otherwise, assume that there is no initial product (the initial mass and moles of MgO would be 0). Additionally, we can calculate the molar masses for each reactant and product by looking at the periodic table:

Mg = 24.31 g/mol
O_2 = 32.00 g/mol
MgO = 40.31 g/mol

TABLE 12.3: Magnesium Table Part I

	Mg	O_2	MgO
Molar Mass	24.31 g/mol	32.00 g/mol	40.31 g/mol
Initial Mass	1.00 g	excess	0 g
Initial Moles		excess	0 mol
Change in Moles	-2x	-x	+2x
Final Moles	0 mol	excess	
Final Mass	0 g	excess	

Now, fill in the remaining values by performing calculations. We can use molar masses to convert between grams and moles for any known amount.

$1.00 \text{ g Mg}(\frac{1 \text{ mol Mg}}{24.31 \text{ g Mg}}) = 0.0411 \text{ mol Mg}$

Once we know the difference between the initial and final moles for any of the reaction components, we can calculate the value of x. Over the course of the reaction, 0.0411 moles of Mg are used up, so

$$-2x = -0.0411 \text{ mol}$$
$$x = 0.0206 \text{ mol}$$

Using this information, we can fill in more of the table:

TABLE 12.4: Magnesium Table Part II

	Mg	O_2	MgO
Molar Mass	24.31 g/mol	32.00 g/mol	40.31 g/mol
Initial Mass	1.00 g	excess	0 g
Initial Moles	0.0411 mol	excess	0 mol
Change in Moles	-0.0411 mol	-0.0206 mol	+0.0411 mol
Final Moles	0 mol	excess	
Final Mass	0 g	excess	

Using our value for x, we can now perform simple addition to determine the final moles of MgO. This can then be converted to grams using the molar mass.

TABLE 12.5: Magnesium Table Part III

	Mg	O_2	MgO
Molar Mass	24.31 g/mol	32.00 g/mol	40.31 g/mol
Initial Mass	1.00 g	excess	0 g
Initial Moles	0.0411 mol	excess	0 mol
Change in Moles	-0.0411 mol	-0.0206 mol	+0.0411 mol
Final Moles	0 mol	excess	0.0411 mol
Final Mass	0 g	excess	1.66 g

Now that the table is complete, we can answer the original questions. We can see directly from the table that 1.66 grams of MgO could be produced from this reaction. We do not yet know the mass of oxygen that is used up, but we do know that 0.0206 moles are consumed. Converting this to grams using the molar mass of O_2 gives us the following:

$0.0206 \text{ mol } O_2 \times (\frac{32.00 \text{ g } O_2}{1 \text{ mol } O_2}) = 0.659 \text{ g } O_2$

1.00 grams of Mg reacts completely with 0.659 grams of O_2 to produce 1.66 grams of MgO.

Limiting Reactant

So far, we have either assumed that all reactants will be completely consumed in a chemical reaction, or we have been told that one reactant is present in excess. In the previous example, 1 gram of magnesium reacted in the presence of excess oxygen. However, we may sometimes be presented with initial amounts of multiple reactants without being told which one will run out first. In such a scenario, the **limiting reactant** (sometimes called a limiting reagent) will be the reactant that is completely consumed. After the limiting reactant runs out, there may still be some of the excess reactants left over, but the reaction can no longer proceed, because one of the ingredients is missing. To determine which reactant is limiting in a chemical reaction, we need to look at how many moles of each are present. These values must then be compared to the coefficients in the balanced equation, which tell us the ratios in which various reactants combine.

Before working with chemical reactions, it may help to explain the concept of limiting reactants in a more familiar context. For example, let's say that you want to make as many cheese sandwiches as possible with the bread and cheese that is available.

Example 12.8

You have 16 slices of bread and 10 slices of cheese. If each sandwich requires two slices of bread and one slice of cheese, how many sandwiches can you make, and what ingredients will be left over? For this "reaction," which reactant is limiting, and which one is present in excess?

Answer:

For this example, we could simply start subtracting bread and cheese as each sandwich is made. After making 8 sandwiches, we would find that we have run out of bread, but there are two slices of cheese left over. Thus, bread is the limiting reactant, and cheese is present in excess. Notice that we actually have more slices of bread than of cheese, but because it gets used up twice as fast, bread runs out first (it is limiting).

An alternative way to look at this problem would be to write this "reaction" out as a chemical equation.

2 Bread + Cheese → Sandwich

We cannot directly compare the amounts of bread and cheese, because they are not used in a 1:1 ratio. However, if we divide each amount by the coefficient from the balanced equation, we get the following:

$$\frac{16 \text{ slices bread}}{2} = 8$$
$$\frac{10 \text{ slices cheese}}{1} = 10$$

These values can be directly compared. After dividing each amount by its coefficient from the balanced equation, the smallest number corresponds to the ingredient that will run out first. In this case, the limiting reactant is bread, because 8 <10. To determine how much of the excess reactant is left over, we need to determine how much will be used up by the limiting reactant. In order to use up all of the limiting reactant (16 slices of bread), we would need:

$16 \text{ slices bread} \times (\frac{1 \text{ slice cheese}}{2 \text{ slices bread}}) = 8 \text{ slices cheese}$

After using 8 slices of cheese, all the bread will be used up, and the "reaction" stops. Subtracting this amount from our original 10 slices of cheese, we can see that there will be two slices left over.

Here is an interactive simulation to help you visualize reactions involving limiting reactants: http://phet.colorado.edu/en/simulation/reactants-products-and-leftovers .

Limiting Reactants and Reaction Tables

Filling out a reaction table will help to double-check that you have found the correct limiting reactant, and it will give you information about theoretical yields and the amounts that will be left over for any excess reactants.

Example 12.9

3.40 g of hydrogen gas and 7.16 g of nitrogen gas react to form gaseous ammonia. Assume that the reaction runs until one of the reactants is fully consumed.

Answer:

First, write the balanced equation for this reaction and set up a reaction table. Fill in the amounts given in the problem, and calculate the molar masses of each reaction component. Recall that the "change in moles" line is based on the coefficients from the balanced equation:

$N_{2(g)} + 3\ H_{2(g)} \rightarrow 2NH_{3(g)}$

TABLE 12.6: NH3 Table Set Up

	N_2	$3H_2$	$2NH_3$
Molar Mass	28.02 g/mol	2.02 g/mol	17.04 g/mol
Initial Mass	7.16 g	3.40 g	0 g
Initial Moles			0 mol
Change in Moles	-x	-3x	+2x
Final Moles			
Final Mass			

Next, use molar masses to convert the known masses to moles:

$$7.16\text{ g N}_2\left(\frac{1\text{ mol N}_2}{28.02\text{ g N}_2}\right) = 0.256\text{ mol N}_2$$
$$3.40\text{ g H}_2\left(\frac{1\text{ mol H}_2}{2.02\text{ g H}_2}\right) = 1.68\text{ mol H}_2$$

Now that we have the moles of each reactant, we can divide by the coefficients from the balanced equation to determine which will run out first.

$$\frac{0.256\text{ mol N}_2}{1} = 0.256$$
$$\frac{1.68\text{ mol H}_2}{3} = 0.560$$

Because the number for N_2 is lower, N_2 is the limiting reactant. Since this reaction is run until a reactant runs out, we now know that the final mass of N_2 will be 0 grams. Putting this new information into the table, we get the following:

TABLE 12.7: NH3 Table Part I

	N_2	$3H_2$	$2NH_3$
Molar Mass	28.02 g/mol	2.02 g/mol	17.04 g/mol
Initial Mass	7.16 g	3.40 g	0 g
Initial Moles	0.256 mol	1.68 mol	0 mol
Change in Moles	-x	-3x	+2x
Final Moles	0 mol		
Final Mass	0 g		

Looking at the difference between the initial and final moles for N_2, it is clear that x must have a value of 0.256 moles. Using this value, we can replace the "Change in Moles" line with specific values, and the "Final Moles" line can be filled in by simple addition or subtraction.

TABLE 12.8: NH3 Table Part II

	N_2	$3H_2$	$2NH_3$
Molar Mass	28.02 g/mol	2.02 g/mol	17.04 g/mol
Initial Mass	7.16 g	3.40 g	0 g
Initial Moles	0.256 mol	1.68 mol	0 mol
Change in Moles	-0.256 mol	-0.768 mol	+0.512 mol
Final Moles	0 mol	0.91 mol	0.512 mol
Final Mass	0 g		

Finally, we can convert moles to grams using the molar masses of each reaction component:

$$0.91 \text{ mol } H_2 \times (\frac{2.02 \text{ g } H_2}{1 \text{ mol } H_2}) = 1.84 \text{ g } H_2$$

$$0.512 \text{ mol } NH_3 \times (\frac{17.04 \text{ g } NH_3}{1 \text{ mol } NH_3}) = 8.72 \text{ g } NH_3$$

TABLE 12.9: NH3 Table Part III

	N_2	$3H_2$	$2NH_3$
Molar Mass	28.02 g/mol	2.02 g/mol	17.04 g/mol
Initial Mass	7.16 g	3.40 g	0 g
Initial Moles	0.256 mol	1.68 mol	0 mol
Change in Moles	-0.256 mol	-0.768 mol	+0.512 mol
Final Moles	0 mol	0.91 mol	0.512 mol
Final Mass	0 g	1.84 g	8.72 g

Note that if we calculate the total mass of all components, it is the same before and after the reaction (10.56 g total). This is consistent with the law of conservation of mass.

Now, we can answer specific questions about this reaction. The limiting reactant is N_2, because it is completely used up before any of the other reactants. We would know that we chose the wrong limiting reactant if any of the other final amounts turned out to be negative numbers. The theoretical yield of ammonia is 8.72 g, and there is 1.84 g of H_2 left over after the reaction is complete.

If the yield is 87.5%, we can perform the following calculation:

$$\begin{aligned}
\text{Percent Yield} &= \frac{\text{Actual Yield}}{\text{Theoretical Yield}} \times 100\% \\
\text{Actual Yield} &= (\text{Theoretical Yield})\left(\frac{\text{Percent Yield}}{100\%}\right) \\
\text{Actual Yield} &= (8.62\ \text{g})\left(\frac{87.5\%}{100\%}\right) \\
\text{Actual Yield} &= 7.54\ \text{g}
\end{aligned}$$

7.54 grams of ammonia were actually produced in this reaction.

Lesson Summary

- Chemical reactions can be studied in terms of the amounts of reactants that are present and the amount of products that are formed.
- The balanced chemical equation describes the relative amounts of reactants and products that are consumed and generated by a given chemical process.
- Reactants combine in fixed mole ratios.
- The amount of each reactant needed to generate a certain amount of product can be determined with stoichiometric calculations.
- In cases where one reactant is used up before the others, we can describe the reaction in terms of a limiting reactant and one or more excess reactants.
- The actual and theoretical yields for a given reaction are often related by calculating a percent yield.
- The reaction table method provides a way to organize the information needed to perform stoichiometry calculations and to answer quantitative questions about various chemical reactions.

Lesson Review Questions

1. Urea $(NH_2)_2CO$ is prepared by reacting ammonia with carbon dioxide according to the following equation: $2NH_3(g) + CO_2(g) \rightarrow (NH_2)_2CO(aq) + H_2O(l)$. In one experiment, 637.2 g of NH_3 is allowed to react with 1142 g of CO_2.
   (a) Which of the two reactants is the limiting reagent?
   (b) Calculate the mass of$(NH_2)_2CO$ that could theoretically be formed by this reaction.
2. Hydrogen gas reacts explosively in the presence of oxygen to produce water.
   (a) Write the balanced chemical equation for this process.
   (b) If 1 mol of hydrogen gas and 1 mol of oxygen gas are placed in a container and ignited, how many moles of water will be produced?
   (c) Which will be the limiting reactant?
   (d) Which will be the excess reactant, and how much of the excess reactant will be left over?
3. If 1.00 grams of hydrogen gas and 1.00 grams of oxygen gas are placed in a container and ignited:
   (a) Which will be the limiting reactant?
   (b) Which will be the excess reactant?
   (c) What is the theoretical yield for water?

   (d) If 0.96 g of water are actually produced, what is the percent yield for this process?

4. Gaseous nitrogen and hydrogen react to form ammonia via the Haber process, which is represented by the following chemical equation: $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$
   (a) If you react 25.0 grams of hydrogen gas in the presence of excess nitrogen gas, how many grams of ammonia should be produced?
   (b) If you produced 140. grams of ammonia, what is the percent yield?
5. Look back to Example 12.8. If you changed the recipe to 2 slices of cheese per sandwich, what would be the limiting reactant and excess reactant given the same reactant amounts as in the example?
6. Magnesium reacts with nitrogen in the air to form magnesium nitride.
   (a) Write and balance the chemical equation.
   (b) What is the limiting reactant if 4.00 g of Mg are mixed with 8.00 g of nitrogen?
   (c) What is the theoretical yield of magnesium nitride in grams?

Further Reading / Supplemental Links

- The Copper Cycle: http://www.youtube.com/watch?v=jVFnzFmsZHk
- Chemical reaction library: http://jchemed.chem.wisc.edu
- Stoichiometry general practice problems: http://www.sciencegeek.net/Chemistry/taters/Unit4Stoichiometry.htm
- Borror, D. (Ed.) (1960) Dictionary of word roots and combining forms: compiled from the Greek, Latin, and other languages, with special reference to biological terms and scientific names. Mayfield Publishing Co.
- Watkins, S. F. (2003). Applying the Reaction Table Method for Chemical Reaction Problems (Stoichiometry and Equilibrium). Journal of Chemical Education, 80(6), 658-null. doi: 10.1021/ed080p658

Points to Consider

1. What are some factors that control whether or not the actual yield of a chemical reaction is 100%? What would it mean for a reaction yield to be less than 100%? More than 100%?

Opening image: User:Millenium187/Wikimedia Commons. http://commons.wikimedia.org/wiki/File:Brno_Underground_-_Cabbage_Square_-_Alchemical_kitchen_I.JPG . Public Domain.

12.4 References

1. Martin Walker (User:Walkerma/Wikimedia Commons). http://commons.wikimedia.org/wiki/File:Lead(II)_chloride.jpg . Public Domain
2. Jodi So. CK-12 Foundation . CC BY-NC 3.0

CHAPTER 13

States of Matter

Chapter Outline

13.1 THE KINETIC-MOLECULAR THEORY OF GASES
13.2 LIQUIDS AND SOLIDS
13.3 CHANGES OF STATE
13.4 REFERENCES

So far, much of our study of the chemical world has focused on investigating elements, compounds, and reactions. We have assessed the characteristics of elements and studied how they combine through chemical reactions to produce new compounds. Now, we are going to shift our attention away from compounds and reactions and look at what happens to matter when it changes state. We are going to study why substances exist as solids, liquids, or gases. We are also going to look at what takes place on the molecular level when matter changes state from one form to another. As you might already imagine, some substances exist as solids at room temperature, others exist as liquids, and still others exist as gases. Life as we know it would be much different, for instance, if water was solid at room temperature, or if oxygen and carbon dioxide were liquid. This chapter will help us understand the different states of matter.

Mike Cline. commons.wikimedia.org/wiki/File:FireholeRiverOjoCalientiBend.jpg. Public Domain.

13.1 The Kinetic-Molecular Theory of Gases

Lesson Objectives

- Describe kinetic energy as it applies to molecules.
- Explain how kinetic energy is related to the mass and velocity of a particle.
- Describe the nature of elastic collisions and the implications for matter at the molecular level.
- Describe the origins and assumptions of the kinetic-molecular theory, and use this model to describe the nature of matter at the molecular level.
- Describe ideal behavior as it applies to a gas.

Lesson Vocabulary

- **kinetic energy**: The energy associated with motion.
- **elastic collision**: A collision in which momentum is conserved.
- **kinetic-molecular theory**: Describes the molecular behavior of an ideal gas.
- **ideal gas**: Gases that conform to the kinetic-molecular theory.

Check Your Understanding

- What are the similarities and differences between different states of matter?

Introduction

Ice, water, and steam appear quite differently to the eye. If you were to look at these three states of matter on the molecular level, you would see that the arrangement of molecules is very different here as well. However, solids and liquids have definite volumes, unlike gases which tend to take on the shape of their container. In this lesson, you will learn about the unique behavior of gas particles on a molecular level and the basis for kinetic molecular theory.

States of Matter - A Microscopic View

If we see matter at the macroscopic level, we can easily tell whether it is solid, liquid, or gas. In **Figure** 13.1, we see a green chlorine gas-liquid equilibrium. The various states of matter can largely be explained by studying interactions between particles that occur at the microscopic level. **Figure** 13.2 shows how the three states of matter differ on the molecular level.

FIGURE 13.1

Chlorine gas.

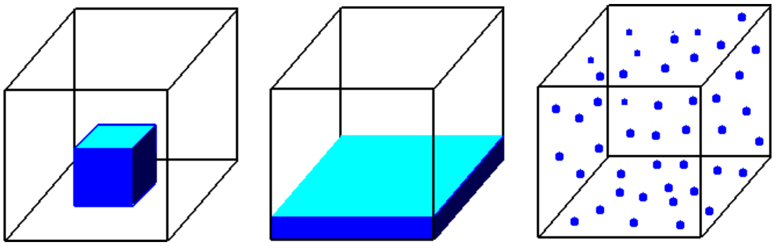

FIGURE 13.2

In this image, we see how atoms of argon interact in the solid, liquid, and gas phases.

As we saw in our chapter on the mole, matter is ultimately composed of particles. We cannot "see" individual molecules, but we can see the effects exerted by the structure of each molecule on the behavior of the bulk material. What accounts for the very different properties exhibited by the same substance when it exists in different phases of matter? The sizes and properties of individual atoms and molecules do not change when a substance changes phase. Rather, it is the interactions between particles that are changing.

Liquids and Solids

As shown in **Figure** 13.2, each state of matter looks quite different at the molecular level. In the case of liquids and solids, the distances between particles are negligible relative to the size of each particle; they are essentially in direct contact with one another. In liquids, particles are free to move and exchange neighbors, resulting in the properties of a fluid. In solids, they are rigidly fixed in space and held tightly to neighboring particles.

Gases

The story is quite different for gases. Gases take the shape of their container, and they are relatively easy to compress. There are fewer gas particles per unit volume than for the same substance in the liquid or solid form. In fact, the liquid form of a given material is generally several hundred times more dense than the gas form at normal pressures. Despite the large amounts of empty space, a sample of a gas contains many particles moving around, colliding and imparting force on their surroundings. For example, in a one mole sample of gas at 0°C and 1 atm of pressure, each cubic centimeter contains roughly 2.7×10^{19} molecules. Each molecule participates in several billion collisions every second, moving only about 10-100 nanometers between collisions. Additionally, these gas particles move at very high speeds. For example, at 25°C, the average speed of hydrogen molecules in a sample of hydrogen gas is 1960 m/s.

These are just some of the differences we see when we look at the molecular level and study the different states for a particular chemical species. The following simulation illustrates how particles behave over time in the liquid, solid, and gas states: http://phet.colorado.edu/en/simulation/states-of-matter .

In this simulation, you can watch different types of molecules form a solid, liquid, or gas. Add or remove heat to watch the phase change. Change the temperature or volume of a container and see a pressure-temperature diagram respond in real time.

One of the concepts shown by this animation is that particles are constantly moving and vibrating. This is an important assumption that we make when we study matter at the molecular level. Anything that is moving and has mass also possesses some amount of **kinetic energy**, or the energy of motion. Kinetic energy increases as the molecular mass increases and as the velocity of the particle increases.

Another thing we can see in this animation is that particles are constantly colliding with one another. One assumption that we make when talking about collisions between gas particles is that they are completely elastic collisions. In an **elastic collision**, momentum is conserved, which means that none of the kinetic energy of the colliding particles is lost in some other form (such as the emission of light). This makes sense, because if energy were lost in collisions, the speeds of the particles would gradually decrease over time, and eventually everything would condense down into a solid form.

The Kinetic-Molecular Theory of Gases

Some of the observations and assumptions we just made about particle behavior at the molecular level were proposed in independent works by August Kroning (1856) and Rudolf Clausius's 1857 work titled "the theory of moving molecules." This work became the foundation of the **kinetic-molecular theory** of gases. The kinetic-molecular theory of gases makes the following assumptions:

1. Gases are comprised of large numbers of particles that are in continuous, random motion and travel in straight lines.
2. The volume of gas particles in a sample is extremely small compared to the total volume occupied by the gas.
3. Attractive and repulsive forces between gas molecules are negligible.
4. Energy can be transferred between molecules during collisions. Collisions are completely elastic.
5. The average kinetic energy of the molecules is proportional to the temperature of the sample.
6. Gases that conform to these assumptions are called **ideal gases**.

By applying these principles to gases, it is possible to show that the properties of gases on the macroscopic level are a direct result of the behavior of molecules on the microscopic level.

Lesson Summary

- Differences between solids, liquids, and gases depend upon the interactions between the individual particles.
- Kinetic energy is directly proportional to the mass and velocity of a particle; that is, as mass and/or velocity increase, so does the kinetic energy.
- The kinetic-molecular theory describes the behavior of an ideal gas.
- Assumptions of the kinetic-molecular theory include the following:
  - Gas particles are in constant, random motion.
  - The volume of gas particles is negligible in comparison to the volume of the container.
  - There are no attractive forces between gas particles.
  - Collisions of gas particles are elastic, so no energy is lost.
  - The speed of a gas particle is directly proportional to the temperature of the system.

Review Questions

1. What do we mean when we say molecular view of matter? Can you draw a diagram to describe what particles might look like at the molecular level for solids, liquids, and gases?
2. What is kinetic energy? Does kinetic energy increase or decrease as particle speed increases?
3. Describe what is meant by an elastic collision. What would happen to particles over time if most collisions were not elastic?
4. Summarize the major points of the kinetic-molecular theory.
5. How are ideal gases and the kinetic-molecular theory related?
6. Determine whether or not the following gases would be ideal; that is, do they fit the points of kinetic-molecular theory?

a. As a gas is heated, its particles start to move more slowly.
b. When one gas particle bumps into another, no energy is lost.
c. The gas particles follow predictable, circular paths within a container.

Further Reading / Supplemental Links

- Brenner, H. C. (1992). The kinetic molecular theory and the weighing of gas samples. Journal of Chemical Education, 69(7), 558-null. doi: 10.1021/ed069p558
- Hildebrand, J. H. (1963). An introduction to molecular kinetic theory - Selected topics in modern chemistry The University of California, Berkeley. New York: Reinhold Pub. Corp.
- Timm, J. A. (1935). The kinetic-molecular theory and its relation to heat phenomena. Journal of Chemical Education, 12(1), 31-null. doi: 10.1021/ed012p31
- TedEd "The Invisible Properties of Gases": http://www.youtube.com/watch?v=EHxdVtygP1g

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Points to Consider

- One of the assumptions of the kinetic-molecular theory is that collisions between particles are elastic –that momentum is conserved. Can you think of collisions you have witnessed in your everyday life that are completely elastic? Are collisions that you typically see elastic or not? Give examples.

13.2 Liquids and Solids

Lesson Objectives

- Compare and contrast the properties of liquids and solids both at the macroscopic level and at the molecular level.
- Explain the concept of viscosity and give examples of substances that are more viscous and less viscous than water.
- Define surface tension and vapor pressure.
- List the four types of solid crystals based on how the particles are bonded together, and give examples of each.

Lesson Vocabulary

- **viscosity**: Measures a fluid's resistance to flow.
- **surface tension**: The amount of energy required to increase the surface area of a liquid.
- **adhesion**: A liquid that displays more attraction between the liquid and the glass than attraction between the liquid particles.
- **cohesion**: A liquid that that displays more attraction between the liquid particles than attraction between the liquid and the glass
- **vapor pressure**: A measure of the pressure exerted by a gas above a liquid in a sealed container.
- **crystalline solids**: Solid substances in which the arrangement of particles is highly ordered.

Check Your Understanding

- Would particles in the solid, liquid, or gas phase have the greatest average kinetic energy?

Introduction

You encounter solids and liquids in many forms in your everyday life. Solids, unlike liquids, hold a definite shape. Both solids and liquids hold a definite volume. However, on a molecular level, these two states of matter are quite different. In this lesson we will introduce some of the properties of liquids and solids that affect your interactions with the substances all around you.

Liquids

Liquids have a definite volume, but no definite shape. A gallon of milk will keep the same volume whether it is stored in a one-gallon milk jug or a ten-gallon barrel. The volume is the same, but the fluid will either fill the jug or

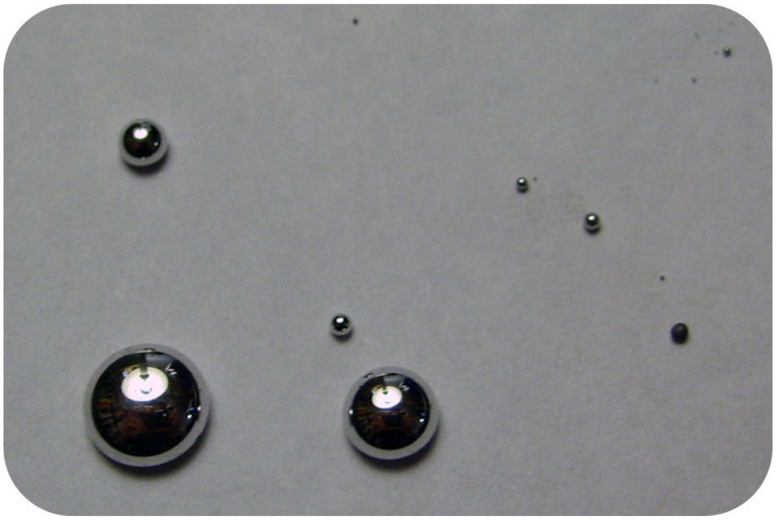


FIGURE 13.3

In this image, you see small pools of elemental mercury. The Latin name for mercury is hydrargyros, a compound word meaning "water-silver" (hydr- = water, -argyros = silver), since it is liquid like water but shiny like silver. Mercury is the only pure metal that exists as a liquid at room temperature.

spread out over the bottom of the barrel.

Intermolecular Forces in Liquids

Molecules in the liquid state are held in close proximity to one another by intermolecular forces. Any molecule containing an –OH group (such as water and the various alcohols) will form hydrogen bonds with adjacent molecules, causing a group of molecules to take on the liquid state. A polar molecule like CH_2Cl_2 cannot form hydrogen bonds, but molecules are held together in the liquid state by dipole-dipole interactions. Br_2 is not polar, but interactions with other Br_2 molecules through dispersion forces cause Br_2 to be a liquid at room temperature as well. Intermolecular forces are also responsible for various properties of liquids, such as viscosity, surface tension, and vapor pressure.

Viscosity

Viscosity measures a fluid's resistance to flow –the higher the viscosity, the slower the flow of the material. One factor that affects viscosity is the strength of the intermolecular forces in the material. Molecules that exhibit higher intermolecular forces tend to have higher viscosities. Temperature also influences viscosity. A higher temperature results in a decrease in viscosity, since molecules are moving faster and the intermolecular forces are more easily disrupted. Most cooking oils are more viscous than water, but when heated, the viscosity decreases and the oil spreads more easily. Motor oils are ranked by viscosity. Lower viscosity oils provide less drag on the engine, but they are also used up faster than a higher-viscosity material.

Surface Tension

Surface tension is a physical property of liquids that is caused by the attraction of liquid molecules due to various intermolecular forces. This property is allows the surface of a liquid to resist an external force, and is a measure of the amount of energy required to increase the surface area of a liquid. Surface tension is basically a measure of the "pull" of surface molecules on one another.

Intermolecular forces on a molecule in the interior of a liquid are exerted in all directions. The forces on a surface molecule are more directional, causing the molecule to be pulled toward other surface molecules and down toward the interior of the liquid. This property has consequences both for the behavior of the liquid in contact with solids and the influence of temperature on the liquid.

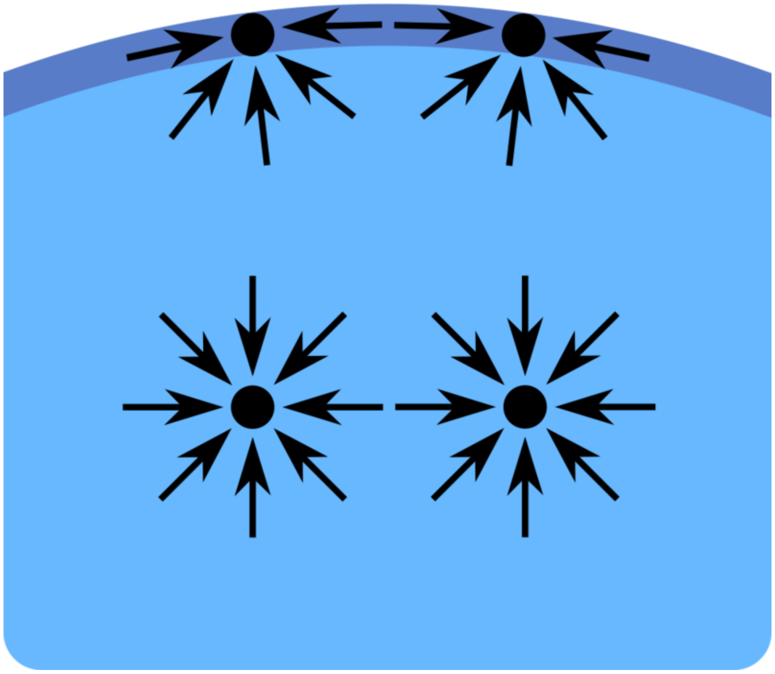


FIGURE 13.4

A liquid that can interact with glass displays the property of **adhesion**. The attraction of the glass to the molecules is stronger than the attraction of the liquid molecules to each other. The liquid molecules are pulled up due to their stronger attraction to the glass. Water is one liquid that displays this property.

Some liquids, such as mercury, display more attraction between the liquid particles than attraction between the liquid and the glass. This is known as **cohesion**. The pull between the liquid particles is stronger, so the liquid pulls away from the glass.

Vapor Pressure

Vapor pressure is a measure of the pressure exerted by a gas above a liquid in a sealed container. While viscosity and surface tension increase as the strength of intermolecular forces increase, vapor pressure *decreases*. This is because the stronger the intermolecular forces are, the harder it is for liquid molecules to escape into the gas phase. Vapor pressure a measure of how much of a substance is in the gas phase when that substance is at equilibrium; that is, the number of molecules in the gas and liquid phases are not changing. The more molecules that are able to escape into the gas phase, the higher the vapor pressure. Vapor pressure is also proportional to temperature. As temperature increases, vapor pressure also increases.

Solids

Solids are materials that have both a defined shape and a defined volume. They do not take on the shape of their container, as liquids and gases do. Solids can be either amorphous or crystalline. Amorphous solids (such as glass) do not have a well organized three-dimensional arrangement of molecules or atoms, so they lack a high level of

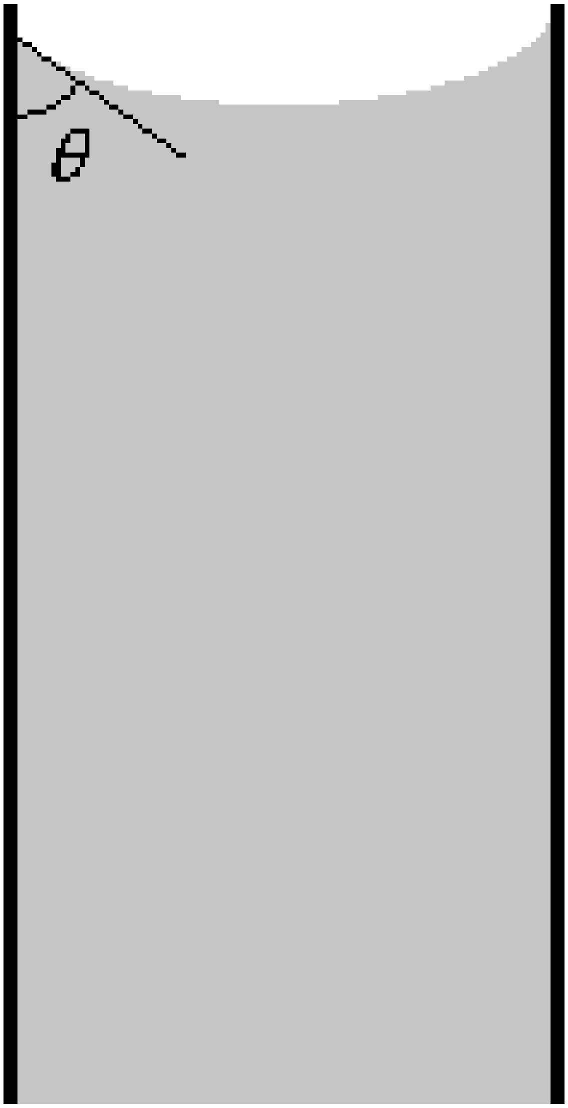


FIGURE 13.5

order. On the other hand, **crystalline solids** display a highly ordered and predictable three-dimensional structure. In this section we will discuss the different types of crystalline solids.

Types of Solids

Solids can be categorized by the forces holding the individual atoms, ions, or molecules together. The **Table** 13.1 summarizes the properties of different solids:

TABLE 13.1: Crystal Types in Solids

Type	Connecting Forces	Properties	Examples
ionic	ionic bonds	brittle, high melting points, poor conductors	NaCl, LiBr
molecular	intermolecular forces	soft, low melting points, poor conductors	water, glucose

TABLE 13.1: (continued)

Type	Connecting Forces	Properties	Examples
covalent	covalent bonds	hard, high melting points, poor conductors	diamond, quartz
metallic	metallic bonds	variable hardness and melting points, good conductors	Cu, Fe, other metals

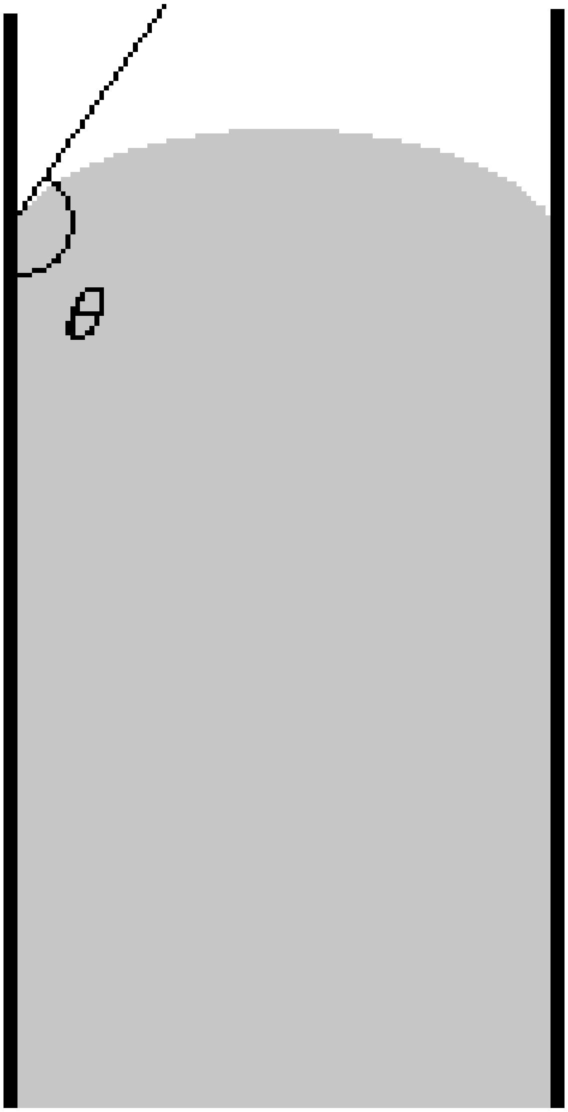


FIGURE 13.6

Ionic crystals have very strong interactions between individual particles, due to the electrostatic attraction between oppositely charged ions. This is reflected in the very high melting points of most ionic solids. The shape of the solid depends upon the relative sizes of the ions and the ratio of cations to anions. Although ionic substances are poor conductors in the solid state, the ions become mobile upon melting, and the resulting liquid is a very good conductor of electricity.

Molecular solids are held together by weak dispersion forces or other polar interactions. Because these are based on attractions between partial charges, they are not as strong as ionic forces. Due to the weaker forces involved, this class of solids will melt at much lower temperatures than ionic crystals.

Covalent solids are composed of atoms connected by covalent bonds in a three-dimensional network. This extensive series of strong connections produces a very stable structure that is not affected much by changes in temperature. The hardness and stability of diamond is a reflection of the many strong carbon-carbon bonds that form its covalent network.

Metallic solids are composed entirely of metallic atoms. In other solid structures, the electrons involved in bonding tend to be localized, or fixed in place in the covalent bonds. However, the electrons in metallic bonds are delocalized over the entire crystal. The fact that the electrons are free to move between different atoms causes metallic solids to be very good conductors of electricity.

Crystalline solids can also be characterized by their shape. The diagram below illustrates some of the common crystal forms. The crystal shapes are determined by the type and arrangement of the individual atoms, ions, or molecules from which they are constructed.

TABLE 13.2: Seven Basic Crystal Systems

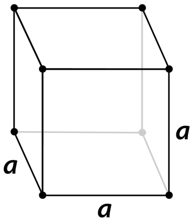
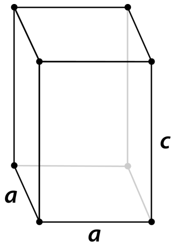
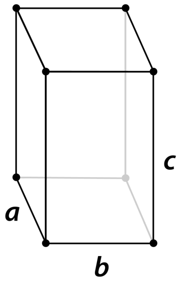
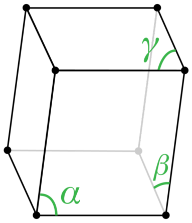
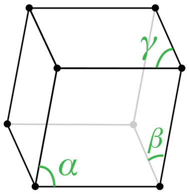
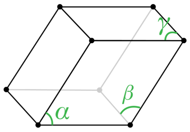
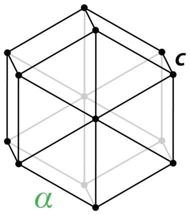
Crystal System	Diagram
Cubic $a = b = c; \alpha = \beta = \gamma = 90°$	
Tetragonal $a = b \neq c; \alpha = \beta = \gamma = 90°$	
Orthorhombic $a \neq b \neq c; \alpha = \beta = \gamma = 90°$	
Monoclinic $a \neq b \neq c; \alpha \neq 90° = \beta = \gamma$	

TABLE 13.2: (continued)

Crystal System	Diagram
Rhombohedral $a = b = c; \alpha = \beta = \gamma \neq 90°$	
Triclinic $a \neq b \neq c; \alpha \neq \beta \neq \gamma \neq 90°$	
Hexagonal $a = b \neq c; \alpha = \beta = 90°, \gamma = 120°$	

Lesson Summary

- At the molecular level, the major difference between solids and liquids is based on how freely the particles can move within the substance.
- Viscosity measures a liquid's resistance to flow.
- Surface tension results from the directional pull on surface molecules towards the interior of a liquid.
- Adhesion and cohesion are demonstrated by liquids as they interact with the surface of a container.
- Vapor pressure is the pressure resulting from the gas molecules above a liquid in a closed container at equilibrium.
- Ionic, molecular, covalent, and metallic solids are characterized by the types of bonds holding the substance's particles together in the solid form.

Review Questions

1. Define viscosity. Give an example of how temperature influences viscosity.
2. Define surface tension. Would you expect water to have a stronger or weaker surface tension than olive oil?
3. Draw a picture of a liquid displaying adhesion and a liquid displaying cohesion in a glass jar.
4. What does vapor pressure measures? Does vapor pressure increase or decrease as intermolecular forces when intermolecular forces grow stronger?

5. What distinguishes crystalline and amorphous solids?
6. List and define the four different types of crystalline solids.
7. Order the four types of crystalline solids from lowest to highest melting point.
8. Research to find one example for each type of crystalline solid, different from those provided in the text.

Further Reading / Supplemental Links

- Surface tension –"sticky water": http://www.exploratorium.edu/ronh/bubbles/sticky_water.html
- Types of solids: http://chemistry.about.com/od/matter/a/Types-Of-Solids.htm
- Identifying states of matter: http://www.edinformatics.com/math_science/states_of_matter.htm
- Adhesion and cohesion, in space!: http://www.youtube.com/watch?v=oAY3yISf-24

Points to Consider

- In this lesson, we studied the differences between liquids and solids at the molecular level. As we will see, these differences can be accounted for by looking at the amount of energy within a given system.
- How do you suppose pressure might affect particles at the molecular level in terms of the phase that a given substance exhibits?

13.3 Changes of State

Lesson Objectives

- Describe how the phase of a material is affected by changes in the temperature.
- Describe how the phase of a material is affected by changes in pressure.
- Draw phase diagrams to relate the pressure, temperature, and the phase of a substance.
- Describe the energy changes associated with changes of state.

Lesson Vocabulary

- **heating curve**: A curve where supplying heat to a solid substance will gradually raise its temperature, and eventually, it will melt.
- **melting point**: The temperature of a point where heat is used to break up the attractive forces holding them rigidly in place.
- **boiling point**: The temperature of a point where particles start to enter the gas phase.
- **phase diagram**: A plot of temperature vs. pressure that indicates the states of matter present at each point.
- **triple point**: A point where all three states can exist simultaneously.

Check Your Understanding

1. Compare and contrast the properties of liquids, solids, and gases.
2. Which of the following statements about solids and liquids are true? (There may be more than one.)
   a. Solids and liquids are virtually incompressible; their volume is constant.
   b. Solids are typically more dense than liquids.
   c. All liquids have the same density.

Introduction

In the last lesson, we studied the characteristics of liquids and solids at a macroscopic level and at the molecular level. Increasing the temperature of a solid transforms the particles from a rigid arrangement to a fluid (a liquid or gas). Conversely, decreasing the temperature of a liquid or gas slows the particles down, going back from free movement to a fixed arrangement. In this section, we will further explore how temperature and pressure affect the characteristics and behavior of matter. Pressure has a larger effect on gases, which are very compressible, than liquids and solids. However, changes in pressure are still relevant to solids and liquids. For example, **Figure** 13.7 shows ice skates on ice. Because your entire weight is all concentrated on a thin blade, ice skates exert quite a bit of pressure on the ice below them. An interesting property of water is that increasing the pressure on its solid form

FIGURE 13.7

(ice) will eventually convert it to liquid water. The pressure exerted by ice skates makes small amounts of liquid water on the surface, allowing the skates to glide smoothly.

Heating Curves

Supplying heat to a solid substance will gradually raise its temperature, and eventually, it will melt. Heating the resulting liquid will cause a further increase in temperature until the liquid begins to boil. If we were to graph the temperature of a substance against the amount of heat added, it would look something like the **Figure** 13.8.

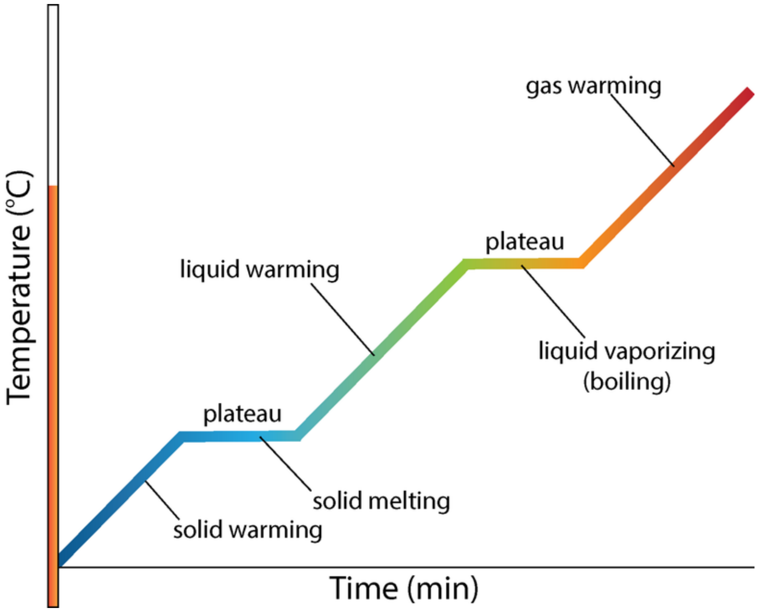


FIGURE 13.8
Heating curve depicting phase changes between the solid, liquid, and gas forms of a given substance.

The above graph is referred to as a **heating curve**. The most notable feature is that the temperature rise is not steady;

there are plateaus during which heat is being added, but the temperature is not increasing. What is happening here? Let's start with the first slope on the left. At this point, the substance is in its solid form. Adding heat causes the particles to move faster. Faster particles means more kinetic energy, which also means a higher temperature. At the first plateau, the vibrations of the particles become energetic enough to break free of the rigid solid form, and the substance converts to a liquid. Heat continues to be added, but instead of increasing the kinetic energy of the particles, it is used to break up the attractive forces holding them rigidly in place. This process is known as melting, and the temperature at which it occurs is the **melting point**. Because the added heat is used to break up attractive forces instead of adding to the kinetic energy of the particles, the temperature of the material stays constant until the phase change is completed.

Further heating then adds energy to the liquid particles, increasing their speed, kinetic energy, and temperature. This is the second slope on the curve. Once the particles are energetic enough to completely break free of each other, they start to enter the gas phase. Boiling occurs at the second plateau of this curve, and the temperature at this point is referred to as the **boiling point**. Again, the added heat is being used to break up the interactions between particles instead of increasing their kinetic energy, so no temperature increase is observed until all particles are in the gas phase. Finally, adding even more energy will further speed up the gas particles, increasing the kinetic energy and temperature of the substance.

The reverse process can also be diagrammed, where we start with a gas and gradually remove heat until it condenses to a liquid and then freezes into a solid. For a given amount of a certain substance at a given pressure, heating and cooling curves should be mirror images. The melting point will be equal to the freezing point, and the boiling point will be equal to the condensation point. Additionally, the amount of heat added to completely melt the sample is the same as the amount that must be removed to completely freeze it.

Two other changes of state can occur under at appropriate pressures. The direct conversion of a solid to a gas without becoming a liquid is called sublimation. The reverse process (gas to solid) is known as deposition. Depositions of hot metal vapors are often used in the electronics industry to produce thin films of metal on solid bases. Most substances require reduced pressures (less than one atmosphere) for these processes to occur. At higher pressures, substances would transition through the liquid phase. However, some materials, such as carbon dioxide, will sublime even at standard pressure. Iodine and naphthalene (found in mothballs) are other substances that can sublime at only slightly reduced pressures.

The **Figure** 13.9 summarizes the different processes involved in phase changes.

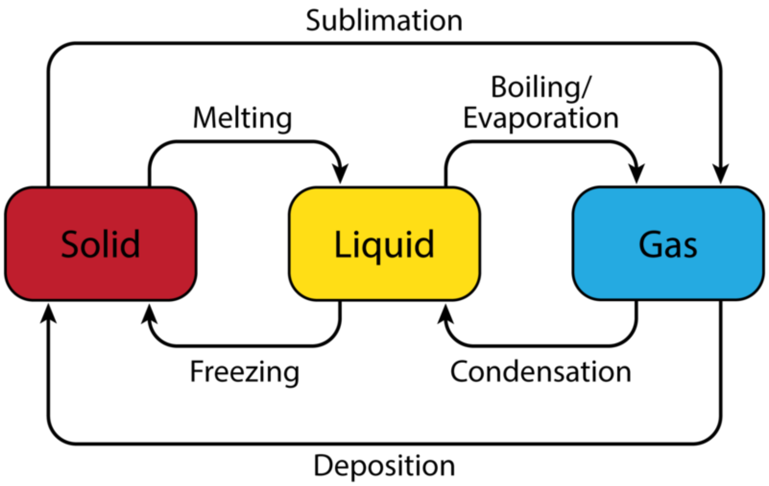


FIGURE 13.9

Summary of phase changes.

Phase Diagrams

Both temperature and pressure have an effect on the phase in which a given substance exists. A plot of temperature vs. pressure that indicates the states of matter present at each point is known as a **phase diagram**. **Figure** 13.10 shows the phase diagram for water.

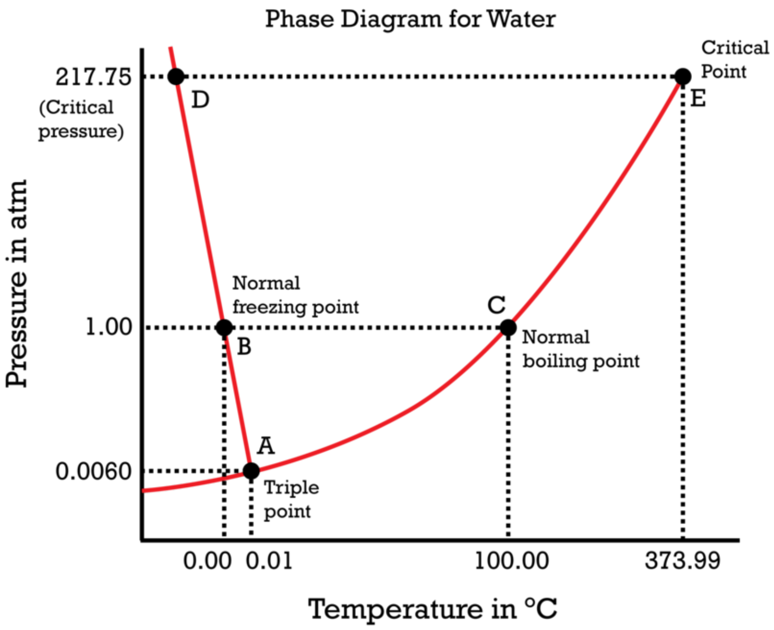


FIGURE 13.10

The lines on this diagram show the boundaries between the three states of matter for water. Notice that there is one point where all three states can exist simultaneously; this is called the **triple point**. Also look at the slope of the solid-liquid boundary. For most substances, this line has a positive slope, which means that increasing the pressure of a liquid will eventually form a solid. Water is unusual in that it has a negative slope for this boundary. This has to do with the fact that the liquid form of water is more dense than the solid form (ice). As a result, putting large amounts of pressure on ice at a given temperature will cause it to melt. We already discussed this phenomenon at the beginning of the lesson in the context of ice skating. The phase diagram gives us a more detailed way to look at this occurrence.

Example 13.1

A pressure cooker operates by keeping water in its liquid form at temperatures above its normal boiling point. Can you use the phase diagram to explain this behavior?

Answer:

The pressure cooker maintains a pressure that is above one atmosphere. At this higher pressure, the boundary between the liquid and gaseous forms of water occurs at a higher temperature.

If we look at the phase diagram for carbon dioxide, we can see that its triple point occurs at approximately 5 atm and -56°C. Below this pressure, liquid CO_2 cannot exist. At one atmosphere of pressure, only the solid and gas forms are possible, which explains why solid CO_2 sublimes instead of melting at standard pressures. Also note that the solid-liquid boundary has a positive slope, which is normal for most substances.

Example 13.2

Why is solid CO_2 is called dry ice? Use the phase diagram to explain.

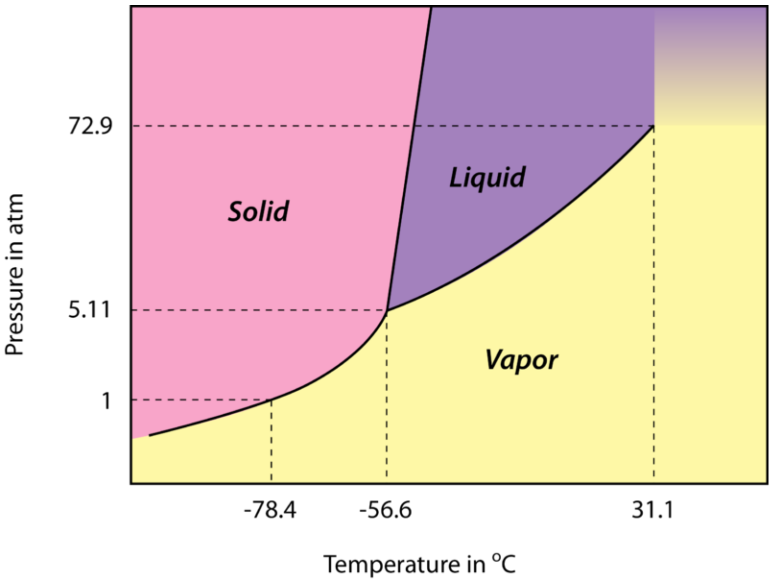


FIGURE 13.11

Answer:

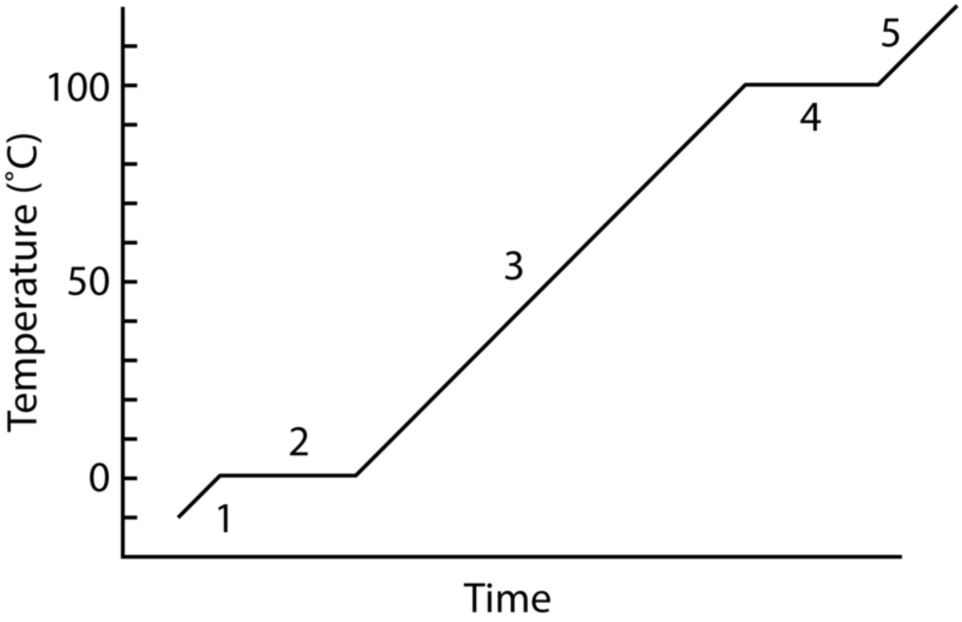
Solid CO_2 exists at temperatures below -78°C at the standard pressure of 1 atm. When solid CO_2 is allowed to warm to room temperature at this pressure, the solid changes to a gas without going through the liquid form. Because it does not become a liquid, it is considered "dry."

Lesson Summary

- Phase transitions occur as heat is added or removed from a substance.
- The solid to liquid transition is called melting.
- The liquid to gas transition is called boiling.
- Sublimation and deposition involve direct transitions between solid and gas without going through the liquid state.
- A phase diagram gives information about the conditions under which a material can exist as a solid, a liquid, or a gas.

Review Questions

1. The following heating curve of an unknown substance shows several phase changes that take place as heat is added. Label each section indicated by a number.



2. What would happen if you tried to make an ice rink using dry ice? Would you be able to skate? Compare the phase diagrams of water and dry ice to justify your answer.
3. What would you see if you were to observe water at its triple point?
4. Referring to the phase diagram of water, what phases can exist at a temperature of 0°C and a pressure of 0.006 atm?
5. Referring to the phase diagram for CO_2, at what temperature must liquid CO_2 exist if the pressure is 100 atm?
6. What temperature must carbon dioxide be in order to remain solid at 7 atmospheres of pressure? Would it melt or sublime at this pressure?

Further Reading / Supplemental Links

- Observe the triple point of an organic compound, tert-Butyl alcohol: http://www.youtube.com/watch?v=BLRqpJN9zeA
- Materials and their properties: http://www.abpischools.org.uk/resources/solids-liquids-gases/index.asp
- Review on matter and change of state: http://www.chem4kids.com/files/matter_intro.html

Points to Consider

- Can you think of some substances commonly encountered in their gaseous state?
- How might you check for the presence of a gas?

Opening image: Mike Cline. http://commons.wikimedia.org/wiki/File:FireholeRiverOjoCalientiBend.jpg . Public Domain.

13.4 References

1. User:Workingclass91/Wikimedia Commons. http://commons.wikimedia.org/wiki/File:Liquid_chlorine_in_flask.jpg . CC BY 3.0
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CHAPTER 14 The Properties of Gases

Chapter Outline

14.1 GAS PROPERTIES
14.2 GAS LAWS
14.3 GAS MIXTURES
14.4 REFERENCES

When the weather is right, you might see a brightly colored balloon floating far above you. The technology that goes into a hot air balloon is one that we may not pay much attention to these days. It works by trapping hot gases in a container that remains upright over time. It is the oldest human-carrying flight technology and is still used today for many important applications, such as weather monitoring. In this chapter, we are going to study the properties of gases and the effects that altering one of these properties has on various others.

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14.1 Gas Properties

Lesson Objectives

- List some substances that are gases at 25°C and some characteristics that they have in common.
- Define and give examples of diatomic gases.
- Describe how pressure is measured, and be able to carry out conversions between different units of pressure.

Lesson Vocabulary

- **diatomic gas**: Any two-atom molecules that exist in the gas phase around room temperature.
- **pressure**: A measure of the total amount of force divided by the surface area over which it is exerted.
- **barometer**: An instrument used to measure pressure.
- **atmospheric pressure**: The pressure exerted by the weight of the atmosphere at a given altitude.
- **millimeters of mercury (mm Hg)**: A common unit of pressure originating from the mercury barometer.
- **torr**: A unit of pressure equal to mm Hg named after Italian physicist Evangelista Torricelli.

Check Your Understanding

1. What evidence might there be to demonstrate the presence of gases in our atmosphere?
2. Can you think of examples from your life suggesting that there are gases we depend on for survival?

Introduction

Figure 14.1 shows a nitrogen gas discharge lamp, where nitrogen gas is energized to produce light that appears lavender in color. Nitrogen gas is the most abundant gas on Earth. However, despite the fact that approximately 78% of the air we breathe is nitrogen, we may hardly notice it as we navigate our daily lives. Although nitrogen-containing compounds have been known since ancient times, pure elemental nitrogen in its gaseous form was not discovered until 1772, by Daniel Rutherford. This discovery, along with Joseph Priestley's discovery of oxygen in 1774, greatly influenced our modern understanding of gases and matter in general.

Nitrogen has a melting point of -210°C and a boiling point of -196°C. It is colorless, odorless, tasteless, and fairly unreactive at normal temperatures and pressures. It exists as N_2 molecules, in which two nitrogen atoms are held together by a strong triple covalent bond. Its lack of reactivity is derived from the large amount of energy that would be required to break this bond. Nitrogen is an example of a **diatomic gas**, which refers to any two-atom molecules that exist in the gas phase around room temperature.

In this lesson, we are going to study some properties exhibited by gases, with a special focus on the pressure they exert and how pressure is measured.

FIGURE 14.1

Nitrogen gas lamp.

Physical Characteristics of Gases

All matter, under the right conditions, can exist in a gaseous state. Some substances, such as carbon dioxide, oxygen, and nitrogen, exist as gases at room temperature under standard atmospheric pressure. Gases have the following characteristics:

1. **Gases assume the volume and shape of their container.** When placed in a container of any size and shape, the gas molecules will quickly distribute themselves evenly throughout the container.
2. **Gases are compressible.** The volume and pressure of a particular sample of gas can fluctuate greatly simply by changing the size of its container.
3. **Gases mix homogeneously when confined to same container.** When several gases are added to a container, the individual gas particles mix freely, forming a homogeneous mixture in which each type of gas is randomly distributed throughout all the available volume.
4. **Gases have much lower densities than liquids and solids.** For example, liquid water is over 1000 times more dense than water vapor at STP.

The following simulation demonstrates the properties of gases listed above: http://phet.colorado.edu/en/simulation/states-of-matter .

Pressure

According to the kinetic-molecular theory, momentum is conserved in collisions between particles at the molecular level. The same can be assumed to be true for collisions between gaseous particles and the wall of their container

In the chapter opener, we saw a hot air balloon traveling through the air. The walls of the balloon are pushed outward by the hot air inside. On the molecular level, this outward force is due to countless tiny collisions between gas molecules and the walls of the balloon. **Pressure** is a measure of the total amount of force divided by the surface area over which it is exerted. If the total force of the collisions inside the balloon is greater than the force of collisions exerted by the atmosphere on the outer surface of the balloon, it will expand. Equivalently, if the pressure inside the balloon is higher than the pressure outside, the balloon will expand.

Pressure can be measured with an instrument called a **barometer** (**Figure** 14.2).

The word barometer comes from the Greek roots *baro*, meaning *pressure*, and *–meter*, meaning to *measure*. Evangelista Torricelli (1608-1647) is credited with inventing the barometer in 1644. The invention consisted of a mercury-filled container attached to a glass tube into which mercury flowed. As shown in **Figure** 14.2, atmospheric gases exert a downward force on the fluid reservoir, and the fluid rises in the tube. The height of the fluid is one way to measure **atmospheric pressure**. If the tube is connected to an enclosed sample of gas instead of open to the atmosphere, the fluid will change height to a different level that is proportional to the pressure of the sample. Because this was one of the first standardized ways to measure pressure, **millimeters of mercury (mm Hg)** is actually a common unit of pressure. This unit is also sometimes referred to as a **torr**, short for Torricelli. Standard atmospheric pressure (1 atm) is defined as 760 mm Hg, which is approximately equal to the average atmospheric pressure at sea level. The SI unit for pressure is the Pascal, where (1 Pascal = 1 newton/m^2). Because this is such a small unit, kilopascals (kPa) are also commonly used. The relationships between various units of pressure are shown below:

1 atm = 1.01325 bar = 101.325 kPa = 760 mm Hg = 760 torr = 29.92 in Hg = 14.696 psi

Example 14.1

The pressure in a bicycle tire is measured to be 46 psi at room temperature. What is this pressure in atm?

$46 \text{ psi} \times \frac{1 \text{ atm}}{14.7 \text{ psi}} = 3.1 \text{ atm}$

Atmospheric Pressure

Atmospheric pressure can be thought of as the force exerted by a hypothetical column of gas that stretches from sea level to the outer reaches of the atmosphere. If we divide the total weight of the air in the column (the force) by the area that it is pressing down on, we get a pressure of about 1 atm. **Figure** 14.3 illustrates this type of calculation.

If we go up in altitude, there is less air in between the ground and the edge of the atmosphere. The smaller amount of force means that atmospheric pressure is lower at higher altitudes (see **Figure** 14.4).

As shown here, pressure decreases to less than 25% of ground-level atmospheric pressure when we get to an altitude of about six miles. Since this is a common cruising altitude for commercial airplanes, pressurized cabins are needed for the comfort and survival of the passengers. This is because the density of the air decreases along with the decreasing air pressure, so there is less oxygen in a breath of air. You've probably noticed this effect in high-mountain areas, as it often feels harder to breath.

Example 14.2

If you were to ascend from sea level to the top of a 10,000-foot high mountain (about 2 miles), what would the atmospheric pressure be? What percent of standard atmospheric pressure is this value?

Answer:

Looking at the altitude-pressure curve above, we can see that the pressure would be approximately 500 mb. Since the pressure at sea level is 1000 mb, the new atmospheric pressure would be 500/1000 × *100% = 50% of the standard atmospheric pressure.*

FIGURE 14.2

Diagram of a mercury barometer.

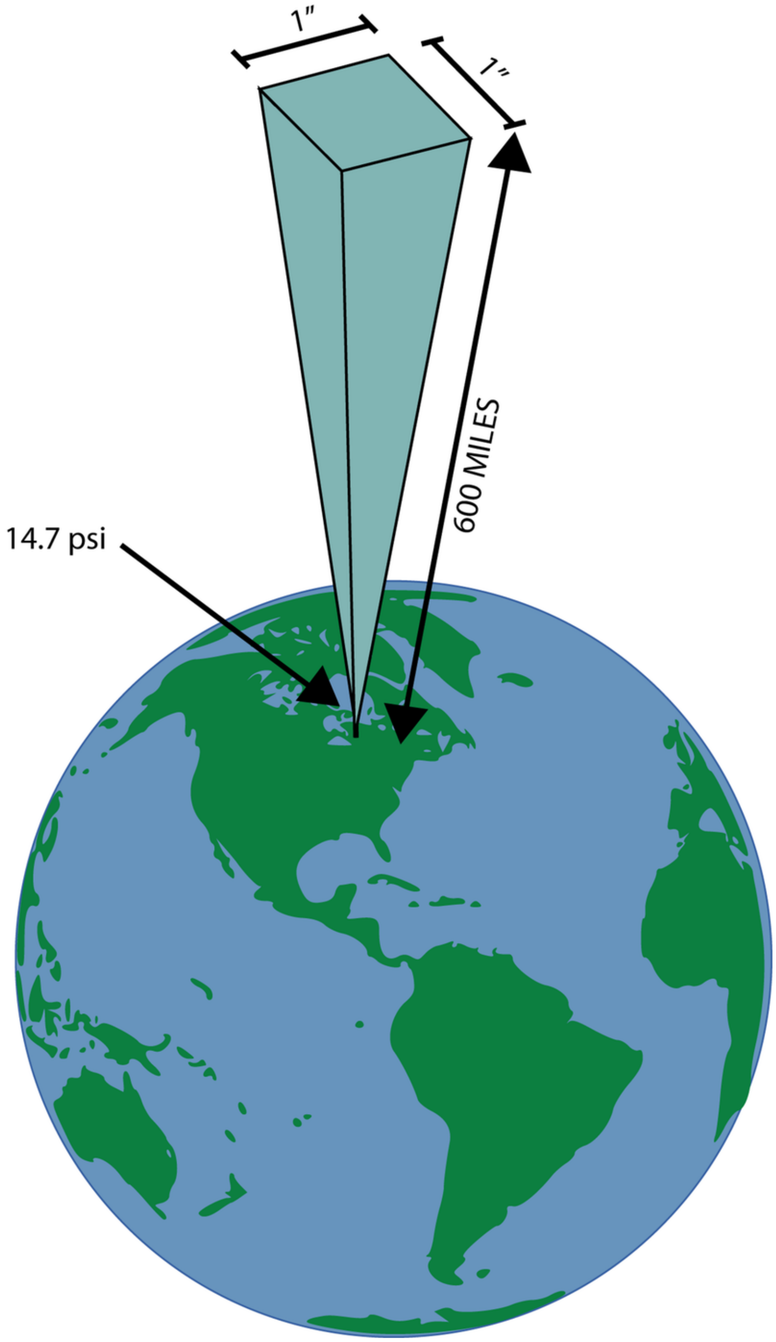

FIGURE 14.3

Illustration of atmospheric pressure

Lesson Summary

- Gases assume the shape of their container.
- Gases are compressible.
- Gas particles demonstrate elastic collisions between themselves and with container walls.
- Pressure is equal to force/area.
- Atmospheric pressure can be measured with a barometer.
- Atmospheric pressure at sea level is 14.7 psi (1 atm) at 25°C.

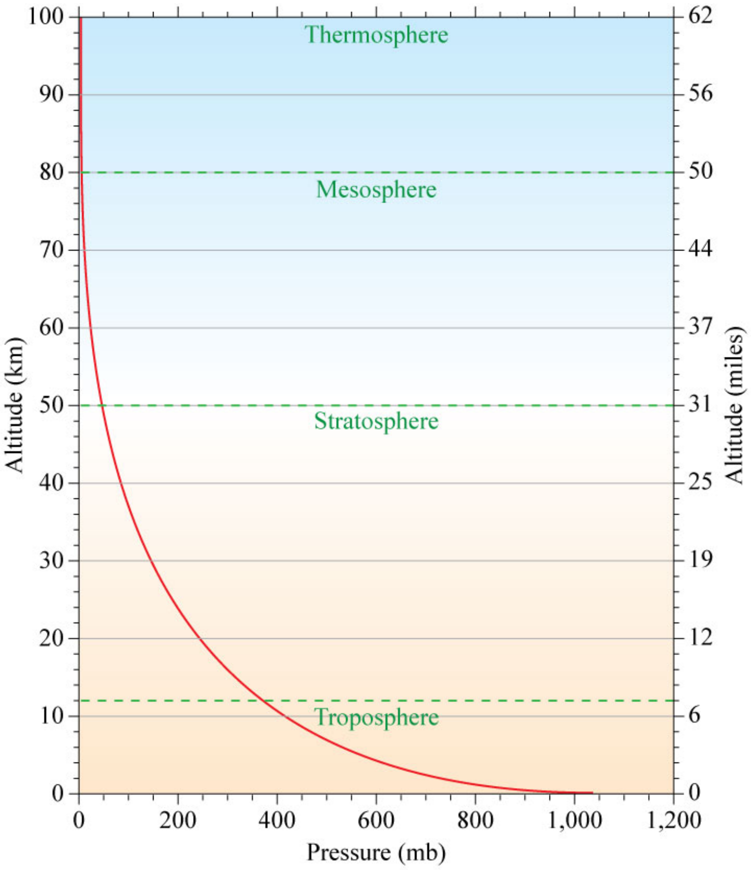

FIGURE 14.4

This is a pressure vs. altitude curve that displays altitude in kilometers on the left axis and miles on the right. Pressure is reported in millibars (mb) on the bottom or inches of mercury (in Hg) on the top.

- Atmospheric pressure decreases as the altitude increases.

Review Questions

1. Why do you suppose the pressure of atmospheric gases increases with proximity to earth? Why aren't the gases evenly distributed throughout the entire reaches of the atmosphere? Study the PhET simulation for further illustration here: http://phet.colorado.edu/en/simulation/states-of-matter .
2. Draw a diagram showing how particles exert pressure on the wall of a container.
3. If you were to double the pressure of the bicycle tire from 46 psi to 92 psi, what would be the new pressure in atm?
4. The average atmospheric pressure in Denver is 0.830 atm. Express this pressure in mm Hg.
5. Convert a pressure of 570. torr to atmospheres.
6. Convert 8.5 psi to torr.

Further Reading/Supplemental Links

- Weeks, M. E. (1934). Daniel Rutherford and the discovery of nitrogen. Journal of Chemical Education, 11(2), 101. doi: 10.1021/ed011p101

- Properties of gases: http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch4/properties2.html
- Review of air pressure: http://kids.earth.nasa.gov/archive/air_pressure/

Points to Consider

- In this lesson we studied gas pressure and how it is measured. How do you think pressure is affected by changes in temperature, amount of gas, and volume?

14.2 Gas Laws

Lesson Objectives

- Describe various observed relationships between the pressure, volume, temperature, and amount of a gas, including Boyle's law, Charles's law, Gay-Lussac's law, and Avogadro's law. Be able to perform calculations using these relationships.
- Be able to derive a combined gas law, and utilize this expression to calculate volume, temperature, and pressure changes in gas systems.
- Describe the ideal gas equation PV=nRT and perform calculations using this relationship.

Lesson Vocabulary

- **Boyle's Law**: States that for a fixed amount of gas at a constant temperature, the volume occupied is inversely proportional to its pressure.
- **absolute zero**: The lower limit for possible temperatures, a value of 0 Kelvin or -273°C.
- **Charles's Law**: States that for a fixed amount of gas at a constant pressure, the volume is directly proportional to its absolute temperature.
- **Gay-Lussac's Law**: States that pressure is directly proportional to the absolute temperature.
- **Avogadro's Law**: Stats that if you compare two samples of an ideal gas at the same temperature, pressure, and volume, they contain the same number of molecules.
- **ideal gas law**: The equation of state that describes the relationship between temperature, pressure, volume, and amount of an ideal gas. Derived from a combination of Boyle's, Charles's, Gay-Lussac's and Avogadro's gas laws.

Check Your Understanding

- One of the earliest air pumps was made by Robert Boyle. **Figure** 14.5 is a diagram of his early pump.

What do you suppose the relationship is between pressure and volume as shown here?

Introduction

In the last lesson, we studied the properties and characteristics of gases. Many of these properties can be explained by the fact that gases are mostly empty space but contain large numbers of particles with certain masses and velocities. Now we are going to study how gases behave when exposed to changes in temperature, pressure, and volume. We will also see how the development of instruments that measure pressure and temperature led to new discoveries in our understanding of gases. The origins of the absolute temperature scale will be discussed, and we will examine the empirical relationships between volume, temperature, pressure, and amount that were discovered by early chemists.

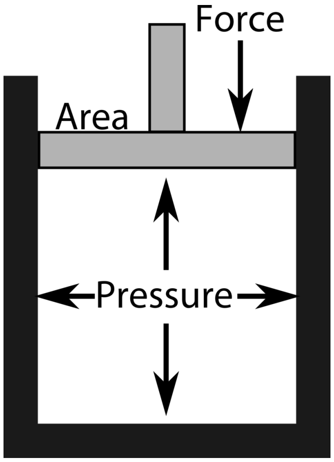

FIGURE 14.5

Air pump made by Robert Boyle.

FIGURE 14.6

Soap bubble in flight.

Boyle's Law: Pressure vs. Volume

With the development of the barometer in 1644 came a series of experiments and investigations aimed at understanding the nature of gases. Robert Boyle (1627-1691) was particularly interested in the relationships between the volume occupied by a sample of gas and the pressure it exerted on its container. He invented one of the earliest air pumps, which allowed him to create low-pressure environments. Boyle devised experiments to study the pressure-volume relationship. For example, he observed that reducing the volume of a balloon by half doubles its volume. In other words, volume is inversely proportional to pressure ($V \propto 1/P$).

For a fixed amount of gas at a constant temperature, the volume occupied is inversely proportional to its pressure. Stated mathematically, the product of the pressure and volume is equal to a constant:

$P \times V = k$

where k is a constant that depends on the temperature and amount of the gas in a given sample. This observation was published in 1662 and is now known as **Boyle's Law**.

This equation can be used to quantitatively predict how changes in pressure will affect the volume of a sample, and vice versa. Let's assume that a sample of gas undergoes a change to one of these variables while the temperature and amount are held constant. The initial pressure (P_1) and the initial volume (V_1) can be related to the final pressure (P_2) and the final volume (P_2) as follows:

$P_1 \times V_1 = k$

$P_2 \times V_2 = k$

Therefore,

$P_1 \times V_1 = P_2 \times V_2$

Example 14.3

A sample of oxygen gas has a volume of 150. mL when its pressure is 0.647 atm. What will the volume of the gas be at a pressure of 0.987 atm if the temperature remains constant?

Answer

$$\begin{aligned}
&P_1 \times V_1 = P_2 \times V_2\\
&V_1 = 150.\text{ mL}, V_2 = ?\\
&P_1 = 0.647\text{ atm}, P_2 = 0.987\text{ atm}\\
&V_2 = \frac{P_1 \times V_1}{P_2}\\
&V_2 = \frac{(0.647\ \text{ atm})(150.\ \text{ mL})}{0.987\ \text{ atm}}\\
&V_2 = 98.3\ \text{ mL}
\end{aligned}$$

Temperature

The thermometer was developed a short time after the barometer made it possible to study pressure in a quantitative manner. Although crude thermometers had been available for quite some time, Daniel Fahrenheit constructed a more accurate thermometer in 1724 using mercury in glass. Because the height of the mercury in the thermometer was a relative measure, certain fixed points needed to be defined. Originally, Fahrenheit defined a 1:1:1 mixture of ice, salt, and ammonium chloride as 0°F, and the freezing/melting point of ice as 32°F. On this scale, the normal temperature of the human body is 96°F, and the boiling point of water is 212°C. The modern Fahrenheit scale is defined in terms of the normal freezing and boiling points of water.

Anders Celsius (1736) devised a slightly different scale, which also had two fixed values based on the freezing and boiling points of water. Originally, he suggested a value of 0°C for the boiling point and 100°C for the freezing point. Shortly after his death, the scale was reversed, resulting in the form that is used today. The Celsius scale is the standard way to measure temperature in most parts of the world. **Figure** 14.7 compares these two different scales.

Absolute Zero

The ideas of absolute zero and absolute temperature were conceived in 1848 by Lord Kelvin. Kelvin had observed that for every 1°C drop in temperature, a sample of gas contracted by a uniform amount, specifically, 1/273th of its volume at 0°C. If this data is extrapolated, or projected, to the point where the gas would reach a volume of zero, we reach a lower limit for possible temperatures. Kelvin interpreted this to mean that -273°C is the lowest achievable temperature. In contrast to other scales, where the temperature can be below zero, the value of zero Kelvin represented an **absolute zero**. **Figure** 14.8 Below shows Kelvin's extrapolation. The Kelvin scale is used for all gas law calculations.

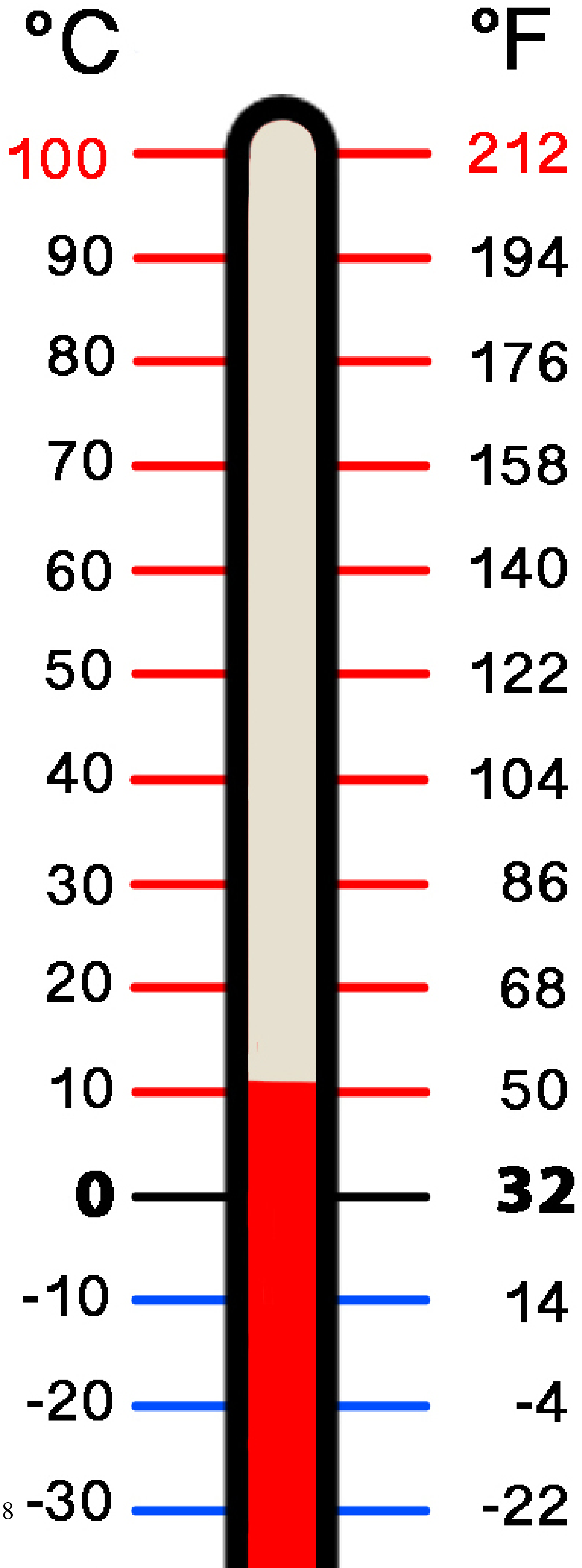
°C
°F
100
212
90
194
80
176
70
158
60
140
50
122
40
104
30
86
20
68
10
50
0
32
-10
14
-20
-4
-30
-22

FIGURE 14.7

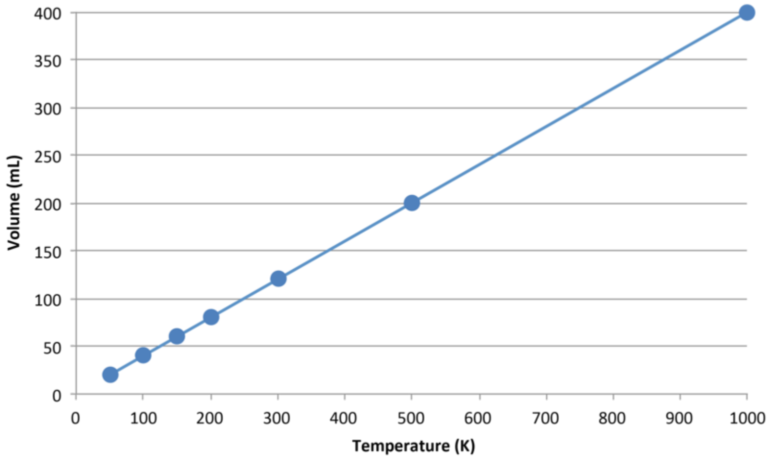

FIGURE 14.8

Temperature Relationships

Charles's Law

Various studies were done on the effects of temperature changes on both pressure and volume by two prominent French scientists, Jacques Charles (1746-1823) and Joseph Louis Gay-Lussac (1778-1850). In 1802, Charles and Gay-Lussac both proposed that for a fixed amount of gas at a constant pressure, the volume is directly proportional to its absolute temperature (V ∝ T). **Figure** 14.9 illustrates the volume-temperature relationship.

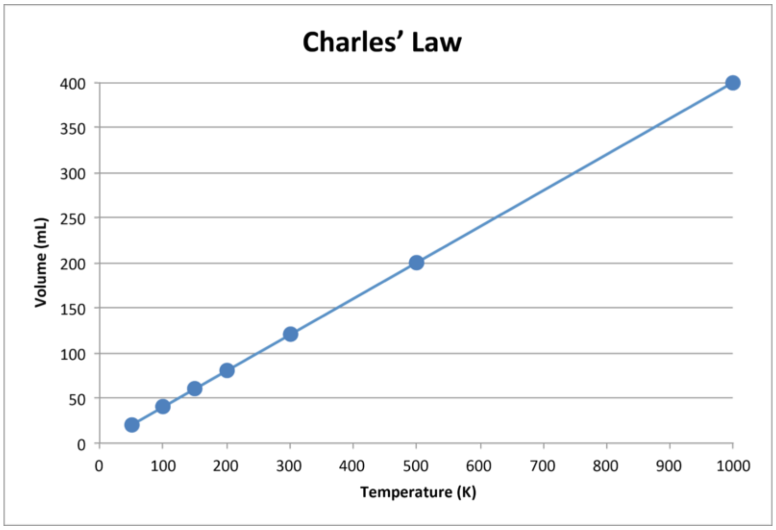

FIGURE 14.9

This relationship between volume and pressure is commonly known as **Charles's Law**. It can be expressed mathematically as follows:

$\frac{V}{T} = k$

where k is a constant that depends on the pressure and amount of the gas sample. As in the case of Boyle's Law, this can also be used to generate a way of comparing two different states for a given sample at constant pressure:

$\frac{V_1}{T_1} = \frac{V_2}{T_2}$

Example 14.4

A sample of neon gas occupies a volume of 752 mL at 25°C. What volume will the gas occupy at 50°C if the pressure remains constant? Before you begin, think about whether or not the volume should go up or down.

Answer:

Don't forget that all temperatures must be converted to absolute temperature (Kelvin).

$$\begin{aligned}
T_1 &= 25^\circ\text{C} + 273 = 298\text{ K} \\
T_2 &= 50^\circ\text{C} + 273 = 323\text{ K} \\
V_1 &= 752\text{ mL} \\
V_2 &= ? \\
\frac{V_1}{T_1} &= \frac{V_2}{T_2} \\
V_2 &= \frac{V_1 T_2}{T_1} \\
V_2 &= \frac{(752\text{ mL})(323\text{ K})}{298\text{ K}} \\
V_2 &= 815\text{ mL}
\end{aligned}$$

Gay-Lussac's Law

Gay-Lussac's Law describes the relationship between pressure and absolute temperature:

$\frac{P}{T} = k$

$\frac{P_1}{T_1} = \frac{P_2}{T_2}$

Gay-Lussac's law says that at a constant volume, the pressure of a gas is directly proportional to its absolute temperature. This relationship is also sometimes attributed to Guillaume Amontons (1663–1705). Although his work predated that of Gay-Lussac by over a century, the data on which he based his ideas were considerably less precise, due to the cruder instrumentation available at the time.

Example 14.5

The gas in an aerosol can exerts a pressure of 3.00 atm at 25°C. Directions on the can warn the user not to keep the can in a place where the temperature exceeds 52°C. What would the gas pressure in the can be at 52°C? Before you begin, do you think the pressure should go up, down or stay the same?

Answer:

Again, don't forget that all temperatures must be converted to absolute temperature (Kelvin).

$$\begin{aligned}
T_1 &= 25^\circ\text{C} + 273 = 298 \text{ K}\\
T_2 &= 52^\circ\text{C} + 273 = 325 \text{ K}\\
P_1 &= 3.00 \text{ atm}\\
P_2 &= ?\\
\frac{P_1}{T_1} &= \frac{P_2}{T_2}\\
P_2 &= \frac{P_1 T_2}{T_1}\\
P_2 &= \frac{(3.00 \text{ atm})(325 \text{ K})}{298 \text{ K}}\\
P_2 &= 3.27 \text{ atm}
\end{aligned}$$

Note that the pressure increases, which would be expected if the temperature were to go up.

Combined Gas Law

We can combine the relationships described in Boyle's law, Charles's law, and Gay-Lussac's law to create a combined gas law that relates pressure, volume, and temperature.

$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

We can use this expression to predict changes to these variables for a given chemical system.

Example 14.6

A helium-filled balloon has a volume of 50.0 L at 25°C and 1.08 atm. What volume will it have at 0.855 atm and 10.°°C?

$$\begin{aligned}
P_1 &= 1.08 \text{ atm}, P_2 = 0.855 \text{ atm}\\
V_1 &= 50.0 \text{ L}, V_2 = ?\\
T_1 &= 25^\circ\text{C} + 273 = 298 \text{ K}, T_2 = 10^\circ\text{C} + 273 = 283 \text{ K}\\
V_2 &= \frac{P_1 T_2 V_1}{P_2 T_1}\\
V_2 &= \frac{(1.08 \text{ atm})(283 \text{ K})(50.0 \text{ L})}{(0.855 \text{ atm})(298 \text{ K})} = 60.0 \text{ L}
\end{aligned}$$

Avogadro's Law

In 1811, shortly after the work of Charles and Gay-Lussac, Amadeo Avogadro (1776-1856) was also studying the relationships between pressure, volume, and temperature. He postulated that if you compare two samples of an ideal gas at the same temperature, pressure, and volume, they contain the same number of molecules. This became known as **Avogadro's Law**. This means that at a given pressure and temperature, the volume of a sample is directly proportional to the number of molecules present.

$\frac{V}{n} = k$

Where:

V is the volume of the gas
n is the amount of gas particles (generally measured in moles)
k is a proportionality constant

Ideal Gas Law

If we add Avogadro's Law into the combined gas law, we get the following equation:

$\frac{PV}{Tn} = constant$

Unlike the constants for the other gas laws, this constant is given a special name. The ideal gas constant (R) has the same value for any sample of any ideal gas. A more common way to write the **ideal gas law** is the following:

$PV = nRT$

Recall that 1 mol of an ideal gas at 1 atm of pressure and 0°C (standard temperature and pressure) occupies a volume of 22.4 L. We can use this information to calculate the value of R:

$R = \frac{P \times V}{T \times n} = \frac{(1 \text{ atm})(22.4 \text{ L})}{(273 \text{ K})(1 \text{ mol})} = 0.0821 \text{ L} \cdot \text{atmK}^{-1} \cdot \text{mol}^{-1}$

Using more precise measurements, the ideal gas constant is found to have a value of 0.08206 L•atm•K^{-1}•mol^{-1}.

Example 14.7

Sulfur hexafluoride (SF_6) is a colorless, odorless, and very unreactive gas. Calculate the pressure (in atm) exerted by 1.82 moles of the gas at 69.5°C when confined to a rigid steel vessel with a volume of 5.43 L.

Answer:

$$\begin{aligned}
T_1 &= 69.5^\circ\text{C} + 273 = 342.5 \text{ K} \\
P &= \frac{nRT}{V} \\
P &= \frac{(1.82 \text{ mol})(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(342.5 \text{ K})}{5.43 \text{ L}} \\
P &= 9.42 \text{ atm}
\end{aligned}$$

Note that, in order for all of the units to cancel correctly, the pressure must be expressed in atmospheres, the volume must be in liters, the amount must be in moles, and the temperature must be in Kelvin. If different units were used, the ideal gas constant would have a different value.

Lesson Summary

- Pressure and volume are inversely proportional at a constant temperature.
- Volume and temperature are directly proportional at a constant pressure.
- Pressure and temperature are directly proportional at a constant volume.
- Pressure, volume, and temperature are related by the combined gas law.
- The volume occupied by a gas at a given temperature and pressure is proportional to the number of gas molecules present.
- For any ideal gas, PV=nRT, where R is a constant with a value of 0.08206 L•atm•K^{-1}•mol^{-1}.

Review Questions

1. A sample of a gas has a volume of 4.22 L at 27.8°C and 734 mmHg. What will its volume be at 24.6°C and 755 mmHg?
2. How many molecules of nitrogen gas are in a 5.20 L vessel at 136°C and 0.43 atm?
3. A 34.8 L tank of Ar gas is connected to an evacuated 87.5 L tank. If the final pressure is 640 mmHg, what must have been the original gas pressure in the 34.8 L tank?
4. A 54.0 L cylinder contains 798 g of chlorine gas at 29°C. What mass of chlorine must be released to reduce the pressure to 0.78 atm?
5. A sample of gas at 1 atm has a temperature of 15°C and a volume of 2.58 L. The temperature is then raised to 38°C at 1 atm.
   a. Does the volume of the gas increase or decrease?
   b. Calculate the new volume.
6. An automobile engine contains a vaporized sample of gasoline. The initial volume in the cylinder is 0.725 L. After compression, the volume is reduced to 0.075 L. The fuel mixture initially exerts a pressure of 1.00 atm. Calculate the pressure of the compressed fuel-air mixture (assuming temperature and the amount of gas remain constant).
7. If a gas is cooled from 333.0 K to 273.0 K at a constant volume, what would the final pressure be if the original pressure was 780.0 mm Hg?
8. A bag of potato chips is packaged at sea level (1.00 atm) and has a volume of 315 mL. If this bag of chips is transported to Denver (0.820 atm), what will the new volume of the bag be? Assume the temperature remains the same.
9. Calculate the volume (in L) occupied by 2.12 moles of nitric oxide (NO) at 6.54 atm and 76°C.

Further Reading/Supplemental Links

1. Charles's Law Practice Simulator: http://science.widener.edu/svb/tutorial/charleslaw.html
2. Nobel Prize 2001 for studies in absolute zero: http://www.colorado.edu/NewsServices/nobel/background.html
3. The gas laws: http://misterguch.brinkster.net/gaslaws.html

Points to Consider

- As we studied gases in this lesson, we assumed that all gases exhibit ideal behavior (collisions between particles are completely elastic, the particles do not attract or repel one another, and the volume of the gas particles is negligible compared to the volume they occupy). If some of these assumptions were not quite true, how would it affect the observed gas laws?
- What properties of gases are affected by the speeds of the individual particles?

14.3 Gas Mixtures

Lesson Objectives

- Define partial pressure.
- Describe Dalton's law of partial pressures and perform calculations using this equation.
- Define and perform calculations using mole fractions.
- Define diffusion and effusion and how they relate to other properties of gases.

Lesson Vocabulary

- **partial pressure**: The pressure that each individual gas exerts in a gaseous mixture.
- **Dalton's Law of Partial Pressures**: States that if two or more gases are mixed in a container, each one will exert the same amount of pressure that it would if it were by itself in a container of the same size.
- **mole fraction**: Expresses what fraction or percentage a particular substance contributes to the total number of gas particles present.
- **diffusion**: When the random motions of gas particles in a large container results in an even distribution throughout all the available space.
- **effusion**: The process of a confined gas escaping through a tiny hole in its container.
- **Graham's law of effusion**: States that the rate of effusion or diffusion of a gas is inversely proportional to the square root of the molar mass of the gas.

Check Your Understanding

1. Which of the following statements are true about gases?
   a. Gases always form a solid coating on the interior of the container which they are bounded by.
   b. Gas particles move fairly quickly, often at speeds of more than 100 miles per hour.
   c. In environments with multiple gases, there will be two layers formed –the heaviest gases on the bottom, lightest on top.
   d. Gases mix homogeneously, regardless of which gases are combined.

Introduction

In our previous lesson, we studied the relationships that exist between pressure, temperature, volume, and amount for gases. One assumption we made was that the gases behave ideally, which means that the collisions between gas particles are completely elastic, the particles do not attract or repel one another, and the particle volumes are negligible compared to the overall volume that they occupy. Many properties of ideal gases do not depend on the identity of the gas. For example, we know that one mole of any ideal gas takes up 22.4 L at STP, regardless of the chemical makeup of the individual particles. However, not all properties are like this. For example, the particles of different gases have different average speeds, even if the samples are kept at the same temperature. In this lesson, we will examine how molecular speed is determined for a given sample and use this information to investigate what happens to gas behavior when molecular speeds vary.

Gas Mixtures

Gases are frequently encountered as mixtures. For example, the air we breathe is a mixture of several gases. It is mostly nitrogen and oxygen, but water vapor, argon, carbon dioxide, and various other gases are also present in small amounts. Suppose we place a sample of air in a rigid container. If we were to visualize what is happening at the molecular level, we would see various gas particles mixed together in a homogeneous fashion. Each gas is evenly distributed throughout the entire container, just as they would be if there were no other substances present. The following simulation will help us visualize this setup: http://phet.colorado.edu/en/simulation/gas-properties .

Based on your observations of the above simulation, would you say the mixture of heavy and light gases was homogeneous or heterogeneous? Were the collisions elastic? What are the similarities and differences between the heavy gas particles and light gas particles?

Dalton's Law of Partial Pressures

In our hypothetical gas mixture, we could measure the total pressure exerted by the mixture using a barometer or other instruments. However, we cannot directly measure the pressure exerted by each individual component. How can we determine this information? The concept of **partial pressures** was first described in 1801 by John Dalton (1777-1844). **Dalton's law of partial pressures** states that if two or more gases are mixed in a container, each one will exert the same amount of pressure as it would if it were by itself in a container of the same size. As a result, the total pressure of the mixture will be the sum of the partial pressures. For example, here is an image that shows what happens at the molecular level when two different gases are mixed.

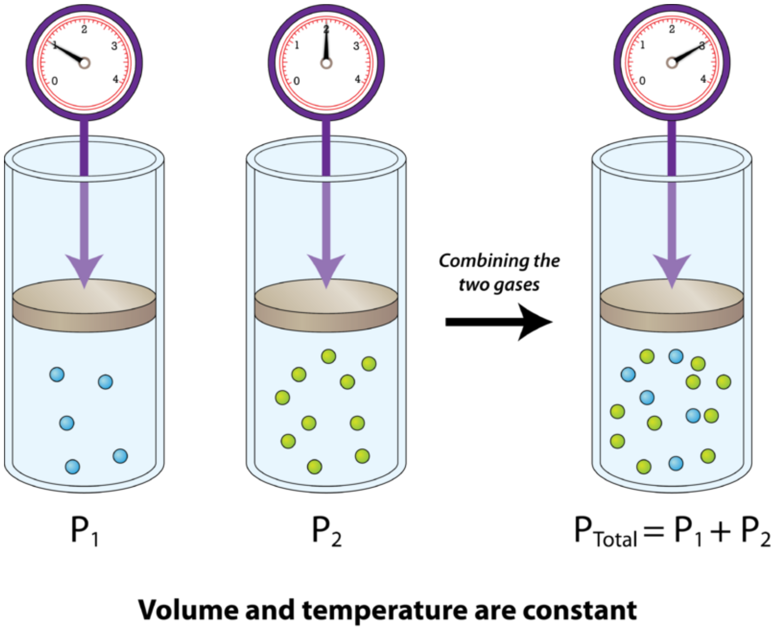

FIGURE 14.10

The partial pressure is the pressure that each individual gas exerts. If we assume that a certain sample of air contains only nitrogen, oxygen, and argon, we could express the total pressure of the mixture as a sum of three partial pressures:

$P_t = P_{O_2} + P_{N_2} + P_{Ar}$

P_t=total pressure

P_O2=partial pressure of O_2

P_N2=partial pressure of N_2

P_{Ar}=partial pressure of Ar

The percentage of the total pressure that is due to one gas in a mixture is proportional to its mole fraction. A **mole fraction** expresses what fraction or percentage the moles of a particular substance contribute to the total number of moles present. It can be calculated as follows:

$X_A = \frac{\text{moles } A}{\text{total moles}}$

Example 14.8

If you had a gas mixture that contained 3.0 moles of argon gas and 6.0 moles of oxygen gas, what is the mole fraction of the argon? If the total pressure is 760 mm Hg, what is the partial pressure of argon?

Answer:

First, calculate the mole fraction of argon:

$$X_{Ar} = \frac{\text{moles Ar}}{\text{total moles}}$$
$$X_{Ar} = \frac{3.0 \text{ moles Ar}}{9.0 \text{ total moles}} = 0.33$$

Partial Pressure:

$$P_{\text{Ar}} = (X_{\text{Ar}})(P_t)$$
$$P_{\text{Ar}} = (0.33)(760 \text{ mm Hg}) = 253 \text{ mm Hg}$$

Partial Pressures and the Ideal Gas Law

We could also determine partial pressure by solving for P in PV = nRT, by using a value for n that only accounts for one of the gases present.

Example 14.9

A gaseous mixture consists of 380 g of F_2 and 100 g of Ne. If the volume of the container is 112 L and the temperature is 273 K, calculate:

a. The moles of each gas.
b. Total moles of all gases.
c. Mole fraction of each gas.
d. Total pressure of mixture.
e. Partial pressure of each gas.

Answer:

a. *Moles of each gas*:

$$n_{\mathrm{F_2}} = 380 \text{ g } \mathrm{F_2} \times \frac{1 \text{ mol } \mathrm{F_2}}{38 \text{ g } \mathrm{F_2}} = 10. \text{ mol } \mathrm{F_2}$$
$$n_{\mathrm{Ne}} = 100 \text{ g Ne} \times \frac{1 \text{ mol Ne}}{20 \text{ g Ne}} = 5 \text{ mol Ne}$$

b. *Total moles of all gases*:

$$n_t = n_{\mathrm{F_2}} + n_{\mathrm{Ne}}$$
$$n_t = 10 + 5 = 15$$

c. *Mole fraction of each gas*:

$$X_{\mathrm{F_2}} = \frac{10 \text{ mol}}{15 \text{ mol}} = 0.67$$
$$X_{\mathrm{Ne}} = \frac{5 \text{ mol}}{15 \text{ mol}} = 0.33$$

d. *Total pressure of the mixture*:

$$P_t = \frac{nRT}{V} = \frac{(15 \text{ mol})(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(273 \text{ K})}{(112 \text{ L})}$$
$$P_t = 3.0 \text{ atm}$$

e. *Partial pressure of each gas*:

$$P_{\mathrm{F_2}} = X_{\mathrm{F_2}} P_t = (0.67)(3.0 \text{ atm}) = 2.0 \text{ atm}$$
$$P_{\mathrm{Ne}} = X_{\mathrm{Ne}} P_t = (0.33)(3.0 \text{ atm}) = 0.99 \text{ atm}$$

Diffusion and Effusion

Gas molecules are always in motion. We can measure the movement of gases in various ways. We have already seen that the temperature is related to the average speed of the gas particles. Because individual particles are all moving in random directions, the sample as a whole does not move this fast from place to place. However, we can also look at the speed at which an entire gas sample moves. What if a gas is transferred to a larger container? Eventually, the random motions of the gas particles will result in an even distribution throughout all the available space. This process is referred to as **diffusion**.

Another related process is effusion. **Effusion** is the process of a confined gas escaping through a tiny hole in its container. Effusion can be observed by the fact that a helium-filled balloon will stop floating and sink to the floor after a day or so. This is because the helium gas effuses through tiny pores in the balloon. Both diffusion and effusion are related to the speed at which various gas molecules move. Gases that have a lower molar mass effuse and diffuse at a faster rate than gases that have a higher molar mass. While they are similar processes, there is a key difference between diffusion and effusion. Diffusion describes the process of a gas spreading out at a constant pressure, such as throughout a room. Effusion, on the other hand, describes the process of a gas spreading out from a high pressure surroundings to lower pressure surroundings.

Scottish chemist Thomas Graham (1805-1869) studied the rates of effusion and diffusion for various gases. **Graham's Law of Effusion** states that the rate of effusion or diffusion of a gas is inversely proportional to the square root of the molar mass of the gas.

$Rate_{effusion} \propto \frac{1}{\sqrt{MM}}$

Relative rates of effusion for gases of different molecular masses can be studied by looking at the time needed for a given gas to effuse through a pinhole in a vacuum (**Figure** 14.11). The lighter the gas molecules are, the smaller the number in the denominator, and the faster the gas effuses and diffuses.

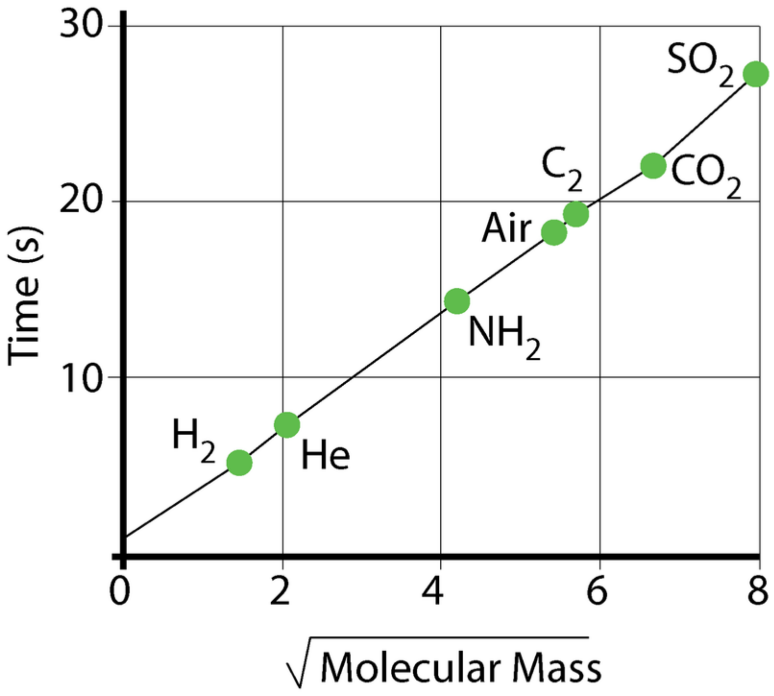

FIGURE 14.11

Molecular Mass vs. Time.

Lesson Summary

- Dalton's law of partial pressures states that the total pressure of a gas mixture is the sum of the partial pressures of each gas component.
- Mole fractions describe the fraction or percentage of a mixture that is made up of a particular substance.
- The rates of diffusion and effusion for a gas are inversely proportional to the square root of its molar mass.

Review Questions

1. Say you have a closed container containing 10 moles of a mixture of gases. If you removed 2 moles of one of the gases and replaced it with 2 moles of a lighter gas, would the total pressure in the container increase, decrease, or remain the same?
2. A gaseous mixture consists of 5.2 moles of helium and 2.1 moles of nitrogen. If the volume of the container is 11.2 L and the temperature is 273 K, calculate the following:
   1. The total moles of gas particles
   2. The mole fraction of each gas
   3. The total pressure of the mixture
   4. The partial pressure of each gas
3. A gaseous mixture consists of 11.0 g of CO_2 and 48.0 g of O_2. If the volume of the container is 2.24 L and the temperature is 273 K, calculate the following:
   1. The moles of each gas
   2. The total moles of gas particles
   3. The mole fraction of each gas

   4. The total pressure of the mixture
   5. The partial pressure of each gas

4. A gaseous mixture consists of 80 g of chlorine and 21 g of nitrogen. If the volume of the container is 11.2 L and the temperature is 273 K, calculate:
   1. The moles of each gas.
   2. The total moles of gas.
   3. The mole fraction of each gas.
   4. The total pressure of the mixture.
   5. The partial pressure of each gas.
5. Compare and contrast diffusion and effusion. Does the aroma of a sprayed perfume represent diffusion or effusion?
6. A sharp object punctures a bike tire. Explain which process is responsible for the loss of air from the tire that causes a flat.
7. The mole fraction of CO in the air in a garage where a charcoal grill is operating can be dangerously high, about 5×10^{-5}. If the barometric pressure is 745 mm Hg, what is the partial pressure of CO in atmospheres?

Further Reading / Supplemental Links

- Dutton, F. B. (1961). Dalton's law of partial pressures. Journal of Chemical Education, 38(8), A545. doi: 10.1021/ed038pA545.1
- Kenney, T. (1990). Graham's law: Defining gas velocities. Journal of Chemical Education, 67(10), 871. doi: 10.1021/ed067p871
- Practice with partial pressures: http://www.khanacademy.org/science/chemistry/ideal-gas-laws/v/partial-pressure
- Gas Encyclopedia-Learn about the properties of various gases: http://encyclopedia.airliquide.com/Encyclopedia.asp?GasID=59

Points to Consider

- In this chapter, we investigated the properties of gases and gas mixtures. How do you think the properties of liquid mixtures might be similar or different from those of gas mixtures?

14.4 References

1. User:Jurii/Wikimedia Commons. http://commons.wikimedia.org/wiki/File:Nitrogen-glow.jpg . CC BY 3.0
2. User:Danomagnum/Wikimedia Commons. http://commons.wikimedia.org/wiki/File:MercuryBarometer.svg . Public Domain
3. Jodi So, using world map clip art by Jenny Boyd. CK-12 Foundation (clip art available at http://www.clker.com/clipart-world-map-32.html) . CC BY-NC 3.0 (clip art in public domain)
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CHAPTER 15 Water

Chapter Outline

15.1 PROPERTIES OF WATER
15.2 AQUEOUS SOLUTIONS
15.3 COLLOIDS AND SUSPENSIONS
15.4 REFERENCES

Water is a major contributor to shaping the earth's surface. Whether through dissolving of materials and the wearing away of solids (as seen in the image above) or moving materials to build up deposits (stalagmites and stalactites in caves), water exerts a significant influence on our environment.

Wolfgang Staudt. www.flickr.com/photos/wolfgangstaudt/2252688630/. CC BY 2.0.

15.1 Properties of Water

Lesson Objectives

- Explain the different characteristics that water exhibits in its solid, liquid, and gaseous forms.
- Explain the processes by which water, ice, and steam interconvert.
- Describe the arrangement of water molecules in ice.
- Describe the molecular model of liquid water, and use this to explain some of its properties.
- Compare the density, surface tension, and heat capacity of water to other common liquids.

Lesson Vocabulary

- **crystalline solid**: A solid in which molecules are fixed in an arranged pattern.
- **frost**: A type of ice produced by the deposition of water vapor.
- **amorphous solid**: A solid in which molecules are in a fixed place but lack the organization of a regular, repeating pattern.
- **surface tension**: A property of liquids describing the tendency of surface molecules to be pulled in towards the liquids center, creating a surface that is tightened like a film.
- **heat capacity**: An inherent property of a given substance indicating how much heat the substance must absorb to cause a certain increase in temperature.

Check Your Understanding

1. Explain the similarities and differences between polar and nonpolar substances. What intermolecular forces do each of these substance types exhibit?
2. Some substances, like solid carbon dioxide, sublime at room temperature. Write an equation describing this process. What is the opposite of sublimation called?
3. An ice cube is cold to the touch because heat from our hands is going into the ice cube, heating and eventually melting the ice. How would it feel if we were to touch something while it was in the process of freezing?
4. The following substances are placed into a graduated cylinder, in no particular order: mercury, copper BBs, and water. Over time, the substances separate based on density. How will these substances layer themselves in the cylinder, from top to bottom?
5. Are the following substances amorphous or crystalline?:
    a. hard candy
    b. diamond
    c. glass in a windowpane

Introduction

Water is truly an amazing substance. It can exist in all three states under normal pressures and temperatures. At room temperature, it is a tasteless, odorless, colorless liquid, although it exhibits a blue hue when present in large volumes. Approximately 70% of the Earth's surface is covered in water. For a small molecule, water molecules are highly attracted to one another, due to particularly strong hydrogen bonds. This leads to a number of properties, such as a relatively high surface tension. Unlike most other substances, water expands when it freezes. Water is also able to absorb relatively large amounts of heat with only minimal changes in temperature. This can be seen on a small scale, such as the coolant in your car, or on a larger scale, such as the more moderate climates in coastal areas. The water in the oceans acts as a tremendous heat sink, which influences global weather patterns. The clouds that form above lakes and oceans originate from the evaporation of lake and ocean water. They are byproducts of water's thermal regulating capacity. Additionally, water is not only found here on Earth; scientists have found evidence of water on a number of extraterrestrial planets. In this lesson, we are going to take a look at this unique and important substance.

Water, Ice and Steam

As we saw in the *States of Matter* chapter, all substances can transform from one state to another, depending on the temperature and pressure of the environment. The solid, liquid, and gaseous forms of water all play an important part in our everyday lives.

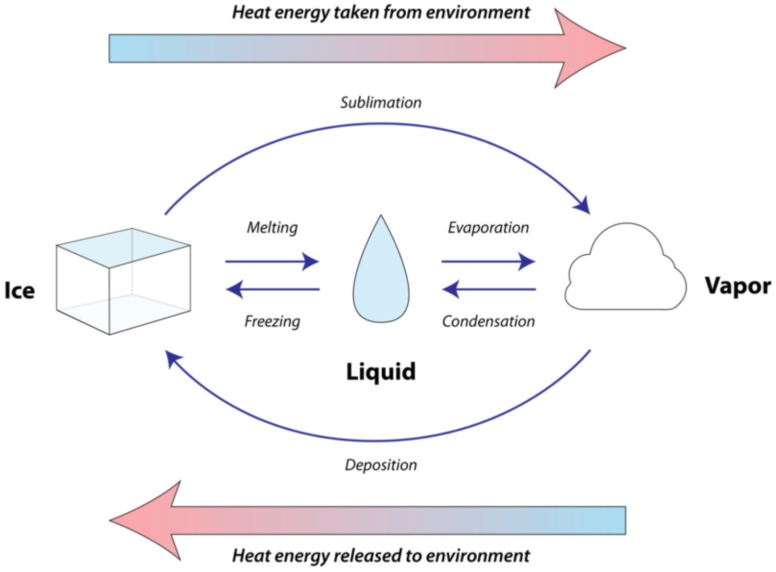

FIGURE 15.1

Example 15.1

Which of the processes in **Figure** 15.1 require the absorption of heat? Which release heat?

Answer:

Melting, sublimation, and evaporation absorb heat from their surroundings. Freezing, deposition, and condensation release heat.

Ice - H

Water in its solid form is generally referred to as ice. Other common terms for solid water include snow, sleet, hail, or frost. The use of a different term generally depends on how and where the water was frozen. Ice plays a major role in activities as diverse as skiing and skating, rain making, polar marine transportation, and offshore drilling. It also plays an important role in the degradation of concrete and other porous materials. Liquid water gets into the cracks of such materials, which can then fracture if the water freezes and expands. Icing on airplanes and electrical transmission lines can also interfere with their functioning.

Water can freeze into both crystalline and non-crystalline (amorphous) forms. **Crystalline solids** refer to solids in which the atoms or molecules are packed in a precisely arranged order. The environmental conditions under which the transition occurs dictate whether this phase change produces regular crystals or not. In its crystalline form, water molecules are generally arranged in a hexagonal array, as shown in **Figure** 15.2.

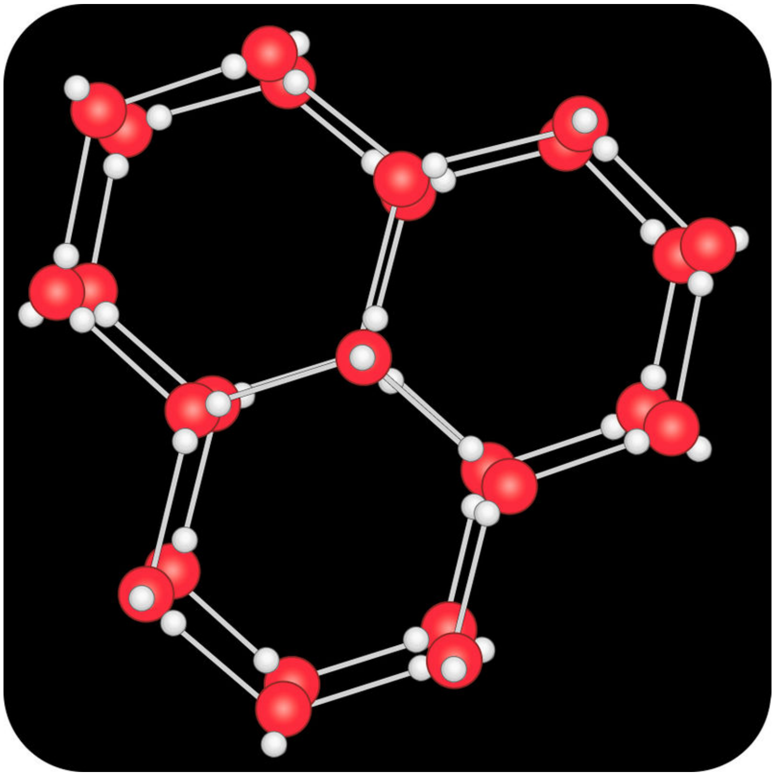

FIGURE 15.2

Ice on Earth generally forms when liquid water freezes. However, it can also be produced by the deposition of water vapor (i.e., $H_2O(g) \rightarrow H_2O(s)$). When this is the case, the ice is often referred to as **frost** (**Figure** 15.3).

When water freezes in a non-crystalline, amorphous form as frost, the water molecules are fixed in place, but not in a regular, repeating pattern. Frost and other **amorphous solids** are characterized by their unorganized and unpredictable structure. Because ice comes in both amorphous and crystalline forms, there are differences in the physical properties of ice such as its hardness and density.

Example 15.2

Can you think of another substance that has an amorphous geometry? Can you think of another substance that has a crystalline geometry?

Answer:

FIGURE 15.3

Some types of candy, such as gummi bears or taffy, are amorphous solids. Table salt has a crystalline geometry.

Liquid Water –H

Liquid water is formed when water vapor condenses (i.e., $H_2O(g) \rightarrow H_2O(l)$ or when ice melts (i.e., $H_2O(s) \rightarrow H_2O(l)$). Because water is a molecular substance, it is a poor conductor of electricity in its pure form. However, as we will see later, its conductivity can be improved by the addition of certain substances. Water molecules are polar, and this overall polarity gives rise to many of the properties of water. For example, an interesting effect is seen when water is placed in a static electric field, as shown in the **Figure** 15.4 and the video below. This phenomenon can be explained in terms of the polarity of water molecules.

MEDIA

Click image to the left for more content.

Density

The molecular structures of solid and liquid water are shown in **Figure** 15.5.

Interestingly, due to the "open" nature of the rigid solid form, the density of liquid water is actually higher than that of solid ice. As a result, ice floats on water. This is relatively rare; most other substances are more dense in their solid form. The density of water as a function of temperature can be graphed, as shown in **Figure** 15.6.

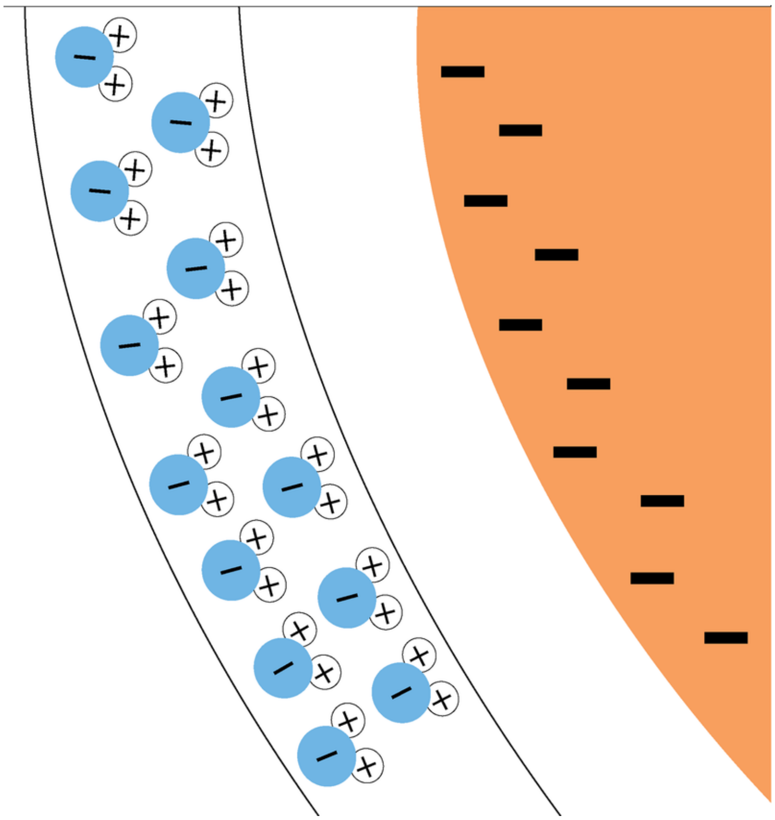

FIGURE 15.4

Water bending in a field of static electricity

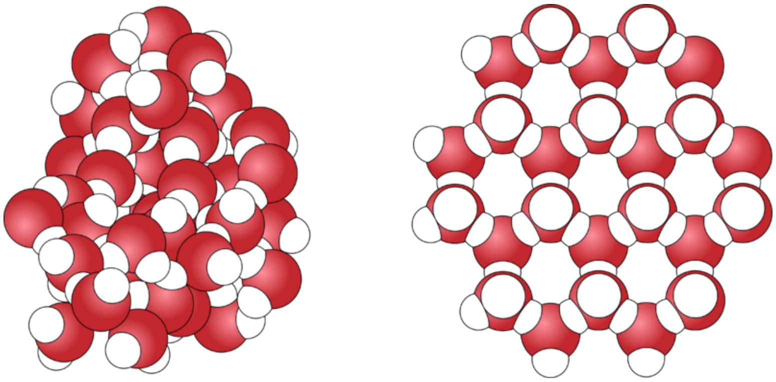

FIGURE 15.5

Molecular arrangement of H_2O molecules in the solid (*right*) and liquid (*left*) phases.

Surface Tension

As we saw in our chapter on *Covalent Bonding*, water molecules attract each other through dipole-dipole interactions and hydrogen bonds. An example of a favorable arrangement is shown in **Figure** 15.7.

Molecules within a liquid are pulled equally in all directions by intermolecular forces. However, molecules at the surface are pulled downwards and sideways by other liquid molecules, but not upwards away from the surface. The overall effect is that the surface molecules are pulled into the liquid, creating a surface that is tightened like a film. This phenomenon is referred to as **surface tension**. Liquids that have strong intermolecular forces, like the hydrogen bonding in water, exhibit the greatest surface tension. **Table** 15.1 shows surface tension values for various common liquids.

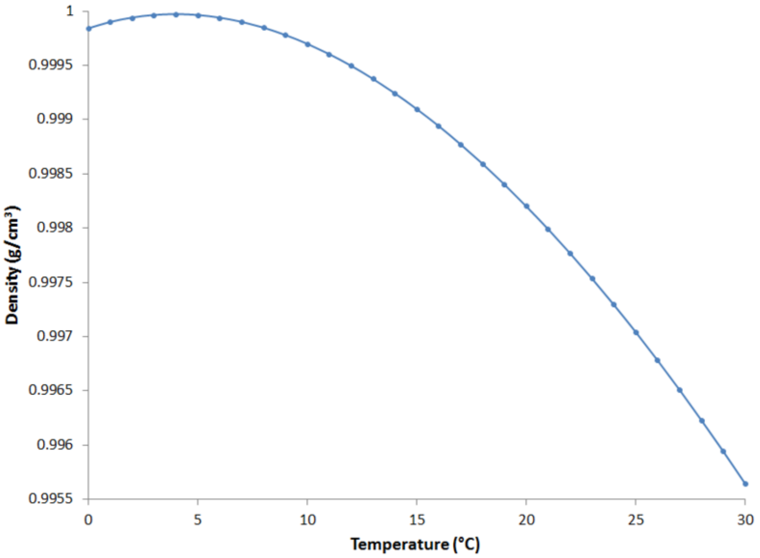

FIGURE 15.6

Density vs. temperature curve for water.

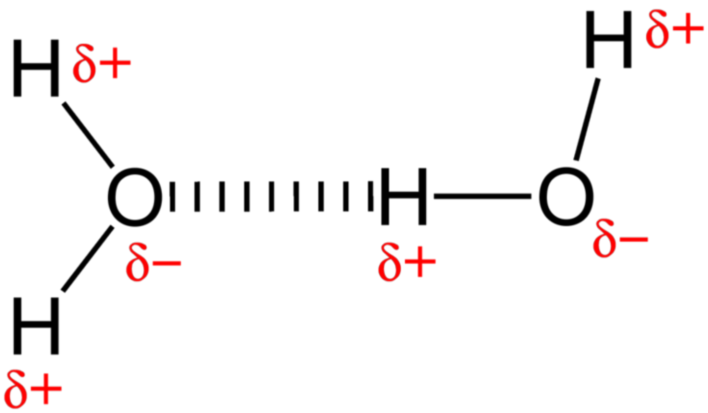

FIGURE 15.7

Hydrogen bonding between water molecules.

TABLE 15.1: Surface Tension of Common Fluids

Fluid	Surface Tension (N/m)
benzene	0.0289
diethyl ether	0.0728
carbon tetrachloride	0.027
chloroform	0.0271
ethanol	0.0221
ethylene glycol	0.0477
glycerol	0.064
mercury	0.425
methanol	0.0227
propanol	0.0237
toluene	0.0284
water at 20°C	0.072

TABLE 15.1: (continued)

Fluid	Surface Tension (N/m)

The surface tension of water is illustrated by a number of common occurrences. For example, water spiders are able to walk across bodies of water because of surface tension. Even though the spiders are denser than water, they do not sink, because the small amount of weight pressing down on the surface is not enough to break the strong hydrogen bonds that hold the surface together.

Heat Capacity

The **heat capacity** of a substance measures how much heat it needs to absorb to cause a certain increase in temperature. Substances with high heat capacities can absorb large amounts of heat with only a minimal temperature increase. Compared to other common liquids, water has a relatively high heat capacity. The heat capacities of some common substances are listed in **Table** 15.2:

TABLE 15.2: **Heat Capacity of Common Materials**

Material	Heat capacity (calories•g^{-1}•°C^{-1})
Acetone	0.51
Aluminum	0.22
Ammonia	1.13
Copper	0.09
Grain alcohol	0.23
Lead	0.03
Mercury	0.03
Silicon	0.18
Silver	0.06
Water	1.00

Example 15.3

How much heat must be absorbed by 1 gram of water to raise its temperature by 5°C?

Answer:

Water has a heat capacity of 1.00 calories•g^{-1}•°C^{-1}. Raising the temperature of 1 gram of water by 5°C would require the absorption of 5 calories of energy.

Steam –H

Water vapor, or steam, can be produced either through the vaporization of liquid water (i.e., $H_2O(l) \rightarrow H_2O(g)$ or the sublimation of solid water (i.e., $H_2O(s) \rightarrow H_2O(g)$). When water changes from a liquid to a gas at normal temperatures and pressures, we refer to the process as evaporation. When we sweat, we take advantage of this process. Vaporization requires an input of energy, so when our sweat evaporates, it absorbs some of the energy from our bodies, thus cooling us. When water is vaporized by heating it to its boiling point, we generally refer to it as boiling instead.

Steam is a very useful form of water that can be used to do mechanical work, like powering steam engines and turbines. Such devices are important for the generation of electricity.

Lesson Summary

- Water can exist in all three states under normal pressures and temperatures. It is tasteless, odorless, and exists as a liquid at room temperature and standard atmospheric pressure.
- In its solid form, water is frequently referred to as ice. The terms snow, sleet, hail, or frost may also be used, depending on the conditions under which the water solidified. Ice can exist as an amorphous solid or as a crystalline solid.
- In its pure liquid form, water is a poor conductor of electricity. Unlike most substances, water is more dense in its liquid state than its solid state. As a result, water expands when it freezes, and ice floats on water.
- Compared to other liquids, water has a relatively high surface tension and heat capacity. Both of these properties are partially a result of the strong hydrogen bonds that hold water molecules together.

Review Questions

1. Why do you suppose a wet cloth that is hung outdoors in freezing weather can be retrieved later in a dry state?
2. Identify the state(s) of water present at each of the points identified in the **Figure** 15.8.

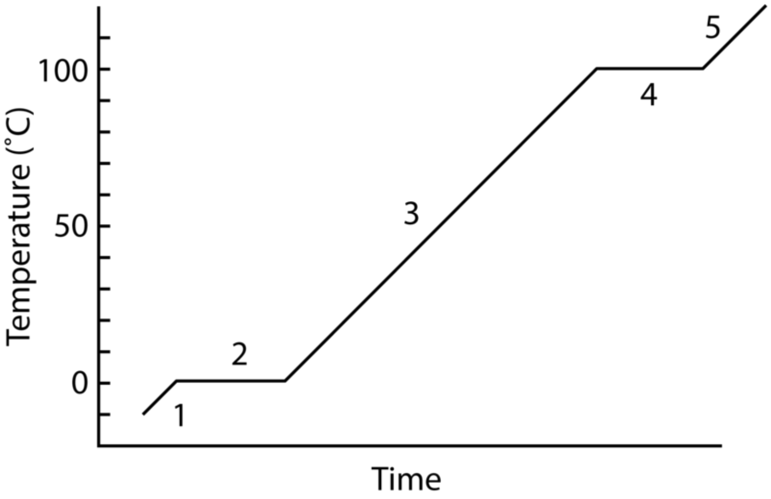

FIGURE 15.8

3. When might you see condensation, evaporation, melting, or freezing as part of a normal weather pattern? What evidence do you have that these changes have occurred?
4. Which of the processes illustrated in **Figure** 15.1 do you suppose are responsible for the formation of hail during a thunderstorm?
5. Give an example other than those mentioned in the chapter of the strong surface tension exhibited by water.
6. How is it possible for water to fracture rock when it freezes?
7. Based on the data in the table of "Heat Capacity," do substances that exhibit hydrogen bonding appear to have larger or smaller heat capacities than other substances?
8. What do you suppose would happen if you placed an ice cube in a beaker containing pure ethanol (density = 0.789 g/mL)? Would it sink or float?
9. What do you suppose would happen if a solid piece of ethanol were placed into liquid ethanol? What about if it were placed in liquid water?

Further Reading / Supplemental Links

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- Measuring surface tension: http://www.sciencebuddies.org/science-fair-projects/project_ideas/Phys_p012.shtml
- SnowCrystals.com: http://www.its.caltech.edu/~atomic/snowcrystals/

Points to Consider

- How might water's intermolecular forces affect its ability to interact with other substances? What types of substances mix well with water? What types of substances do not?

15.2 Aqueous Solutions

FIGURE 15.9

Aqueous Solutions of Transition Metal Compounds

Lesson Objectives

- Explain how water acts as a solvent.
- Describe the process of dissolution and what this looks like at the molecular and macroscopic level.
- Describe the process of dissociation and what this looks like at the molecular and macroscopic level.
- Define and give examples of solvents and solutes.
- Describe and give examples of chemical solutions.

Lesson Vocabulary

- **aqueous solution**: A homogeneous mixture in which the most abundant component is water.
- **solution**: A homogeneous mixture.
- **solvent**: The substance in a solution that is present in the largest amount.
- **solute**: All other substances in a mixture or solution.
- **dissolution**: The process where crystals in a molecule get smaller and smaller until the solution is transparent.
- **soluble**: A homogeneous mixture where a solute dissolves completely into a solvent.
- **dissociation**: The process of separating ions from one another.
- **insoluble**: A heterogeneous mixture where a solute does not dissolve completely into a solvent.

Check Your Understanding

- Give two examples each of ionic compounds and molecular compounds, and explain their similarities and differences.
- Identify one solid and one liquid that mix well with water.
- Give an example of a gas that mixes with water.

Introduction

In our last section, we took a detailed look at water and its physical properties and characteristics. We examined properties like surface tension, heat capacity, and density that are significantly higher for water than for many other liquids. In this lesson, we are going to study water's ability to act as a solvent. Water is particularly good at dissolving ionic compounds and very polar molecular substances. By looking at the properties of a given substance, it is often possible to predict whether it will dissolve in water. This type of analysis is aided by understanding the dissolution process on a molecular level.

Aqueous Solutions

An **aqueous solution** is a homogeneous mixture in which the most abundant component is water. The other substance(s) are typically introduced in a solid or liquid form and mixed into the water until they are evenly distributed. For example, if we placed a sample of ethanol in water and mixed it homogeneously, we would have a solution. Table salt mixed with water is another example of a solution. More generally, a **solution** is a homogeneous mixture. The solution component that is present in the largest amount is called the **solvent**, and all other substances are referred to as **solutes**. In aqueous solutions, water is always the solvent.

Experiments

We are going to visualize some simple experiments to explain how an aqueous solution is created. This involves placing various common substances in water and seeing what happens. The substances we will consider are (1) table salt (NaCl); (2) cane sugar ($C_{12}H_{22}O_{11}$), and (3) sand (SiO_2) (**Figure** 15.10).

FIGURE 15.10

Left: Table Salt; Center: Sugar; Right: Sand

Scenario 1 –Salt Added to Water

What will happen when we add table salt to water? At the macroscopic level? At the molecular level?

If we add a spoonful of table salt to a glass of water, we will notice that the salt crystals immediately begin to disappear. We can also stir the solution to speed up the process. Over time, the crystals get smaller and smaller, and eventually, we will be left with a transparent solution, assuming we have enough water to dissolve all of the salt. This process is called **dissolution**. Because dissolution occurs, we say that salt is **soluble** in water. Any substance that is able to dissolve in water is described as being water soluble.

Where did the salt go? If we were to measure the mass of the salt and the mass of the water before mixing them, we would find that the mass of the solution is simply the sum of its two parts, as expected by the law of conservation of mass. The salt is still there, it is just no longer visible. (Interestingly, volume is not additive in the same way, because the density of the solution is different than the densities of the two starting materials.) Recall that salt is an ionic substance comprised of cations and anions bonded tightly together in a crystal lattice. Because water molecules are polar, they are capable of stabilizing isolated ions by surrounding each one with the appropriate partial charges. The process of separating ions from one another is known as **dissociation**. After the sodium and chloride ions that make up salt have separated from each other, the compound is said to have dissociated. Here is a video clip of what dissociation looks like: http://www.youtube.com/watch?v=EBfGcTAJF4o .

Although they appear identical, a solution of sodium chloride has properties that are significantly different than those of pure water. For example, pure water is a poor conductor. However, if we pass electricity through a solution of sodium chloride, we find that it is quite conductive (see **Figure** 15.11).

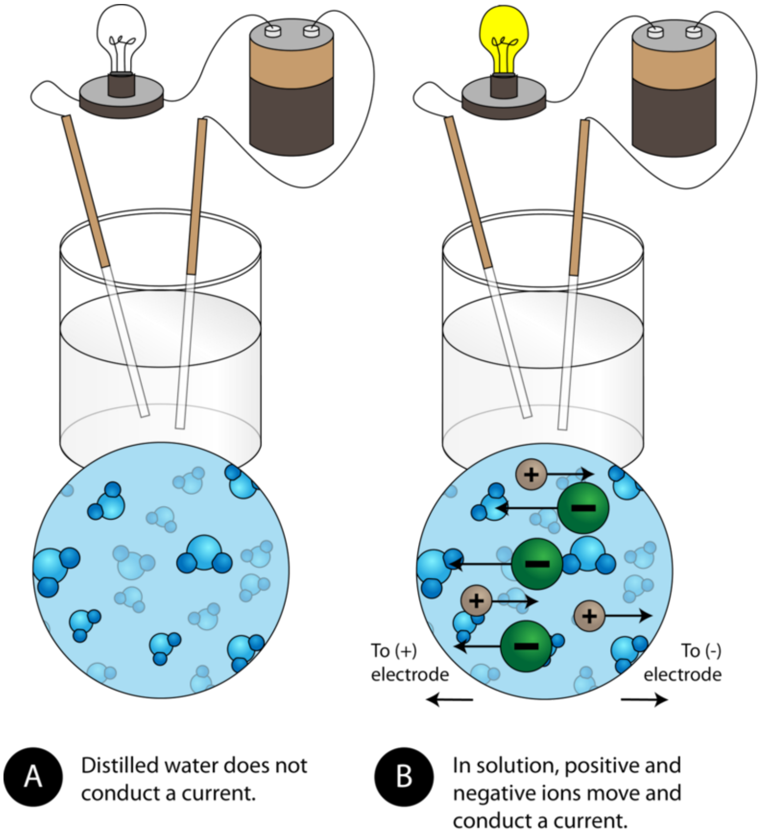


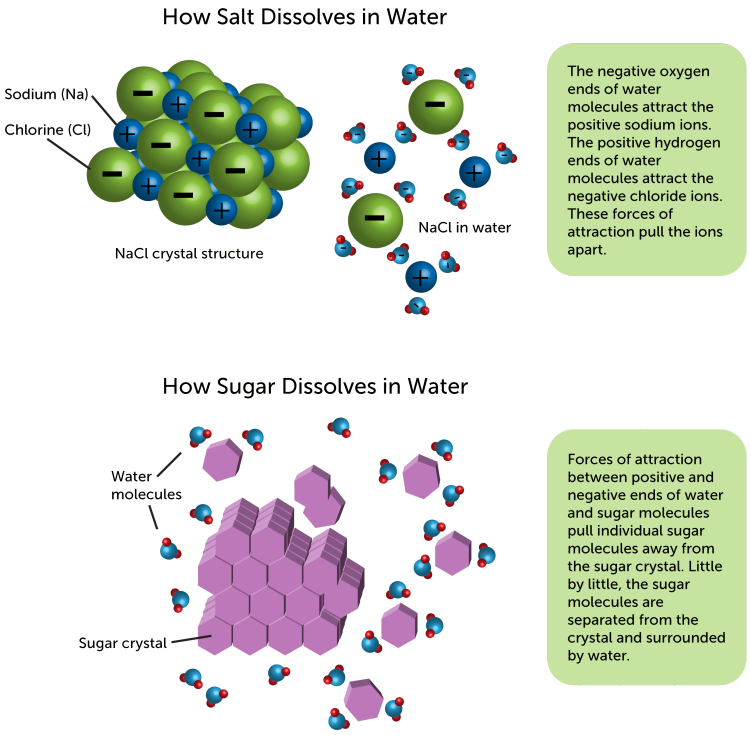
FIGURE 15.11

Conductivity of a solution of sodium chloride.

In **Figure** 15.11, the bulb on the right is fully illuminated. Electricity is able to flow through the circuit because the salt solution is a good conductor. In contrast, the bulb on the left is not lit, because the poorly conductive beaker of water provides too much resistance to the complete electric circuit. Why does this difference occur? In order to conduct electricity, a substance needs to have charge carriers (either ions or electrons) that are able to move freely. In pure water, there are essentially no ions, and all electrons are tightly associated with their corresponding molecules. However, in the salt solution, plenty of positively and negatively charged sodium and chloride ions are available to conduct an electric current. Because this test tells us the relative number of free ions that are in solution, it can be used to determine whether a given substance dissociates into separate ions when dissolved in water.

Scenario 2 –Sucrose Added to Water

In our second scenario, we are going to add cane sugar to water. Again, the solid will gradually disappear over time, and assuming there is enough water to dissolve all of the sugar, we will eventually be left with a clear solution. What would happen if we tested this solution for conductivity? It turns out that the solution of sugar has a conductivity similar to that of pure water. Why is this different than when we dissolved salt? The difference is that sugar is a molecular substance, not an ionic substance. In general, molecular substances do not dissociate when dissolved in water, so no ions are formed that can be used to conduct electricity. (There are some exceptions to this rule. In particular, strong acids, such as HCl, are often molecular substances that dissociate into ions when dissolved in water.) The difference between the dissolution of sodium chloride and sucrose in water is illustrated in the **Figure** 15.12.



The negative oxygen ends of water molecules attract the positive sodium ions. The positive hydrogen ends of water molecules attract the negative chloride ions. These forces of attraction pull the ions apart.

Forces of attraction between positive and negative ends of water and sugar molecules pull individual sugar molecules away from the sugar crystal. Little by little, the sugar molecules are separated from the crystal and surrounded by water.

FIGURE 15.12

Difference between salt and sucrose dissolving in water.

Again, notice that all of the sucrose molecules remain completely intact. No covalent bonds are broken during the dissolution of a non-acidic molecular substance, only the intermolecular interactions that hold individual molecules together are disrupted.

Scenario 3 –Sand Added to Water

If we were to mix sand and water, no solution would form. No matter how long we stirred this mixture, the sand would still settle out to the bottom. Sand and water combine to make a heterogeneous mixture. The **Figure** 15.13 shows this on a large scale.

In order to create a homogeneous aqueous solution, we need the solute to be soluble in water. Sand is **insoluble** in water, and we can easily see that the two substances remain separate when mixed. The conductivity of this system would also be similar to that of pure water, because neither component is conductive on its own, and no real change occurs when they are mixed together.

FIGURE 15.13

Sand mixing with water.

Lesson Summary

- Water is a versatile solvent that can dissolve many ionic and polar molecular solutes to make aqueous solutions.
- The ability of water to dissolve polar and ionic substances is due to its own polarity, which provides partial positive and negative charges to stabilize isolated ions and molecules.
- A homogeneous solution is created when a solute dissolves completely into a solvent. In a solution, we cannot visually distinguish between the solute and solvent.
- Ionic substances dissociate into ions when they dissolve in water, but most molecular substances do not.
- Not all substances are soluble in water.

Review Questions

1. How can a solution be classified as aqueous?
2. What distinguishes solvent and solute?
3. How are dissolution and dissociation related?
4. Construct a diagram showing what happens on the molecular level when the following substances are added to water:
    a. A soluble compound that dissociates into ions
    b. A soluble compound that does not dissociate into ions
    c. An insoluble compound
5. You mix 50 mL of pure water with 30 mL of 95% ethanol and stir until a completely homogeneous mixture is produced. You then measure the new volume of the solution.
    a. What might you expect the new volume to be?
    b. When you put the solution into a graduated cylinder, you see that it has a volume of 76 mL. What might be your explanation for this?
6. Can you think of substances that are soluble in water under some circumstances but not others?
7. Dirt that gets on our hands can be difficult to remove by rinsing with cold water. What are some things that you can do to increase the solubility of dirt, making it easier to dissolve in running water?

8. Can you think of an example in which water is the solute instead of the solvent?

Further Reading / Supplemental Links

- PhET Dissolving Animation: http://phet.colorado.edu/en/simulation/soluble-salts
- Solubility and solubility rules: http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch18/soluble.php
- Practice quiz on solutions: http://www.chem4kids.com/extras/quiz_mattersolution/index.html

Points to Consider

- Some substances only partially dissociate into ions when dissolved in water. How might you test to see the degree to which a substance has dissociated?
- Can you think of a substance that only partially dissolves in water?
- How can you improve water's ability to dissolve a substance?

15.3 Colloids and Suspensions

Lesson Objectives

- Explain how a mixture can be formed from a dispersed phase and a continuous phase and give examples of such mixtures.
- Describe the characteristics and properties of mixtures like foams, aerosols, smoke, suspensions, and sols.
- Describe the relationship between particle sizes in the dispersed phase and the types of mixtures that are produced.
- Describe the different phases that a dispersed medium exhibits.
- Describe the different phases that a continuous medium exhibits.
- Describe the different combinations of dispersed phases and continuous phases, and the resulting mixtures that can be formed from such combinations.
- Describe the Tyndall effect, and give examples of this effect in suspensions and colloids.

Lesson Vocabulary

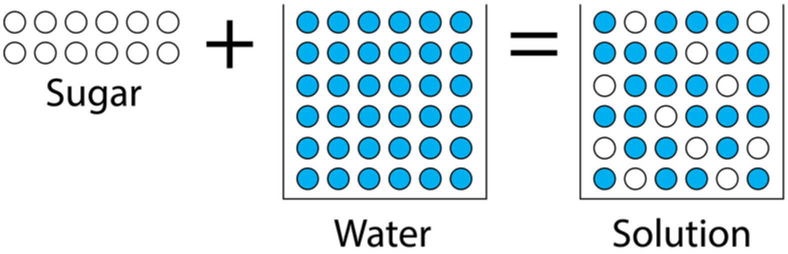
- **dispersed phase**: A substance that is the solute in a colloidal stage.
- **continuous phase**: Also referred to as the dispersion medium, is a solvent in a colloidal stage.
- **colloid**: A homogeneous mixture in which very small particles are distributed evenly throughout another substance; these particles do not settle out of solution.
- **suspension**: A heterogeneous mixture in which solute-like particles separate from the solvent-like particles after being mixed together.
- **Tyndall effect**: The phenomenon in which light is scattered by very small particles in its path.

Check Your Understanding

1. Classify the following items as a homogeneous mixture, a heterogeneous mixture, or neither:

    a. a glass of salt water
    b. oil and vinegar
    c. tomato sauce
    d. milk
    e. smoke from a fire
    f. fog

2. In the following figure, which substance would be the solute, and which would be the solvent?



Introduction

In the previous lesson, we studied how aqueous solutions are formed. Our focus was on solid or liquid solutes being dissolved by liquid water, and we assumed that the solutes were either completely soluble or completely insoluble, producing either homogeneous or heterogenous mixtures, respectively. However, there are other situations that are not as easy to classify. For example, in **Figure** below, we see a small bowl of mayonnaise. Mayonnaise is a colloid –a mixture that is not totally homogeneous nor totally heterogeneous. In this lesson, we are going to expand our study of mixtures to show that solids and gases can also act as solvents. Additionally, we will look at situations in which a solute breaks down into particles that are larger than individual molecules and ions but smaller than, say, a fully intact grain of sand.

FIGURE 15.14

Colloids and Suspensions

Solutions are comprised of a solvent and a solute, mixed homogeneously to produce a transparent fluid. However, there are also mixtures in which the solute is evenly dispersed, but each solute particle is still a cluster of more fundamental particles like molecules or ions. The particle sizes in such mixtures are generally larger than 1×10^{-9} meters. Such a mixture cannot easily be classified as either homogeneous or heterogeneous. In such systems, we often use the terms **dispersed phase** and **continuous phase** (or **dispersion medium**) in place of solute and solvent. Each of these phases can consist of a solid, liquid, or gas. **Table** 15.3 shows various combinations of dispersed and continuous phases.

TABLE 15.3: Dispersed Phase

	Gas	Liquid	Solid
Continuous Gas Phase	*none* gases are miscible	*liquid aerosol* fog, mist	*solid aerosol* smoke
Continuous Liquid Phase	*foam* whipped cream	*emulsion* salad dressing	*suspension or sol* paint, ink
Continuous Solid Phase	*solid foam* styrofoam	*gel* jelly	*solid sol* glass

A mixture of two gases will always be homogeneous. It can be referred to as a solution, but it is often simply called a gas mixture. When a gaseous solute is dispersed within a liquid phase (e.g., whipped cream) or a solid phase (e.g., styrofoam), the result is generally referred to as a foam. A mixture in which liquid particles are dispersed in a gas are called aerosols; examples include fog or hair spray. Liquid particles dispersed into a liquid (e.g., mayonnaise) or solid (e.g., jelly) are called emulsions and gels, respectively. A solid dispersed into a gas, such as smoke, is referred to as a solid aerosol. Solid particles dispersed into liquids (e.g., paint) or solids (e.g., opaque glass) are called sols and solid sols, respectively.

We can further differentiate between different mixtures by looking at the particle size of the dispersed substance (**Figure** 15.15).

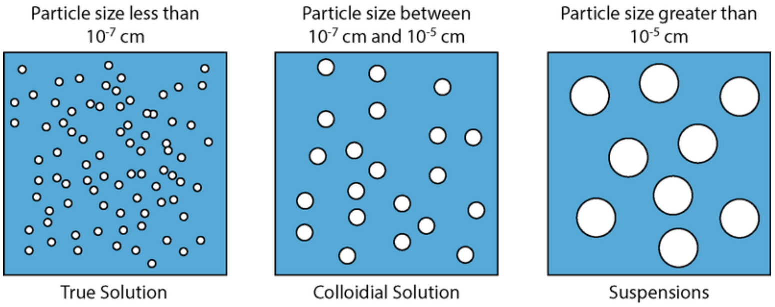


FIGURE 15.15
Particle Size and Solution Type

True solutions generally have particle sizes that are smaller than one nanometer. The particles in these solutions do not settle over time and cannot be separated by filters or semi-permeable membranes. The dispersed particles in **colloids** usually range in size from 10^{-9} to 10^{-7} meters. These solutions are somewhat transparent, and their particles do not settle out over time. However, with fine enough semi-permeable membranes, the dispersed particles in a colloid can be separated from the bulk solvent. **Suspensions** have the largest particles sizes, on the order of 10^{-7} meters or larger. These mixtures are opaque, and the particles can be separated by filtration. Additionally, the particles in a suspension separate over time into different layers based on the relative densities of the dispersed and continuous phases.

Visible Effects of Particle Size

On the macroscopic scale, variations in particle size can be detected by the effect they have on light that passes through the mixture. For example, true solutions are transparent. Some solutions are colored, which means that certain wavelengths of light are absorbed by molecules within the mixture. However, the remaining light is transmitted freely through the mixture. In contrast, the dispersed particles in a colloid scatter light, resulting in an opaque mixture. The difference can be seen in **Figure** 15.16. The phenomenon in which light is scattered by very small particles in its path is known as the **Tyndall effect**.

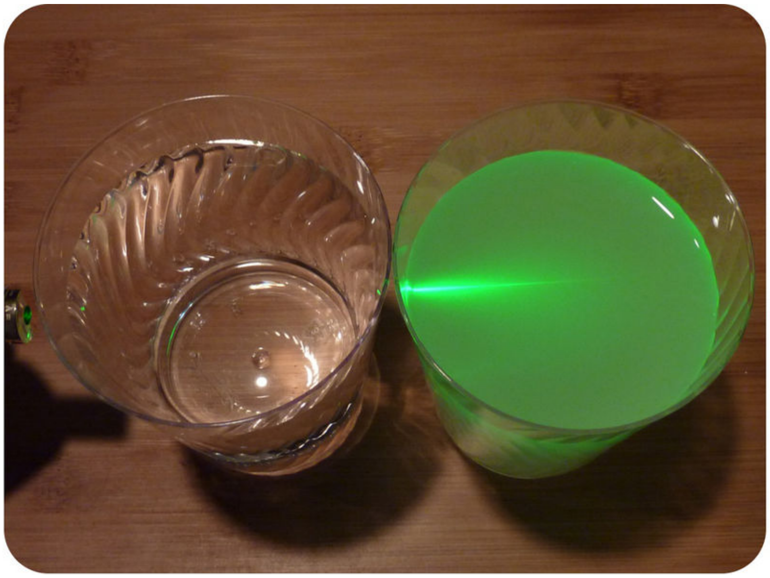


FIGURE 15.16
Light passing through a true solution and a colloidal solution

A suspension scatters light even more effectively than a colloid. Depending on the thickness of the mixture, little to no light will generally make it all the way through a suspension. Suspensions have a very opaque appearance.

Lesson Summary

- The dispersed and continuous phases within a mixture can each be in any state of matter (i.e., solid, liquid, or gas).
- Mixtures are often classified differently based on the combinations of states (solid, liquid, or gas) represented by the dispersed phase and the continuous phase.
- Homogeneous mixtures with particle sizes smaller than 1 nanometer are categorized as true solutions. They are transparent.
- Mixtures with particle sizes ranging from 10^{-9} to 10^{-7} meters are colloidal mixtures. They are partially transparent but exhibit a noticeable Tyndall effect.
- Mixtures in which the particle sizes are larger than 10^{-7} meters are called suspensions. These mixtures are completely opaque.

Review Questions

1. What differentiates the particles that make up colloids and suspensions?
2. How do the dispersed phase and the continuous phase relate to the solution components you have learned about?
3. How can you visibly tell the difference between colloids and suspensions?
4. Categorize each of the following substances as a foam, aerosol, emulsion, gel, sol, or solid sol:
   a. cheese
   b. butter
   c. jelly
   d. shaving cream

   e. car exhaust

5. When driving through fog with your headlights on, you may witness the Tyndall effect. Explain this in terms of the type of mixture that is interacting with the light from the headlights.

Further Reading / Supplemental Links

- Review of the differences between suspensions, colloids, and solutions: http://www.youtube.com/watch?v=3ROWXs3jtQU
- Tyndall effect animation: http://www.youtube.com/watch?v=V7eqD-Jw6m4
- Classification table of colloids: http://en.wikipedia.org/wiki/Continuous_phase

Points to Consider

- If you were to shake a mixture of vinegar and oil, the container will often feel cool to the touch. This indicates that energy in the form of heat has entered the system. What would your explanation for this be?
- We did not discuss whether or not colloids and suspensions have conductive properties. We saw in a previous lesson that some solutions are conductive. How might you test whether or not a colloid or suspension is conductive?

15.4 References

1. Christopher Auyeung. CK-12 Foundation . CC BY-NC 3.0
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3. George. http://www.flickr.com/photos/29171973@N00/336013964/ . CC BY 2.0
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CHAPTER 16 Solutions

Chapter Outline

16.1 SOLUBILITY
16.2 SOLUTION CONCENTRATION
16.3 COLLIGATIVE PROPERTIES
16.4 REFERENCES

Solubility describes the extent to which one substance will dissolve in another. We are going to study factors that affect the solubility of solids, liquids, and gases in various liquid solvents, particularly water. In the opening image, we see crystals forming in a solution, which can occur when the solubility of a given solute-solvent pairing is exceeded. Our understanding of intermolecular forces will help us to explain the extent to which substances are soluble in water by looking at interactions on the molecular level.

Jon Sullivan. Public Domain. http://commons.wikimedia.org/wiki/File:Saltflats_crystals.jpg.

16.1 Solubility

Lesson Objectives

- Define the term solubility and describe factors affecting the solubility of a particular solution.
- Predict whether a substance will dissolve or dissociate in water. Describe what it means for a solution to be saturated, supersaturated, or unsaturated.
- Define and give examples of both miscible and immiscible mixtures.
- Explain the statement "like dissolves like" at the molecular level, and give specific examples of this concept.
- Describe how pressure and temperature affect the solubility of a liquid or solid in solution.
- Describe how pressure and temperature affect the solubility of gases in solutions, and use Henry's Law to predict the solubility of a gas in a solution given the necessary variables.

Lesson Vocabulary

- **solubility**: The degree to which a solute dissolves in a solvent.
- **saturated**: The point at which no more solute is able to dissolve.
- **unsaturated**: A solution in which more solute could be dissolved, solute concentration is less than predicted by solubility properties.
- **supersaturated**: When the amount of solute dissolved exceeds the solubility. Occurs when a solution is saturated and the temperature slowly drops.
- **miscible**: Molecules mix well with one another, and form a homogeneous mixture.
- **immiscible**: Molecules don't mix well together, and form a heterogeneous mixture exhibiting a noticeable bilayer.
- **van't Hoff factor**: Describes the number of moles of particles that dissociate from solid.
- **Henry's law**: Mathematically describes the relationship between the vapor pressure of the solution and the solute concentration.

Check Your Understanding

1. What type of intermolecular forces will exist between molecules of the following substances?
   a. H_2O
   b. CO_2
   c. CH_4
   d. N_2
   e. CO
   f. NH_3

Introduction

Have you ever wondered why it is easier to stir sugar into hot tea rather than into ice tea? Or, why no matter how much you shake a jar of oil and vinegar, it always seems to separate? These observations can be explained by a property of solutions known as solubility. In this section, you'll learn how molecular structure and binding forces contribute to the solubility properties of various solutions and mixtures.

Solubility

Solubility is the degree to which a given solute dissolves in a particular solvent. It depends on various factors, including temperature and pressure. A common way to express the solubility of a given solute-solvent pair is to state the maximum amount of solute that can be dissolved by 100 grams of the solvent. The temperature dependence of the solubilities for various compounds in water is shown in **Figure** 16.1.

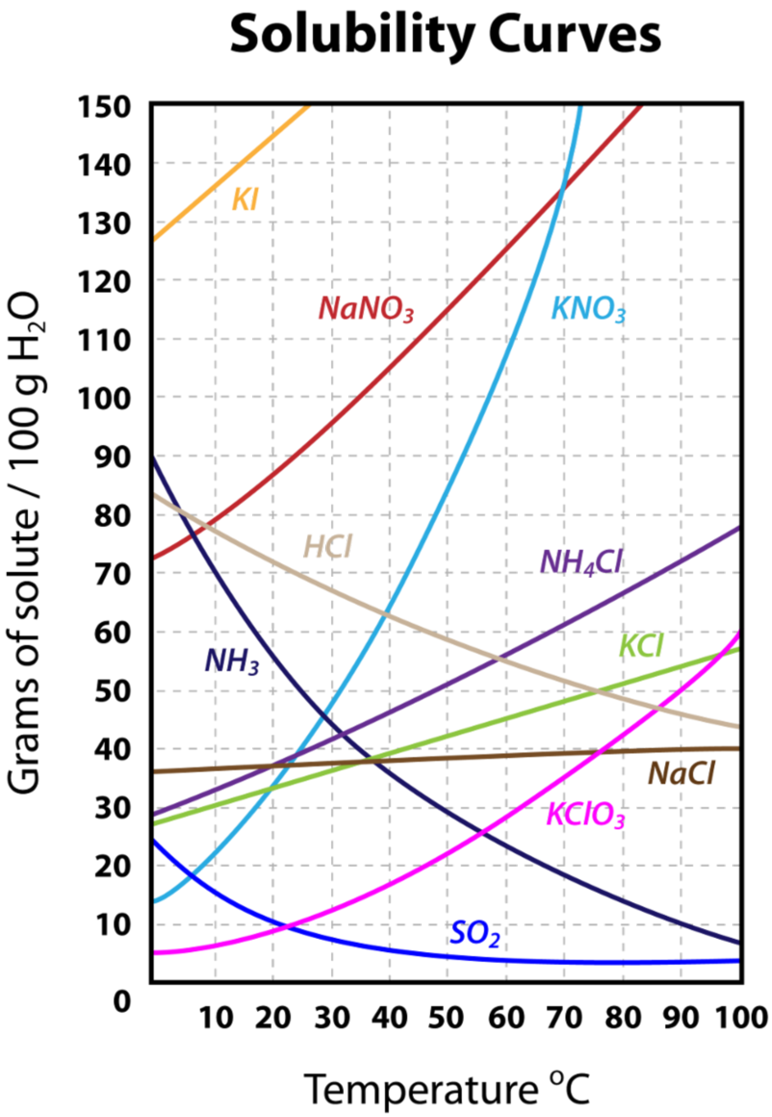

FIGURE 16.1
Solubility Curve for Ionic Solids

The aqueous solubility of a given substance is determined experimentally by dissolving increasing amounts into a known mass of water at a specific temperature until no more solid dissolves. A solution that cannot hold any more of a given solute is said to be **saturated**. For example, in **Figure** 16.1 we see that the solubility of sodium nitrate ($NaNO_3$) is approximately 90 g per 100 g of H_2O at 20°C. At this temperature, a 100 gram sample of H_2O in which 90 grams of sodium nitrate is dissolved would be saturated, and a solution in which less sodium nitrate is dissolved would be **unsaturated**. Note that this ratio also holds for samples in which the solvent is present in different amounts; 50 grams of water would hold 45 grams of sodium nitrate at 20°C, and 300 grams of water would hold 270 g of $NaNO_3$. Notice that even relative solubilities of various compounds are temperature dependent. For example, at 20°C, KCl has a higher solubility than NaCl, but at 50°C, this relationship is reversed.

Solutions can also become **supersaturated**, where the amount of solute dissolved exceeds its solubility. Supersaturation most commonly occurs when a saturated solution is slowly cooled. They occur frequently in geological and meteorological processes. Supersaturated systems are unstable, and eventually, the solute will precipitate until a saturated solution is regenerated. We can quantify supersaturation by looking at solubility curves. If the ratio of solute to solvent is above the saturation curve at the given temperature, the solution is supersaturated. If it is on the curve, the solution is saturated, and if it is below the curve, the solution is unsaturated.

Solubility can be described for any solute-solvent pairing, but because water is such a fundamentally important solvent, we are mainly focusing on aqueous solutions.

Example 16.1

You dissolve 40 g of KCl in 100 g of water at 40°C. You then cool the solution to 20°C, during which you notice solid KCl precipitating. How many grams of KCl would you expect to precipitate?

Answer:

Consult **Figure** 16.1 to find the solubility of KCl at 20°C (approximately 32 g KCl/100 g H_2O). Therefore, we would expect approximately 8 g KCl to precipitate out (40 g –32 g = 8 g).

Factors Affecting Solubility

There are three main factors that control solubility.

1. Identities of the solute and solvent
2. Temperature
3. Pressure (for gases only)

Solute and Solvent

Ultimately, the ability of a solute to dissolve in a particular solvent will be dictated by the relative favorability of solute-solvent interactions compared to solute-solute and solvent-solvent interaction. In particular, the polarity of these two substances has a major effect on whether a significant amount of solute is able to dissolve. Polar solutes are typically quite soluble in polar solvents (e.g., ethanol in water), and nonpolar solutes generally dissolve well in nonpolar solvents (e.g., grease in gasoline). Conversely, polar solutes will have low solubilities in nonpolar solvents (e.g., NaCl in CCl_4), and solubilities will be low for nonpolar solutes in polar solvents (e.g., oil in vinegar).

Temperature

As you can see in **Figure** 16.1, solid and liquid solutes generally become more soluble as the temperature increases. This is true for solvents other than water as well. This effect varies quite a bit by substance. For example, the solubility of KNO_3 has a very strong temperature dependence (its solubility curve has a large slope), whereas the solubility of NaCl is minimally influenced by temperature (its solubility curve is nearly flat). For gaseous solutes, solubility *decreases* at higher temperatures. We will look more at this effect later in the lesson.

Pressure

Higher pressures increase the solubility of gases. You are probably familiar with this concept as it relates to carbonated beverages. Before opening the container, the inside is pressurized, so a large amount of CO_2 is dissolved in the liquid. After opening, the pressure decreases (to the ambient pressure), so the solubility of CO_2 drops, causing it to bubble out of solution. Because they are not compressible like gases, solid and liquid solutes do not have noticeable changes in solubility at different external pressures.

A Review of Intermolecular Forces

Our understanding of the behavior of solutes and solvents can be largely explained at the molecular level using our model of intermolecular forces. Some substances will mix freely while others barely mix at all. This is due to the interactions between particles of the solvent and solute. Recall that nonpolar molecular substances are held together in the solid and liquid phases by relatively weak London dispersion forces, in which induced dipoles line up into a favorable arrangement. An example of this is the interactions found between molecules of iodine (I_2). In contrast, polar molecules are held together by stronger dipole-dipole interactions. Additionally, molecules that contain N-H, O-H, or F-H bonds exhibit a special dipole-dipole interaction called hydrogen bonding, which is unusually strong even for a polar interaction. Ammonia (NH_3) and water are examples of small molecules that exhibit hydrogen bonding. The cations and anions in an ionic compound are held together by very strong ionic bonds, but ion-dipole interactions are nearly as strong. Ion-dipole interactions would be found, for example, when an ionic substance like NaCl is dissolved in water. Each ion is attracted to the appropriate end of the dipole on surrounding molecules of water.

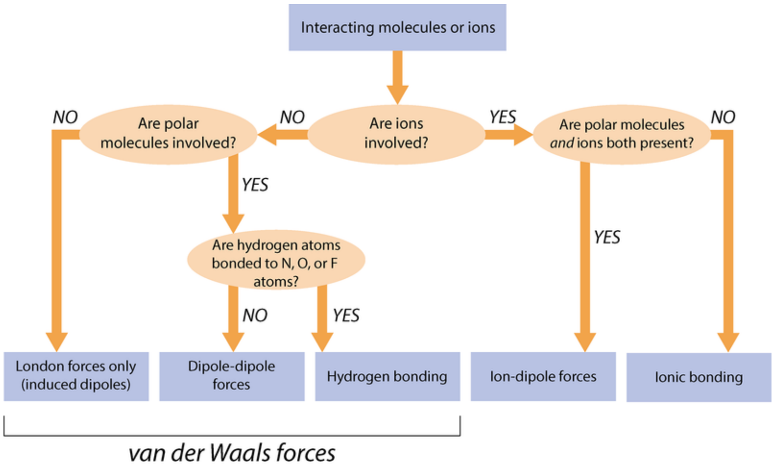

FIGURE 16.2

Decision tree for types of intermolecular interactions

Liquid Solutes

When combining two liquids, we can generally predict whether they will mix to form a homogeneous solution or not by looking at the relative polarity of each substance. We will consider three scenarios: the combination of two polar liquids, the combination of one polar and one nonpolar liquid, and the mixing of two nonpolar liquids.

Polar-Polar Interactions

Polar-polar interactions occur when two or more polar liquids are mixed. An example of this is when methanol mixes with water. Both of these are small polar molecules containing O-H bonds, which means that they can both participate in hydrogen bonding. **Figure** 16.3 shows molecules of methanol and water connected by hydrogen bonds. Because of these strong interactions, the two substances mix freely to form a homogeneous mixture; they are **miscible**. One way to remember this interaction is the phrase "like dissolves like." In this case, a polar solvent dissolves polar solutes.

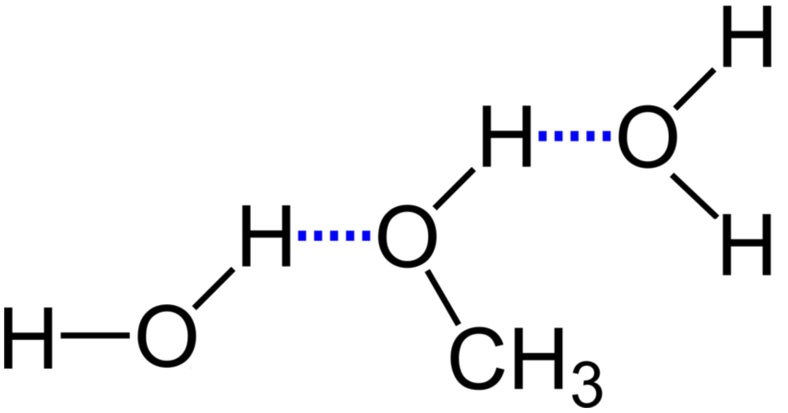

FIGURE 16.3
Hydrogen bonding between methanol and water.

Nonpolar-Polar Interactions

Toluene ($C_6H_5CH_3$ is an organic compound that is often used as a solvent in paint thinners. Toluene is a nonpolar compound. When mixed with water, the two substances will separate into two layers rather than forming a homogeneous solution; these two liquids are **immiscible**. Toluene is a nonpolar chain that cannot form hydrogen bonds with water. Dissolving this chain in water would break up the strong hydrogen bonds between water molecules and replace them with weaker dispersion forces. This is generally not energetically favorable, so the liquids tend to separate themselves to maximize the number of strong attractive interactions.

Example 16.2

Can you think of two other liquids that are immiscible and form a heterogeneous mixture?

Answer:

Another familiar example is the mixing of vinegar and olive oil. Olive oil is a nonpolar substance, while vinegar (which is mostly water and acetic acid) is polar. The result is a heterogeneous mixture that exhibits a bilayer.

Nonpolar-Nonpolar Interactions

Nonpolar-nonpolar interactions occur when two nonpolar liquids are mixed. An example of this is the interaction between toluene and octane (see **Figures** above and 16.5). The interactions between a molecule of toluene and a molecule of octane are relatively weak, but so are the toluene-toluene and octane-octane interactions. Because no strong intermolecular forces (like those between water molecules) need to be broken for mixing to occur, no strong interactions need to be formed in order for mixing to be a favorable process. Toluene and octane will form

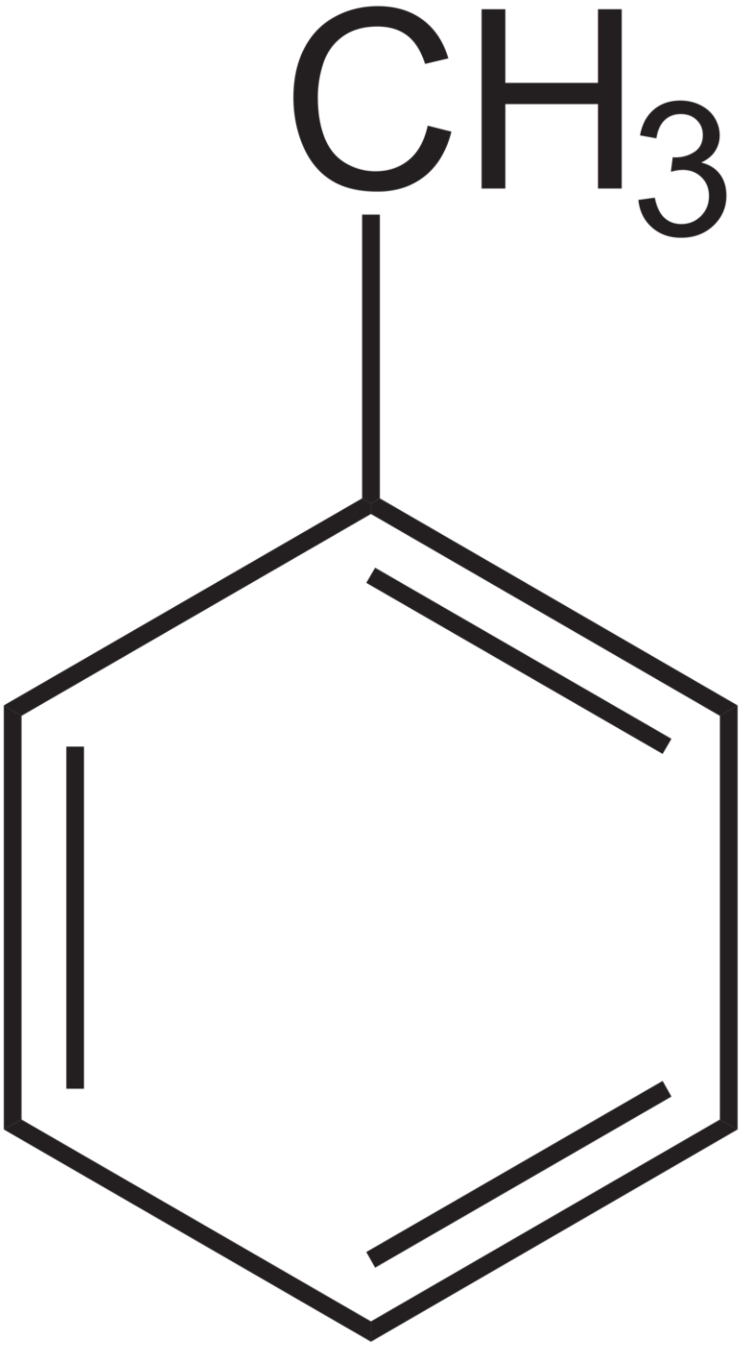

FIGURE 16.4

a homogeneous mixture. The phrase "like dissolves like" applies to these mixtures as well. In this case, nonpolar dissolves nonpolar.

Example 16.3

Can you think of another example of a nonpolar-nonpolar interaction between two different liquids that form a homogeneous mixture?

Answer:

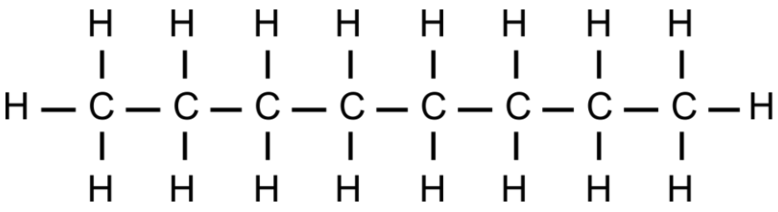

FIGURE 16.5

Another example of a nonpolar-nonpolar interaction between two different liquids would be the mixing of motor oil and gasoline. Both of these substances are nonpolar, so they are miscible and form a homogeneous mixture when combined.

Solid Solutes

Solutions can also be comprised of a solid solute and a liquid solvent. These interactions are governed by the same three interactions we discussed earlier: polar-polar, nonpolar-polar, and nonpolar-nonpolar. The **Table** 16.1 describes these interactions.

TABLE 16.1: **Solution Interactions**

Solid (solute)	Liquid (solvent)	Example	Result
polar	polar	NaCl + H_2O	Homogeneous solution
nonpolar	polar	I_2 + H_2O	Heterogeneous mixture
polar	nonpolar	NaCl + Toluene	Heterogeneous mixture
nonpolar	nonpolar	I_2 + Toluene	Homogeneous mixture

Example 16.4

Using the data in the **Table** 16.1, could you replace the solute or the solvent in the heterogeneous mixtures with another material to make them homogeneous?

Answer:

There are several combinations that could be described. For instance, in the polar-nonpolar mixture between NaCl and toluene, the NaCl could be replaced with a nonpolar solid, like I_2, or the toluene could be replaced with a polar substance, like water.

Ionic Solids in Water

When placed in water, ionic solids dissolve to varying degrees. Some ionic solids have a high solubility in water (e.g., NaCl), while others barely dissolve at all (e.g., AgCl). Still others are moderately soluble (e.g., Ag_2CO_3). The solubility rules we studied in the chapter on *Chemical Reactions* provide guidelines for predicting the relative solubility of a given ionic compound in water. In this chapter, we will focus primarily on water-soluble ionic solids.

When a soluble ionic solid is added to water, it interacts with water molecules and dissociates into isolated ions that diffuse out into the solution. These charged particles become solvated by surrounding water molecules (**Figure** 16.6). Although the strong ionic bonds in the solid are broken up, they are replaced by numerous favorable interactions between the charged ions and the partial charges on the appropriate ends of the polar water molecules.

Notice that for each unit of NaCl that dissolves, two particles are freed into solution, the Na^+ cation and the Cl^- anion. This means that if one mole of NaCl is dissolved, 2 moles of solute particles are found in the homogeneous solution (one mole of each ion). This dissociation is quantified by something called the **van't Hoff factor**. The van't Hoff factor (i) describes the number of moles of solute particles that are found in a solution when one mole of a substance is completely dissolved. The van't Hoff factor for NaCl would be expressed as i = 2.

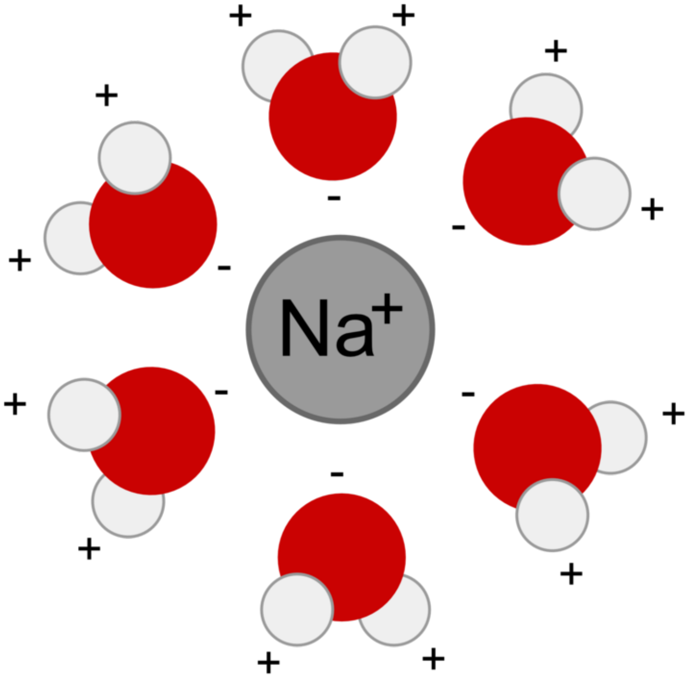

FIGURE 16.6

We can describe the dissociation of magnesium fluoride as follows:

$MgF_2 \rightarrow Mg^{2+} + 2\ F^{-}$

Each unit of magnesium fluoride contains three ions (one Mg^{2+} ion and two F^{-} ions). Using the van't Hoff factor to describe this dissociation, we would say that i = 3, because three moles of ions are produced from the dissociation of one mole of the ionic solid.

Gas Solutes

Gases are also capable of dissolving in liquids. There are many examples of this in our everyday lives. For example, carbonated beverages contain dissolved carbon dioxide. We notice this when bubbles come out of solution when the beverage is opened. Another example is when oxygen from the air we breathe dissolves in our blood, where it is transported throughout the body. Fish and other aquatic organisms use gills to capture dissolved oxygen from their environments.

Because determining the mass of a gaseous sample is generally less convenient than determining how many moles are present, solubilities for gases are often expressed as concentrations instead of as the mass that can be dissolved in a specified amount of solvent. A solution in which one mole of a gas is dissolved in one liter of solution has a concentration of 1 molar (1 M). Because the solubility of most gases is much less than that, the molar solubility is often given in millimolar (mM). A one millimolar solution contains 1/1000 mol of solute per liter of solution. Other methods of expressing concentration, such as parts per million (ppm) or parts per billion (ppb), will be discussed in the following lesson.

Example 16.6

What does it mean if the molar solubility of a gas is 2.0 mM?

Answer:

Each liter of solution can hold a maximum of 2.0 millimoles of that particular gas at the indicated temperature and pressure.

Temperature Effects

As with all substances, the solubility of gases is temperature dependent. However, in contrast to the situation for most solids and liquids, higher temperatures will decrease the solubility of a gaseous solute. **Figure** 16.7 shows this relationship with several common gases.

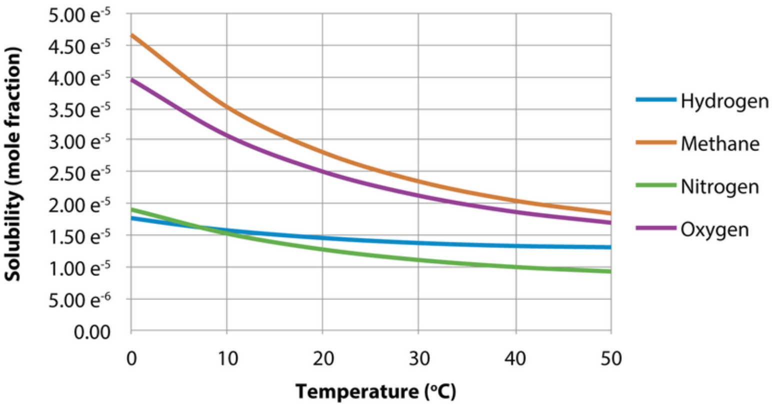

FIGURE 16.7

Solubility-temperature curves for various common gases.

This inverse relationship between solubility and temperature can be understood by looking at a molecular model. Recall that higher temperatures are associated with faster particles. Gas particles are held in solution by attractive interactions with the solvent molecules. If the particles are moving slowly, these attractive forces will pull back any particles that try to escape the surface of the solution and re-enter the gas phase. However, if the gas particles are moving fast enough, these interactions will not be sufficiently strong to prevent this process from occurring. As a result, more particles are able to escape, and the amount of dissolved solute is less than it would be at a lower temperature.

Pressure Effects

At a constant temperature, the amount a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in the area immediately adjacent to the solution. This principle is called **Henry's Law** and is illustrated in **Figure** 16.8.

Mathematically, Henry's Law is expressed as follows:

$\rho = k_H c$

where ρ is the partial pressure of the gas, c is its molar solubility at the given temperature and pressure, and k_H is a constant that depends on the temperature and the identities of both the solute and solvent. Some k_H values for various gases dissolved in water at 298 K are presented in the **Table** 16.2.

TABLE 16.2: kH Values for Various Gases Dissolved in Water at 298 K

Gas	Constant (Pa•mol^{-1}•L)	Constant (atm•mol^{-1}•L)
He	282.7×10^6	2865
O_2	74.68×10^6	756.7

TABLE 16.2: (continued)

Gas	Constant (Pa•mol^{-1}•L)	Constant (atm•mol^{-1}•L)
N_2	$155. \times 10^6$	1600.
H_2	121.2×10^6	1228
CO_2	2.937×10^6	29.76
NH_3	5.69×10^6	56.9

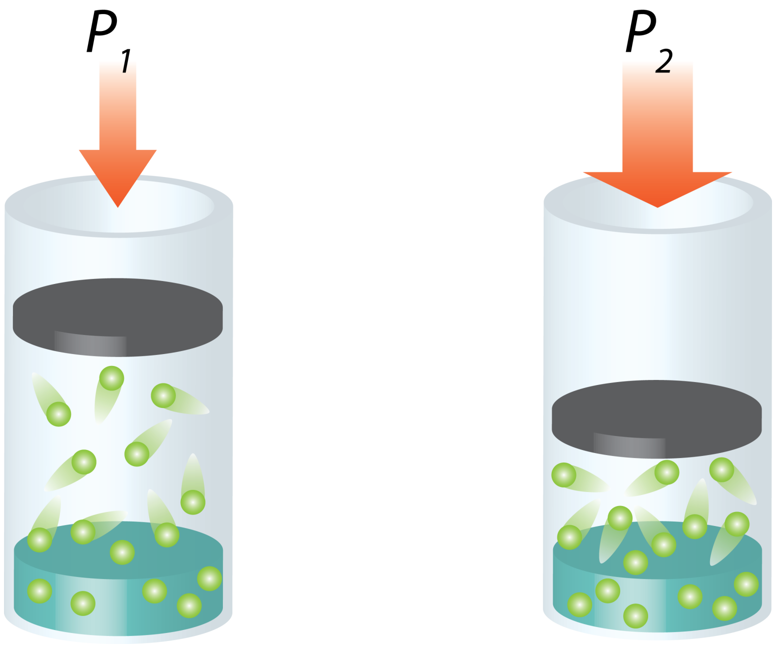

FIGURE 16.8

Illustration of pressure effects on gas solubility.

If we solve the Henry's Law equation for the molar solubility, we get the following useful relationship:

$c = \frac{\rho}{k_H}$

Example 16.7

What are the molar solubilities of oxygen gas and nitrogen gas in pure water at 298 K and 1 atm of pressure? Which gas is more soluble under these conditions?

$$\begin{aligned}
c_{O_2} &= \frac{1 \text{ atm}}{756.7 \text{ atm} \cdot \text{mol}^{-1}\text{L}} \\
&= 0.00132 \text{ mol/L} \\
&= 1.32 \text{ mM} \\
c_{N_2} &= \frac{1 \text{ atm}}{1600. \text{ atm} \cdot \text{mol}^{-1}\text{L}} \\
&= 0.000625 \text{ mol/L} \\
&= 0.625 \text{ mM}
\end{aligned}$$

Oxygen gas is more soluble under these conditions. A saturated solution of O_2 would have a concentration of 1.32 mM, whereas a saturated solution of N_2 would have a concentration of 0.625 mM.

Lesson Summary

- Solubility describes the degree to which a solute will dissolve in a particular solvent.
- Water is a common solvent for dissolving various solids, liquids, and gases.
- The solubilities of solids and liquids are commonly expressed as grams of solute that can be dissolved by 100 g of water at a specified temperature.

- Solutions can be unsaturated, saturated, or supersaturated, depending on the relationship between the solubility of a substance and the amount that is actually dissolved.
- The solubility of gases, liquids, and solids are affected by changes in temperature.
- Solutes and solvents that have similar polarities (i.e., both are polar, or both are nonpolar) tend to mix well, creating homogeneous solutions. Solutes and solvents with very different polarities (i.e., one is polar, and the other is nonpolar) often do not mix well, resulting in the formation of heterogeneous mixtures.
- The solubilities of gases are often described as concentrations (i.e., mM or M) rather than the mass that can be dissolved by a given mass of solvent.
- The solubility of a gaseous solute is inversely related to the temperature of the solvent and directly proportional to the partial pressure of the gas in the surrounding atmosphere.
- Henry's law describes the mathematical relationship between the concentration of a gaseous solute and its partial pressure in the gas above the solution.

Review Questions

1. Draw the mixture that would be formed when oil and water are combined.
2. Give an example of molecular solid that dissolves in water due to polar-polar interactions.
3. Ammonia (NH_3) dissolves well in water. Explain how this interaction might occur and the type(s) of intermolecular forces that would be involved.
4. Using the solubility-temperature curve in **Figure** 16.1, describe conditions under which a solution of potassium chloride would be unsaturated, saturated, and supersaturated at 20°C.
5. A solution is formed by dissolving 10. grams of potassium chlorate in 100. g of water at 30°C. If the solution were heated to 40°C, how many more grams of solute could be dissolved?
6. A solution that is saturated with both methane and oxygen gas at 1 atm and 20°C is then heated to 40°C. What will happen to the dissolved gases as the temperature increases? Referring back to **Figure** 16.7, how much of each gas would leave the solution? How much would remain?
7. Which of the gases in **Table** 16.2 would have the highest solubility in water at 298 K? Which would have the lowest solubility?
8. Urea (CH_4N_2O) is a molecular solid that has a relatively high solubility in water. How would you account for this fact? The molecular structure for urea is shown below.

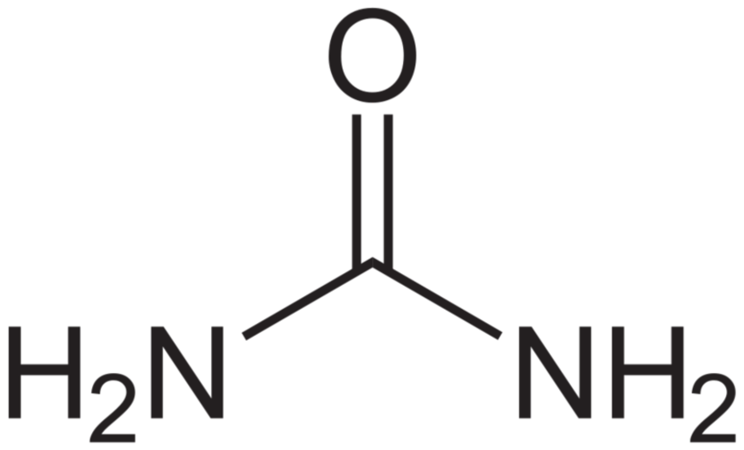

FIGURE 16.9

9. Which of the following substances would dissolve better in water: iodine crystals (I_2) or liquid methanol

(CH_3OH)? How would you categorize the resulting solute-solvent interactions?

Further Reading / Supplemental Links

- Solubility-pressure curves for a variety of gases: http://www.engineeringtoolbox.com/gases-solubility-water-d_1148.html
- Supersaturated solution demonstration: http://www.youtube.com/watch?v=D1PDE5OawuI

Points to Consider

- When you open a can of soda or sparkling water, you can usually see some gas escape or bubble out of the can. Based on the relationship between pressure and gas solubility, why might this occur?
- Why do you suppose it is better to wash your dishes with warm water than with cold water? Explain these effects in terms of solubility.

16.2 Solution Concentration

Lesson Objectives

- Describe the concept of concentration as it applies to solutions, and explain how concentration can be increased or decreased.
- Define molarity and molality, including the most commonly used units for each measurement.
- Define weight percent and be able to determine the weight percent of a solute in a given solution.
- Understand how a dilution changes the concentration of a solution, and be able to perform calculations related to this process.

Lesson Vocabulary

- **molarity (M)**: Moles of solute per liter of solution (mol/L).
- **molality (m)**: Moles of solute per kilogram of solvent (mol/kg).
- **weight percent (w/w)**: The weight of solute divided by the weight of solution, expressed as a percentage.
- **parts per million (ppm)**: The number of particles of a certain solute divided by the total number of particles in a solution, converted to number of particles of solute per one million particles of solution.
- **dilution**: The process of lowering the concentration of a solution by adding more solvent.

Check Your Understanding

1. Which of the following statements is false regarding a solution?
    a. The amount of solute is always less than the amount of solvent.
    b. Water is a common solvent.
    c. You can have a solution where there is zero solute.
    d. Polar solutes will likely dissolve in polar solvents.

Introduction

A solution is comprised of at least two components - the solvent and one or more solutes. Although many different substances (including solids, liquids, and gases) can act as a solvent, we are now going to focus primarily on aqueous solutions, in which water acts as the solvent. Water is the most common solvent that we encounter in our daily lives. In this section, we will explain how to determine the concentration for a given solution and how to create solutions of known concentrations.

Solution Concentration

In its most general form, concentration describes the number of items in a given area or volume. The units generally depend on the types of items being counted. For example, if we were to calculate the concentration of people that live in a city, we would divide the total number of people by the area. If we measured the area in square miles, the units of concentration for this measurement would be people per square mile. Or, we could determine the concentration of fish in a lake by dividing the total number of fish by the volume of the lake. If we measure the volume in cubic meters, the concentration would have units of fish per cubic meter.

To express the concentration of a solution, we can perform a similar calculation. The amount of solute is commonly measured in terms of moles, but it can also be measured by mass or by total number of particles. We can then divide this value by either the amount of solvent or the total amount of solution. These values may have units of mass, volume, moles, or number of particles. Depending on how each component is measured, we get different ways to measure concentration. In this lesson, we will learn about four different ways to describe the concentration of a solution:

1. Molarity - moles of solute divided by volume (in liters) of solution.
2. Molality - moles of solute divided by mass (in kilograms) of solvent.
3. Weight percent - mass of solute divided by mass of solution.
4. Parts per million (or parts per billion) - particles of solute divided by particles of solution.

Each of these ways of describing concentration will be discussed further below.

Molarity

The most common way to express the concentration of a solution is by determining its molarity. The **molarity** of a solution tells us how many moles of solute are present in each liter of solution. It can be calculated as follows:

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

Molarity has units of moles per liter (mol/L). Moles per liter is also given the abbreviated name **molar** (M). For example, a solution that contains 2 moles of solute in each liter of solution would be a 2 molar (2 M) solution.

Example 16.8

What is the molarity (M) of a 3.4 liter sample of a solution that contains 0.32 moles of NaCl?

Answer:

$\text{M}_{NaCl} = \frac{\text{0.32 mol NaCl}}{\text{3.4 L}} = 0.094 \text{ M}$

When indicating solution concentration in molarity, a bracket notation is often used. For instance, from the previous example we could write:

NaCl =0.094

This indicates a 0.094 M solution of sodium chloride.

Making Solutions of a Specific Molarity

To make a solution with a particular concentration of a given solute, the following procedure can be used:

1. Calculate the moles of solute that would be present in the entire desired solution, and then use the molar mass of the solute to calculate the mass that you will need.

2. Weigh out the appropriate amount of solute, and place it in a volumetric flask.
3. Fill the flask about halfway with solvent, and swirl until the solute is completely dissolved.
4. Finally, add enough solvent so that the meniscus of the solution lines up with the calibration mark on the flask.

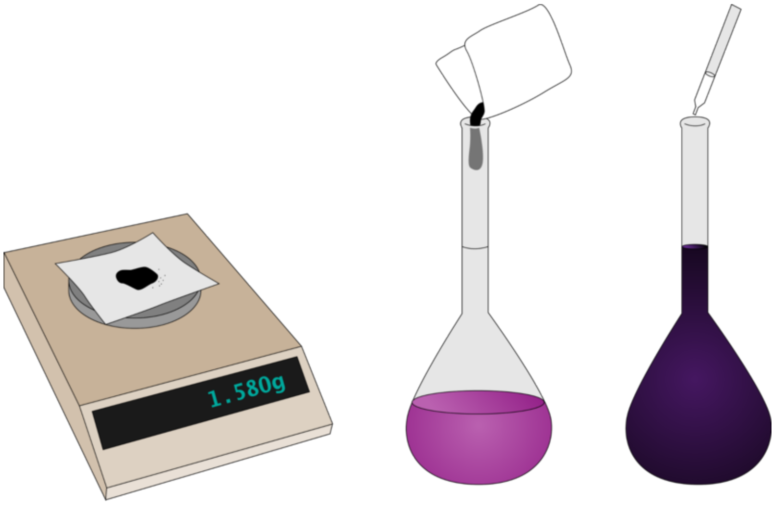

FIGURE 16.10

Example 16.9

You want to make a 0.154 M solution of sodium chloride (the approximate concentration of a standard saline solution). Describe how you would prepare 1.00 L of this solution.

Answer:

Step 1: Calculate

The molarity of our solution is going to be 0.154 M, and the total volume will be 1.00 L. Plugging these values into the definition of molarity will allow us to calculate the necessary moles of solute.

$$\begin{aligned} \text{M} &= \frac{\text{mol}}{\text{L}} \\ \text{mol} &= \text{M} \times \text{L} \\ &= (0.154 \text{ M}) \times (1.00 \text{ L}) \\ &= 0.154 \text{ mol NaCl} \end{aligned}$$

Because we will be measuring out NaCl by mass, we need to determine the mass of 0.154 moles of NaCl using its molar mass (58.44 g/mol).

$0.154 \text{ mol NaCl} \times \frac{58.44 \text{ g NaCl}}{1 \text{ mol NaCl}} = 9.00 \text{ g NaCl}$

Step 2: Weigh out 9.00 g of NaCl and place it in a 1 L volumetric flask.

Step 3: Fill the flask about halfway with water, and swirl until the NaCl is completely dissolved.

Step 4: Add more water until the meniscus of the solution lines up with the calibration mark. Mix well.

Molality

Another way to express the concentration of a solution is by determining its molality. The **molality** (m) of a solution tells us how many moles of solute are combined with each kilogram of solvent. Note that there are two differences between molarity and molality. Molality uses mass instead of volume, and we are looking at the amount of *solvent* instead of the total amount of *solution*. It can be calculated as follows:

molality = $\frac{\text{moles solute}}{\text{kg solvent}}$

Molality is primarily useful for calculating certain physical properties of solutions, such as freezing point, boiling point, and vapor pressure. These will be discussed in the next lesson.

Example 16.10

What would be the molality of an sugar solution in which 4.00 g $C_6H_{12}O_6$ was dissolved in 1.00 L of water? Water has a density of 1.00 g/mL.

Answer:

$$\text{molality} = \frac{\text{moles solute}}{\text{kg solvent}}$$

We need to find the amount of solute (sugar) in moles and the mass of the solvent in kilograms.

$$\text{moles solute} = 4.00 \text{ g } C_6H_{12}O_6 \times \frac{1 \text{ mol } C_6H_{12}O_6}{342.30 \text{ g } C_6H_{12}O_6} = 0.0117 \text{ mol } C_6H_{12}O_6$$
$$\text{kg solvent} = 1.00 \text{ L } H_2O \times \frac{1000 \text{ mL } H_2O}{1 \text{ L } H_2O} \times \frac{1.00 \text{ g } H_2O}{1 \text{ mL } H_2O} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 1.00 \text{ kg } H_2O$$

Substituting these values into our molality expression, we get the following:

$$\text{molality} = \frac{0.0117 \text{ mol NaCl}}{1.00 \text{ kg } H_2O} = 0.0117 \text{ m}$$

Weight Percent

Another way to express the concentration of a solution is by its weight percent. This is commonly used to describe stock solutions of things like acids and bases. **Weight percent** can be calculated by dividing the mass of a solute by the mass of the entire solution:

$$\text{Weight Percent} = \frac{\text{grams of solute}}{\text{grams of solution}} \times 100\%$$

A solution in which 9.3% of the mass is due to NaCl would be referred to as a 9.3% (w/w) NaCl solution. The presence of "(w/w)" indicates that the ratio is between the weight (mass) of the solute and the weight of the total solution. Other ratios in which one or both of the components are measured in terms of volume instead of mass are also common; these percentages are labeled as either weight/volume (w/v) or volume/volume (v/v).

Example 16.11

What is the weight percent of a solution that has 9.01 g of NaCl dissolved in 1000. g of water?

Answer:

Grams of solution = grams of NaCl + grams of water = 9.01 g NaCl + 1000 g H_2O = 1009 g solution

$$\text{Weight Percent} = \frac{9.01 \text{ g NaCl}}{1009 \text{ g solution}} \times 100\% = 0.893\%$$

This mixture could be described as a 0.893% (w/w) solution of NaCl in water.

Parts Per Million

We can also express concentrations by dividing the number of particles of a certain solute by the total number of particles in a solution. These types of values are commonly used to describe small amounts of a substance in a complex mixture. Common units for this type of concentration are **parts per million** (ppm) and parts per billion (ppb). Let's say we have a sample of water in which Pb^{2+} is present at a concentration of 20 ppm. This would mean that if we randomly took a million particles from our solution, 20 of them (on average) would be Pb^{2+} ions. The rest would be mostly water molecules, with a possibility of the presence of various other ions. The maximum allowable concentrations of various toxic gases in the air or heavy metal ions in drinking water are often reported in units of ppm or ppb.

If given information on aqueous solution concentration by ppm, these units can be converted to molarity or molality using the following conversion factor:

1 ppm= 1 mg/ L

This conversion is derived from the fact that ppm is really just a ratio between amount of solute and amount of solution. If you had a 1 ppm solution, this would indicate 1 g of solute per 1×10^6 g of solution. Assuming an aqueous solution density of 1 g/mL as is standard for water, this indicates 1 g of solute per 1×10^6 mL of solution, or 1 mg of solute per 1 L of solution. You can use this conversion unit and a similar conversion method for converting concentration from ppm or ppb.

Dilutions

Many chemicals that we use on a daily basis are transported in a concentrated form but used in a more diluted form. For example, concentrated cleaners are often diluted before they are used. To perform a **dilution**, pure solvent is added to a concentrated solution in order to make a less concentrated (more dilute) solution. The resultant solution will contain the same amount of solute but a greater amount of solvent. It will therefore have a lower concentration than the original solution. When performing a simple dilution, the concentration and volume of the initial solution are related to the new concentration and volume as follows:

$M_1V_1 = M_2V_2$

M_1 = initial molarity, V_1 = initial volume

M_2 = final molarity, V_2 = final volume

This relationship holds true due to the fact that the moles of solute stays constant through a dilution process.

Example 16.12

50.0 mL of a 0.40 M NaCl solution is diluted to 1000.0 mL. What is the concentration of NaCl in the new solution?

Answer:

Determine the values of each variable in the dilution equation above, and then solve for the unknown variable.

V_1 = 50.0 mL, M_1 = 0.40 M, V_2 = 1000.0 mL, and M_2 = ?

Solving the above equation for M_2 gives us the following:

$$\begin{aligned} M_2 &= \frac{M_1V_1}{V_2} \\ &= \frac{(50.0\text{ mL})(0.40\text{ M})}{(1000\text{ mL})} = 0.020\text{ M} \end{aligned}$$

Lesson Summary

- The concentration of a solution can be expressed as the amount of solute present in a given amount of solvent or solution.
- The most common way to express the concentration of a solution is molarity, which is equal to moles of solute per liter of solution.
- Another way to express concentration is molality, which is equal to moles of solute per kilogram of solvent.
- The ratio of solute mass to solution mass, when expressed as a percentage, is known as weight percent.
- The ratio of solute particles to the total number of particles in a solution can be expressed in units of parts per million (ppm) or parts per billion (ppb).
- Concentrated solutions can be diluted by adding pure solvent. The concentration and volume of the initial solution are related to the new concentration and new volume by the equation $M_1V_1 = M_2V_2$.

Review Questions

1. You have 3.50 L of a solution that contains 90.0 g of sodium chloride (NaCl). What is the molarity of the solution?
2. You have 0.8 L of a 0.5 M HCl solution. How many moles of HCl does this solution contain?
3. We want to make 125 mL of a 0.154 M NaCl solution. How many grams of NaCl are needed?
4. A stock bottle of concentrated hydrochloric acid is a 37% (w/w) HCl solution. What is the molarity of this solution? How many moles of HCl are in a 10 mL sample of this concentrated acid? The density of 37% HCl is 1.19 g/mL.
5. To produce 40.0 g of silver chromate, you will need at least 23.4 g of potassium chromate in solution as a reactant. Available to you is 5 L of a 6.0 M K_2CrO_4 solution. What volume of the solution is required to give you the 23.4 g K_2CrO_4 needed for the reaction?
6. 5.85 g of potassium iodide (KI) is dissolved in enough water to make 0.125 L of solution. What is the molarity of this solution?
7. How many moles of H_2SO_4 are present in 0.500 L of a 0.150 M H_2SO_4 solution?
8. Calculate the molality of a solution in which 22.0 grams of KBr is dissolved in 250.0 mL of pure water.
9. What is the molality when 0.75 mol of a substance is dissolved in 2.50 L of water?
10. You have 1.00 L of water. How many grams of sucrose would need to be added in order to make a 1.0 molal solution?
11. Isopropyl alcohol is typically sold as a 70% (w/w) solution in water. What is the molarity of such a solution? Assume that the density of 70% (w/w) isopropyl alcohol is 0.786 g/mL.
12. If a solution contains Pb^{2+} ions at a concentration of 15.0 ppm, what would the molarity of this solution be?
13. The presence of sodium fluoride in drinking water at the level of 2 ppm may cause mottled enamel in teeth, skeletal fluorosis, and may be associated with cancer and other diseases. Calculate the molarity of a 2 ppm solution of sodium fluoride.
14. You want to make 500. mL of 0.050 M HCl by diluting a 6.0 M HCl solution. How much of the concentrated HCl solution is needed?

Further Reading / Supplemental Links

- Making solutions: http://www.science-projects.com/solutions.htm

Points to Consider

- How do you decide which method should be used to express the concentration of a given solution?

16.3 Colligative Properties

Lesson Objectives

- Define and give examples of colligative properties.
- Define vapor pressure and describe the conditions that affect it.
- Calculate changes in vapor pressure using Raoult's law.
- Define boiling point elevation and be able to calculate the boiling point elevation for a particular solution.
- Define freezing point depression and be able to calculate the freezing point depression for a particular solution.
- Determine the molar mass of a solute from boiling point elevation or freezing point depression data.

Lesson Vocabulary

- **vapor pressure**: A measure of the force exerted by a gas above a liquid in a sealed container.
- **colligative propery**: Solution properties which are dependent strictly on the amount of solute added and not the type of solute added.
- **Raoult's law**: States that vapor pressure of a solution equals the product of the vapor pressure of the pure solvent and the mole fraction of solvent, as described by: $P = x_{solvent} P^{\circ}$.
- **mole fraction**: The moles of a solution or mixture component divided by the total amount (in moles) of all components in the solution or mixture.
- **boiling point elevation**: A property describing the increase in boiling point observed when a solute is added to a pure solvent.
- **freezing point depression**: A property describing the decrease in freezing point observed when a solute is added to a pure solvent.

Check Your Understanding

1. Compare and contrast molarity and molality.
2. How many moles of $BaCl_2$ are present in 250 mL of a 2.0 M $BaCl_2$ solution?
3. Calculate the molality of a solution in which 50.0 grams of sodium nitrate have been dissolved in 1.00 L of H_2O.

Introduction

When a solute is dissolved in a liquid solvent to form a homogeneous solution, the behavior of the solution will often be different from that of the pure solvent. For example, the boiling point, freezing point, and vapor pressure of the solution will be different from that of the original solvent. The freezing point of salt water is lower than the freezing point of pure water, and the boiling point of a sucrose solution is higher than that of pure water. In this lesson, we will look at how to calculate the magnitude of these changes based on the concentration of the solution.

Vapor Pressure

As we saw when we studied *States of Matter*, the driving force for particles in the liquid phase to escape into the gas phase depends on both the temperature and identity of the substance. The vapor pressure of a liquid is a measure of this ability. Specifically, **vapor pressure** is the pressure exerted by a vapor that is in equilibrium with its solid or liquid phase. For substances with a stronger drive to enter the gas phase, more vapor particles will be present in the same amount of space, resulting in a higher pressure. At a given temperature, the vapor pressures of various liquids depends primarily on the strength of intermolecular attractions between individual particles. **Figure** 16.11 shows the relative vapor pressures of several different substances.

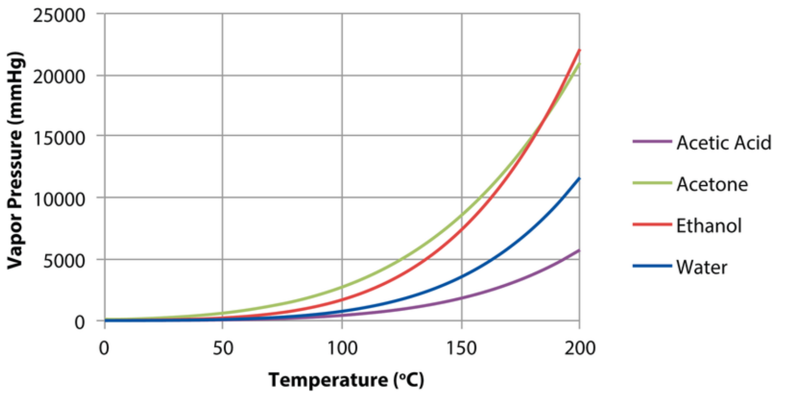

FIGURE 16.11

Vapor Pressure –Temperature Curve

Overall, molecules that can participate in hydrogen bonding, such as acetic acid, tend to have lower vapor pressures at a given temperature than similarly sized molecules without the ability to hydrogen bond, such as acetone.

Vapor Pressure of Solutions

The vapor pressure of a solution is lower than that of the pure solvent at the same temperature. This decrease in vapor pressure is one example of a **colligative property**. Colligative properties are properties of solutions that depend only on the concentration of dissolved particles and not on their identity.

As we see in **Figure** 16.12, the vapor pressure of the solution is lower than the vapor pressure of the pure solvent. This phenomenon can be understood by considering the equilibrium between the liquid and the gas phases for a given solvent. When a pure solvent reaches equilibrium with its vapor, the liquid particles are escaping into the gas phase at the same rate as the gas particles are condensing into the liquid phase. If we add a non-volatile solute (one that does not escape into the vapor phase under standard conditions), the liquid becomes a mixture of solute and solvent particles. The surface will then be composed of solute particles in addition to solvent molecules, which slows the rate at which the liquid particles can evaporate due to fewer solvent molecules in contact with the liquid/vapor interface. However, it does not slow down the rate of condensation. As a result, there is a net shift into the liquid phase. Less solvent is present in its vapor form, so the resulting vapor pressure is lower. This effect is illustrated on the molecular level in **Figure** 16.13.

This effect is quantified by **Raoult's law**, which states that the vapor pressure of a solution is equal to the vapor pressure of the pure solvent multiplied by its mole fraction. Raoult's law can be expressed mathematically as follows:

$P = \chi_{solvent} P^\circ$

where P is the vapor pressure of the solution, $\chi_{solvent}$ is the mole fraction of the solvent, and P° is the vapor pressure

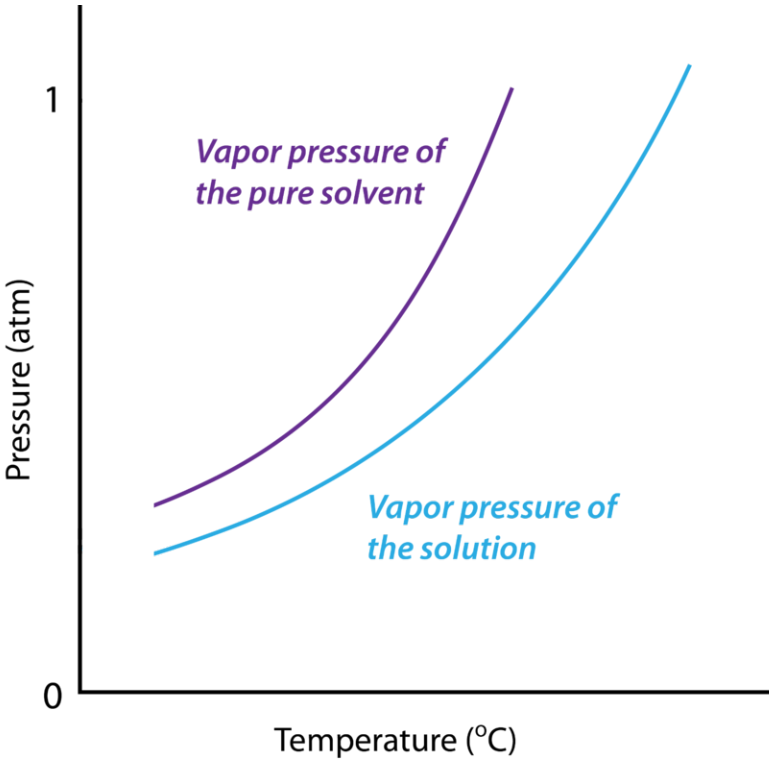

FIGURE 16.12

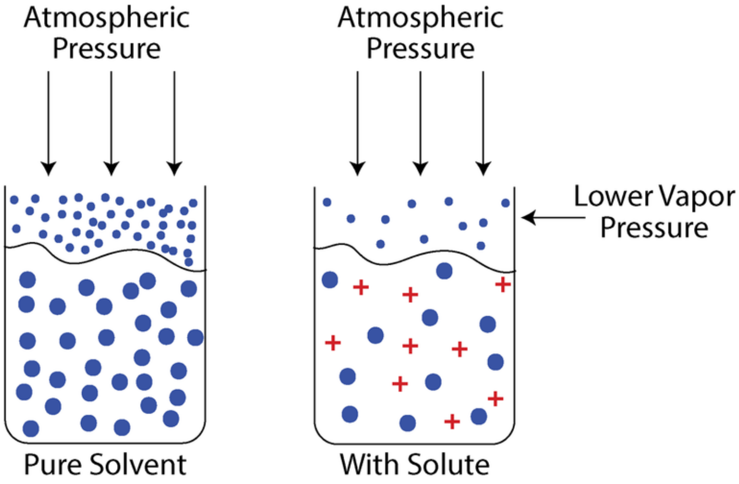

FIGURE 16.13
Vapor-Pressure Lowering in Solution

of the pure solvent.

Mole Fraction

The **mole fraction** (χ) of a component in a mixture is equal to the number of particles of the specified component divided by the total number of particles in the mixture. Alternatively, this ratio can be expressed in moles.

$\text{Ø}_A = \frac{\text{mol A}}{\text{total mol}}$

or

$Ø_A = \frac{n_A}{n_{total}}$

Note that we are dealing with the total number of particles (or moles of particles), so we need to take the dissociation of ionic substances into account. If we dissolve one mole of NaCl in water, we would end up with two moles of independent particles (one mole of sodium ions and one mole of chloride ions). This information needs to be included in any mole fraction calculations.

Example 16.13

22.6 grams of KCl is dissolved in 2000. grams of water. Determine the mole fraction of KCl.

Answer:

$$\begin{aligned}
Ø_A &= \frac{n_A}{n_{total}} \\
n_A &= 22.6 \text{ g KCl} \times \frac{1 \text{ mol KCl}}{74.55 \text{ g KCl}} \times \frac{2 \text{ mol ions}}{1 \text{ mol KCl}} = 0.606 \text{ mol ions} \\
n_{H_2O} &= 2000. \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 111.0 \text{ mol } H_2O \\
n_{total} &= 0.606 \text{ mol} + 111.0 \text{ mol} = 111.6 \text{ mol} \\
Ø_A &= \frac{0.606 \text{ mol}}{111.6 \text{ mol}} = 0.00543
\end{aligned}$$

Boiling Point Elevation

Recall that boiling occurs when the vapor pressure of a liquid is equal to the atmospheric pressure. Since adding a solute lowers the vapor pressure, we would expect a higher temperature to be required before boiling can begin. This phenomenon, known as **boiling point elevation**, occurs whenever a solute is dissolved into a pure solvent.

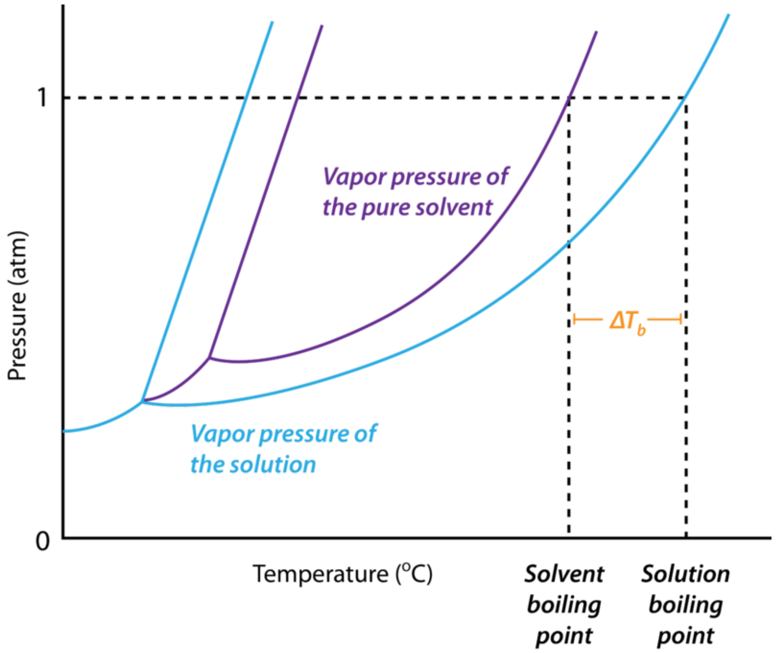

FIGURE 16.14

The boiling point of a solution can be calculated using the following expression:

$$\Delta T_b = k_b \times m \times i$$

where ΔT_b is the increase in boiling point compared to the pure solvent, k_b is the boiling point elevation constant for the given solvent, m is the molality (not molarity) of the solution, and i is the van't Hoff factor.

Example 16.14

Eugenol, the active ingredient in cloves, has the formula $C_{10}H_{12}O_2$. Eugenol is a molecular substance that does not dissociate into ions when dissolved in a solvent. What is the boiling point of a solution in which 0.144 g of eugenol is dissolved in 10.0 g benzene? The k_b value for benzene is 2.53 °C/*m*, and the boiling point of pure benzene is 80.1 °C.

Answer:

$\Delta T_b = k_b \times m \times i$

The van't Hoff factor (i) for a nondissociating substance is 1, and the k_b value for benzene is given, so we only need to calculate the molality of the solution. To do this, we need to determine the moles of the solute and the mass of the solvent in kilograms.

$\text{moles}_{C_{10}H_{12}O_2} = 0.144 \text{ g } C_{10}H_{12}O_2 \times \frac{1 \text{ mol } C_{10}H_{12}O_2}{164.22 \text{ g } C_{10}H_{12}O_2} = 8.77 \times 10^{-4} \text{ mol } C_{10}H_{12}O_2$

$\text{mass of benzene} = 10.0 \text{ g benzene} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 0.0100 \text{ kg benzene}$

$\text{molality} = \frac{8.77 \times 10^{-4} \text{ mol } C_{10}H_{12}O_2}{0.0100 \text{ kg benzene}} = 0.0877\ m$

$\Delta \mathrm{T_b} = 2.53\ °\mathrm{C}/m \times 0.0877\ m \times 1 = 0.222\ °\mathrm{C}$

The boiling point is increased by 0.222 °C compared to the pure solvent. Because the boiling point of pure benzene is 80.1 °C, the boiling point of the solution would be 80.3 °C.

Freezing Point Depression

The addition of solute to a pure solvent affects not only the boiling point of the solution, but the freezing point as well. This phenomenon is called **freezing point depression**, and it can be calculated in essentially the same way as boiling point elevation:

$$\Delta T_f = k_f \times m \times i$$

where ΔT_f is the decrease in freezing point compared to the pure solvent, k_f is the freezing point depression constant for the given solvent, m is the molality (not molarity) of the solution, and i is the van't Hoff factor.

Example 16.15

Calculate the freezing point of a solution in which 5.00 g of biphenyl ($C_{12}H_{10}$) and 7.50 g of naphthalene ($C_{10}H_8$) are dissolved in 200.0 g of benzene. None of these substances dissociate into ions. The normal freezing point of benzene is 5.5 °C, and its k_f value is 5.12 °C/*m*.

Answer:

$\Delta T_f = k_f \times m \times i$

We are given k_f, and i is 1 for nondissociating substances. To determine the molality of the solution, we will need to know the total moles of solute and the mass of the solvent in kilograms. Because colligative properties like freezing point depression do not depend on the identity of the solute, it does not matter that we have two different types of solute molecules.

$\text{moles}_{C_{12}H_{10}} = 5.00 \text{ g } C_{12}H_{10} \times \frac{1 \text{ mol } C_{12}H_{10}}{154.22 \text{ g } C_{12}H_{10}} = 0.0324 \text{ mol } C_{12}H_{10}$

$\text{moles}_{C_{10}H_8} = 7.50 \text{ g } C_{10}H_8 \times \frac{1 \text{ mol } C_{10}H_8}{128.18 \text{ g } C_{10}H_8} = 0.0585 \text{ mol } C_{10}H_8$

$\text{mass of benzene} = 200.0 \text{ g benzene} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 0.2000 \text{ kg benzene}$

$\text{molality} = \frac{0.0324 \text{ mol } C_{12}H_{10} + 0.0585 \text{ mol } C_{10}H_8}{0.2000 \text{ kg benzene}} = 0.455\ m$

$\Delta T_f = 5.12\ ^\circ\text{C}/m \times 0.455\ m \times 1 = 2.33\ ^\circ\text{C}$

The freezing point will be lowered by 2.33 °C. Subtracting this from the normal freezing point of benzene (5.5 °C), this solution will freeze at 3.2 °C.

Values of k_f and k_b for some other common solvents are listed in the **Table** 16.3:

TABLE 16.3: Molal Boiling-Point Elevation and Freezing-Point Depression Constants of Several Common Liquids

Solvent	Normal Freezing Point (°C)	k_f (°C/m)	Normal Boiling Point (°C)	k_b (°C/m)
Water	0	1.86	100	0.52
Benzene	5.5	5.12	80.1	2.53
Ethanol	-117.3	1.99	78.4	1.22
Acetic Acid	16.6	3.90	117.9	2.93
Cyclohexane	6.6	20.0	80.7	2.79

Notice that k_f is generally larger than k_b for a given substance.

Lesson Summary

- The degree to which particles of a given liquid tend to escape into the gas phase is measured by the liquid's vapor pressure. The vapor pressure of a solution is a colligative property, which means that it is affected only by the concentration of solute particles and not their identity.
- The vapor pressure of a solution is lower than the vapor pressure of the pure solvent ($P < P^\circ$).
- Raoult's Law states that the vapor pressure of a solution is equal to the product of the vapor pressure of the pure solvent and the mole fraction of the solvent ($P = \chi_{solvent} P^\circ$).
- The mole fraction of a component in a mixture (χ) can be calculated by dividing the number of particles (or moles) of the component by the total number of particles (or moles) in the complete mixture.
- Adding a solute increases the boiling point of a pure solvent. This change can be calculated using the equation $\Delta T_b = k_b \times m \times i$.
- Similarly, adding a solute decreases the freezing point of a pure solvent. This change can be calculated using the equation $\Delta T_f = k_f \times m \times i$.

Review Problems

1. Would you expect water or ethanol (C_2H_5OH) to have a higher vapor pressure at a given temperature?
2. Based on Figure 16.11 in the lesson above, which substance do you suppose has the strongest intermolecular attractions? Which has the weakest intermolecular attractions? Which substance would evaporate most quickly?

3. What would be the vapor pressure of a 1.0 molal NaCl solution?
4. Calculate the boiling point and freezing point of a 1.0 molal NaCl solution.
5. Calculate the boiling point and freezing point of a 1.0 molal aluminum chloride solution. Compare these values to the boiling and freezing points determined for the 1.0 molal NaCl solution in the previous question. Explain any differences.
6. We want to prepare a solution in which the mole fraction of NaCl is 0.20. If the solution contains 80 grams of NaCl, how many grams of water are required?
7. Calculate the mole fractions of both the solute and the solvent in a saturated solution of hydrogen sulfide in water at 20°C and 1 atm. Use the temperature-solubility curve below to determine the solubility of H_2S.

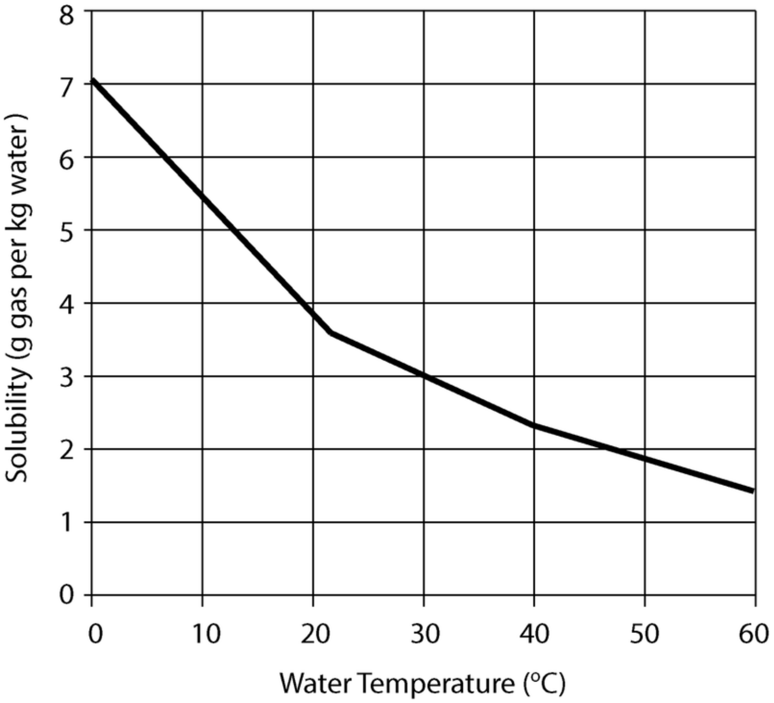

FIGURE 16.15

Solubility –temperature relationship for H_2S

8. How many grams of ethylene glycol ($HOCH_2CH_2OH$) must be added to 5.50 kg of water to lower the freezing point of the water from 0.0°C to -10.0°C? (This is approximately what happens when you put antifreeze in your car.)
9. Vitamin K is involved in the mechanism by which blood clots. When 5.00 g of vitamin K is dissolved in 100.0 g of camphor, the freezing point is lowered by 4.43°C. Calculate the molar mass of vitamin K. K_f for camphor is 37.7°C/*m*, and vitamin K is a molecular substance that does not dissociate into ions.

Further Reading / Supplemental Links

- Freezing-point depression animation: http://group.chem.iastate.edu/Greenbowe/sections/projectfolder/animationsindex.htm
- Boiling-point elevation animation: http://group.chem.iastate.edu/Greenbowe/sections/projectfolder/animationsindex.htm

Points to Consider

- In colder climates, magnesium fluoride is often sprayed on the roads during the winter to reduce icing. What colligative property is being utilized here?
- Would 1 mole of NaCl or 1 mole of MgF_2 have a larger effect on the colligative properties of a given solvent?

16.4 References

1. Christopher Auyeung. CK-12 Foundation . CC BY-NC 3.0
2. Jodi So. CK-12 Foundation . CC BY-NC 3.0
3. User:Jü/Wikimedia Commons. http://commons.wikimedia.org/wiki/File:Methanol_Hydrogen_Bridge_V.2.svg . Public Domain
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CHAPTER 17 Thermochemistry

Chapter Outline

17.1 HEAT FLOW
17.2 ENTHALPY
17.3 ENTHALPY AND PHASE TRANSITIONS
17.4 HESS'S LAW
17.5 REFERENCES

Energy is an integral component of chemical reactions. Some reactions require an input of energy, whereas others release energy as they proceed. When we burn propane, we are oxidizing small hydrocarbons by reacting them with oxygen. This reaction produces heat, which can be used to heat a barbeque for cooking or fill a balloon with hot air so it can soar over the countryside. In this chapter, we will focus primarily on the transfer of heat and energetic changes that occur during chemical reactions.

Adrian Pingstone. commons.wikimedia.org/wiki/File:Flame.inflates.balloon.bath.arp.jpg. Public Domain.

17.1 Heat Flow

Lesson Objectives

- Define thermochemistry.
- Define and give examples of exothermic reactions.
- Define and give examples of endothermic reactions.
- Draw a diagram of a constant-pressure calorimeter.
- Define and perform calculations related to specific heat and heat capacity.

Lesson Vocabulary

- **thermochemistry**: The study of energy relationships in chemical reactions.
- **thermodynamics**: The study of how heat, work, and various forms of energy are related to one another.
- **system**: The chemical reaction being observed, generally within a container.
- **surroundings**: Include everything that is not part of the system.
- **open system**: A system in which both matter and heat can be freely exchanged between the reaction container (the system) and the surroundings.
- **closed system**: A system in which matter cannot enter or leave, but heat can flow between the system and surroundings.
- **isolated system**: An idealized system in which neither matter nor heat can be exchanged between system and surroundings.
- **heat**: A form of thermal energy transferred between two bodies (such as a system and its surroundings) that are at different temperatures.
- **exothermic**: A process in which heat is released to the surroundings.
- **endothermic**: A process in which heat is absorbed from the surroundings.
- **calorimetry**: The measurement of heat transfers, usually through monitoring changes in the temperature of an isolated system.
- **calorimeter**: A device used to measure temperature changes during chemical processes.
- **specific heat**: The amount of energy needed to raise the temperature of one gram of a substance by 1°C.
- **heat capacity**: The amount of heat need to raise the temperature of a specified amount (usually mass) of a material by 1°C.

Check Your Understanding

Recalling Prior Knowledge

- What are the basic types of chemical reactions?
- What is energy?
- What is the law of conservation of energy?

Introduction

Just as the burning of wood releases energy in the form of heat, many other chemical reactions also release heat. There are also chemical reactions, such as photosynthesis in plants, which absorb energy in the form of heat. The study of energy changes in chemical reactions is called **thermochemistry**. The broader term **thermodynamics** also looks at how heat, work, and various forms of energy are related to one another. In this lesson, we will study the difference between reactions that absorb versus release heat as well as how to measure this change in energy.

Chemical Energy and Heat

There are two basic types of energy in the universe: potential energy and kinetic energy. Potential energy is stored energy that is available to do work, but it has not yet been released. The wood in a fireplace possesses potential energy. It is available for producing heat, but has not yet been ignited, so it is not releasing heat into the surrounding environment. Kinetic energy is the energy of motion. A waterfall is an example of kinetic energy. The moving water can erode the rocks in the stream, wearing them down into smaller particles. This same water motion can turn a turbine to generate electricity. In both cases, the movement of the material (water) causes work to be done.

Chemical energy, the energy stored in molecules and atoms, is one type of potential energy. Certain reactions can cause this energy to be released as heat. Other reactions require an input of energy, in which case the products will store more potential energy than the reactants. When we studied phase changes, we saw a relationship between energy and the state of matter. To melt a solid or boil a liquid, energy needs to be added in order to break up the intermolecular forces holding particles together in more ordered states. The reverse processes, condensation and freezing, release energy, because more favorable intermolecular interactions are formed.

When we consider a chemical reaction, we need to take into account both the system and the surroundings. The **system** includes the components involved in the chemical reaction itself. These will often take place in a flask, a beaker, a test tube, or some other container. The **surroundings** include everything that is not part of the system. When potassium reacts with water, part of the heat energy generated in the reaction is released into the surroundings. The boundary between system and surroundings is arbitrary, and it is generally chosen in a way that makes observations and calculations easier.

Depending on the specific setup, a few different types of systems can be described. In an **open system**, both matter and heat can be freely exchanged between the reaction container (the system) and the surroundings. An example would be an open beaker, where any gaseous materials or vaporized molecules are free to leave the system and float off into the atmosphere. In a **closed system**, matter cannot enter or leave, but heat can flow between the system and surroundings. A stoppered reaction flask would be an example of a closed system. Finally, a situation in which neither matter nor heat can be exchanged between system and surroundings is referred to as an **isolated system**. Although truly isolated systems are not really possible, a sealed, vacuum-insulated reaction flask would come very close.

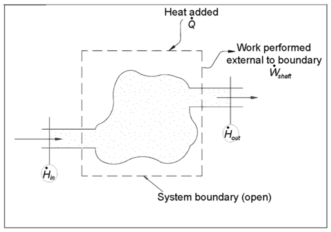

FIGURE 17.1

Open system

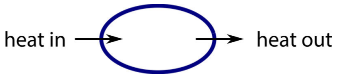

FIGURE 17.2

Closed system. Heat can be exchanged between the system and the surrounding environment, but matter cannot move from one part of the system to another.

Exothermic and Endothermic Processes

Heat involves the transfer of thermal energy between two bodies that are at different temperatures. If you held a flask containing a reaction that releases energy, you would be able to feel the heat being transferred from the reaction into your hand. A process in which heat is released is referred to as **exothermic**. Conversely, reactions that absorb energy will remove energy from the surroundings, causing the container to feel cold. For example, dissolving ammonium nitrate in water will significantly lower the water temperature. Processes that absorb energy from their surroundings are called **endothermic**.

For example, the reaction between potassium and water is very exothermic:

$2K + 2H_2O \rightarrow 2KOH + H_2 + \text{heat}$

Another exothermic reaction involves combining elemental sodium with chlorine:

$2Na + Cl_2 \rightarrow 2NaCl + \text{heat}$

Endothermic reactions are also quite common. An example would be the splitting of water by electrolysis:

$2H_2O + \text{heat} \rightarrow 2H_2 + O_2$

We will explore the details of the energy changes that take place during exothermic and endothermic reactions later in this chapter.

Calorimetry

The subfield of thermochemistry studies the energy changes that occur over the course of various chemical reactions. We will first look at how these changes are measured and then go into quantitative descriptions of heat transfer. **Calorimetry** is a term used to describe the measurement of heat transfers, usually by monitoring changes in the temperature of an isolated system. A **calorimeter** is a device used to measure temperature changes during chemical processes. The simplest type of calorimeter is the constant-pressure device illustrated in **Figure** 17.3.

A basic calorimeter includes the following components:

1. a thermometer to measure temperature changes.
2. a stirring rod to mix materials thoroughly
3. an insulated lid
4. an inner container
5. an outer container
6. spacers to separate the inner and outer containers

To use a calorimeter, the components of a reaction are placed in the inner container and mixed. As the reaction proceeds, the temperature change can be measured with the thermometer. The space between the inner and outer containers provides insulation to minimize heat loss.

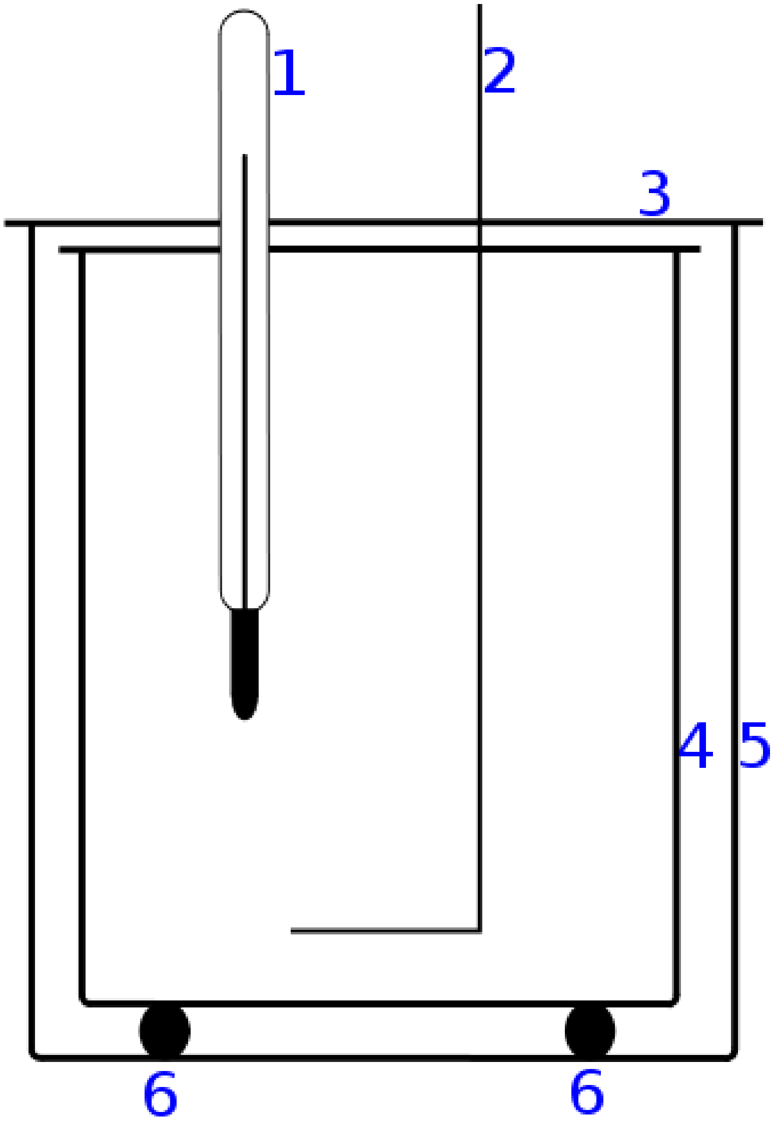

FIGURE 17.3

Units of Heat

The SI unit for heat, and for any form of energy, is the joule. Officially, one joule is the amount of energy needed to move an object by one meter while exerting a force of one newton. Although this definition is based on the concept of work, we can also talk about the amount of heat (in joules) required to change the temperature of a given material by a specific amount.

A related unit is the calorie. This term arose prior to the establishment of the SI system and is now replaced by the joule in most situations. One calorie is defined as the amount of energy needed to increase the temperature of one gram of water by 1°C. One calorie equals 4.184 joules. Note that this calorie is not exactly the same as the calories listed on food products. One food Calorie (usually written with a capital C) is equal to 1000 "regular" calories. Thus, a 140-Calorie snack can be fully digested to produce 140,000 calories of energy. We will use the SI unit joules in our discussions of heat energy.

Heat Capacity and Specific Heat

We mentioned earlier that 4.184 joules (1 calorie) is the amount of energy needed to raise the temperature of one gram of liquid water by 1°C. This value is known as the **specific heat** of liquid water, and it has units of J/g•°C. Other materials have different specific heat values. The **Table** 17.1 lists the specific heats of several substances:

TABLE 17.1:

Material	Specific Heat (J/g•°C)
aluminum	0.900
gold	0.129
graphite	0.720
diamond	0.502
copper	0.385
iron	0.139
water (liquid)	4.184

Note that the heat capacity of a substance depends on its state of matter. Except for water, all of the values in the **Table** 17.1 refer to the specific heat for the solid form of that substance. Also note that water has an unusually high heat capacity. Much more heat is needed to raise the temperature of water by a given amount than to cause the same temperature increase in an equal mass of graphite, diamonds, or various metals.

A related term is **heat capacity**, which is defined as the amount of heat need to raise the temperature of a specified amount of material by 1°C. Heat capacity can be calculated using the following formula:

Heat capacity $= mc$

where m is the mass of the material and c is the specific heat of the material. Heat capacity has units of J/°C.

We can calculate the amount of heat required to cause a specific temperature change by using the following equation:

$q = m \times c \times \Delta T$

where q is the amount of heat added to the system, m is the mass of the substance, c is the specific heat of the substance, and ΔT is the change in temperature.

Example 17.1

How much heat is required to increase the temperature of a 150-gram block of aluminum by 42°C?

Answer:

$$
\begin{aligned}
q &= m \times c \times \Delta T \\
q &= 150 \text{ g} \times 0.900 \text{ J/g} \cdot {}^{\circ}\text{C} \times 42^{\circ}\text{C} \\
q &= 5670 \text{ J}
\end{aligned}
$$

Lesson Summary

- Chemical reactions essentially always involve a transfer of heat energy.
- Exothermic reactions release heat into their surroundings.
- Endothermic reactions absorb heat from their surroundings.
- Specific heat and heat capacity measure the amount of heat energy needed to change the temperature of a material by a given amount.

Lesson Review Questions

1. What is true of all chemical processes?
2. How can you distinguish a system and its surroundings?
3. What are the required characteristics of an isolated system?
4. Explain the difference between exothermic and endothermic processes.
5. Indicate which of the following processes are exothermic and which are endothermic:
    a. ice melting
    b. burning a candle
    c. cooking an egg
    d. the evaporation of sweat
6. Calculate the amount of heat needed to increase the temperature of 125 g of water from 22°C to 59°C.
7. Calculate the specific heat of copper, given that 204.75 J of energy raises the temperature of 15 g of copper from 35°C to 70°C.
8. 432 J of energy is required to raise the temperature of a block of aluminum from 20°C to 60°C. Calculate the mass of aluminum present.
9. 300 g of liquid ethanol at 22°C is supplied with 6480 J of heat. What is the final temperature of the ethanol? (The specific heat of ethanol is 2.44 J/g•°C).

Further Reading / Supplemental Links

- Exothermic and endothermic reactions: http://www.docbrown.info/page03/3_51energy.htm
- Interactive practice with specific heat: http://hyperphysics.phy-astr.gsu.edu/hbase/thermo/spht.html
- Heat, work, and energy: http://www.engineeringtoolbox.com/heat-work-energy-d_292.html

Points to Consider

- How can we determine if a specific reaction is exothermic or endothermic?
- How is enthalpy related to heat?

17.2 Enthalpy

Lesson Objectives

- State the first law of thermodynamics.
- Define enthalpy.
- Explain how enthalpy changes relate to exothermic and endothermic reactions.
- Perform calculations using enthalpy values for various reactions.

Lesson Vocabulary

- **first law of thermodynamics**: States that energy can be converted from one form to another, but cannot be created or destroyed.
- **enthalpy**: A thermodynamic function of a system that is the internal heat content of a substance or system that is at a constant pressure.
- **enthalpy of reaction**: The change in enthalpy resulting from a mole of matter altered by a chemical reaction under standard conditions.
- **standard enthalpy of formation**: The enthalpy change that would be necessary to form a compound from its elements in their standard states at 25°C; has a value of zero for any element in its most stable form.

Check Your Understanding

Recalling Prior Knowledge

- What are endothermic and exothermic reactions?
- How is heat transfer measured?

Introduction

One of the most fundamental scientific laws is that the total amount of energy in the universe is constant. The **first law of thermodynamics** says that energy can be converted from one form to another, but it cannot be created or destroyed. This law is very difficult to prove, since we cannot measure the energy of the entire universe. However, we can measure energy changes as various physical and chemical processes occur, and this allows us to show that the total amount of energy in an isolated system remains constant. Our discussion in this lesson will focus on differences in energy between one state and another.

Enthalpy

In the previous lesson, we looked at how heat transfers are measured. In practice, only changes in energy and heat can be measured; we cannot measure the "energy" of a substance or system by itself. For practical reasons, most reactions are run at a constant pressure, with the reaction vessel open to the external atmosphere. **Enthalpy** is an energetic concept that can be thought of as the internal heat content of a substance or system that is at a constant pressure. Technically, it is defined as follows:

$$H = E + PV$$

where H is the enthalpy of the system, E is the internal energy, P is the pressure, and V is the volume. It can be difficult to distinguish "heat" and "enthalpy." Heat measures the transfer of thermal energy between two objects, and enthalpy measures the flow of heat. When heat flows out of a system, the change in enthalpy is negative; when heat flows into a system, the change in enthalpy is positive. Enthalpy is a useful tool for characterizing chemical reactions.

Enthalpy of Reaction

Any chemical reaction can be written in the form reactants → products. Although the enthalpy of an isolated component cannot be directly measured, the enthalpy change over the course of a chemical reaction can be measured. We can define the **enthalpy of reaction** as follows:

$$\Delta H_{reaction} = H_{products} - H_{reactants}$$

The enthalpy of reaction allows us to determine if a given reaction is exothermic or endothermic. An exothermic reaction, in which heat is released by the reaction to the surroundings, has a negative ΔH value.

A plot of enthalpy vs. reaction progress would take the following form for an exothermic reaction:

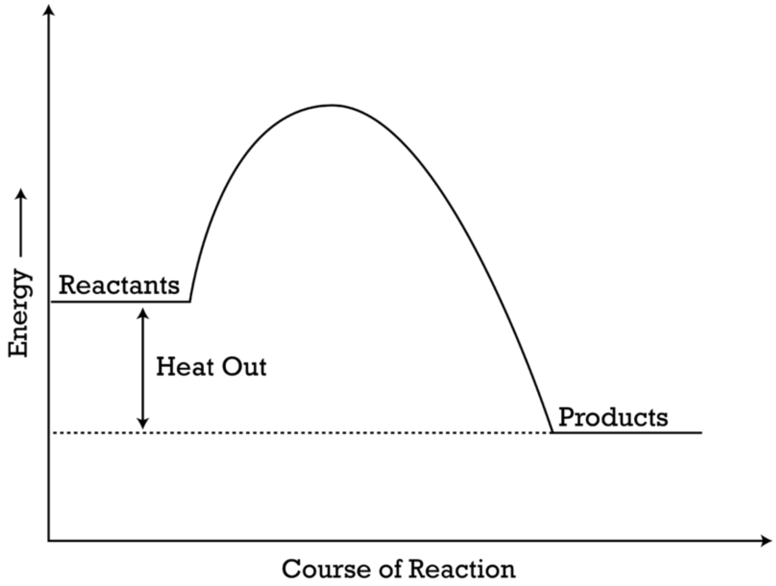

FIGURE 17.4
Energy profile of an exothermic reaction.

The enthalpy of the reactants is greater than the enthalpy of the products. During the course of the reaction, heat is released to the surroundings.

If a net input of heat is required for the reaction to proceed, then ΔH is positive, and the reaction is endothermic. In an endothermic reaction, the reactants are lower in enthalpy than the products, which is why heat must be added to the system in order for the reaction to proceed. An enthalpy vs. reaction progress plot for an endothermic reaction would have the following form:

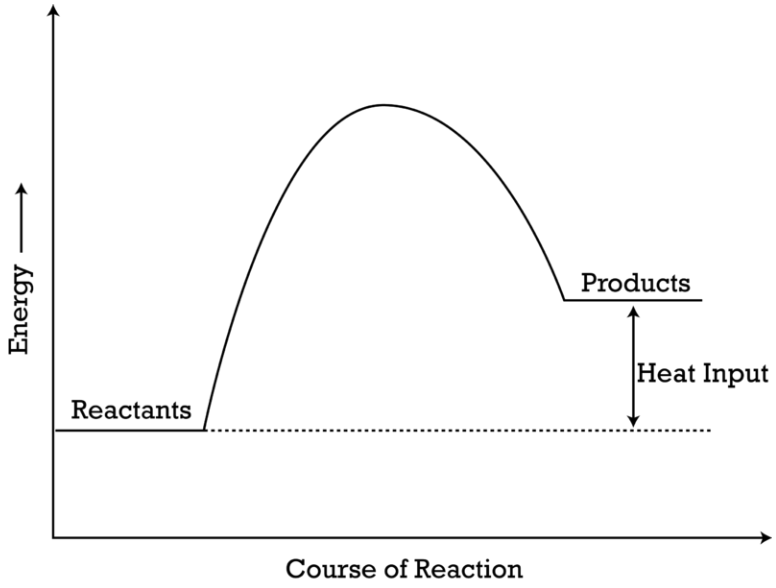

FIGURE 17.5

Energy profile of an endothermic reaction.

Standard Enthalpy of Formation

Although we cannot directly measure the enthalpy content of a single substance, we can determine the enthalpy change that would be necessary to form a compound from its elements in their standard states at 25°C. This value is referred to as the **standard enthalpy of formation** (ΔH_f). The term standard heat of formation can be used interchangeably; although, heat and enthalpy are technically not the same quantity. These values are tabulated for a large number of substances, and knowledge of the ΔH_f values for each component in a reaction allows you to predict the total enthalpy change for that reaction, as we will see in the following section.

The standard states for most elements can be determined just by finding out what state of matter they are in at 25°C, such as Ag(s), Hg(l), or Xe(g). However, some nonmetals have more complicated standard states. In particular, seven elements exist as diatomic substances in their standard states. $H_2(g)$, $N_2(g)$, $O_2(g)$, $F_2(g)$, $Cl_2(g)$, $Br_2(l)$, and $I_2(s)$ each represent the standard forms of these elements.

Because standard enthalpy of formation values represent the change from elements in their standard state to a final substance, any element that is already in its standard state has a ΔH_f value of 0.

Calculations Using Thermochemical Equations

The total enthalpy change for a reaction can be predicted using the following equation:

$$\Delta H_{rxn} = \Sigma n \Delta H_f(products) - \Sigma n \Delta H_f(reactants)$$

Essentially, if we add together the standard enthalpy of formation values for each product (multiplied by its coefficient in the balanced equation) and then subtract the ΔH_f for each reactant (again, multiplied by their coefficients), we are left with ΔH for the overall reaction.

When performing enthalpy calculations, a few points need to be remembered:

- ΔH_f values are generally given in kJ/mol, so we need to multiply each value by the total number of moles of each component in the reaction.
- The standard enthalpy of formation for any element in its most stable form at 25°C is zero.
- The state of the compound must be noted so the correct enthalpy value can be used. For example, ΔH_f is -285.8 kJ/mol for liquid water and -241.8 kJ/mol for water vapor.
- Keep close track of the signs of each value, since many ΔH_f values are negative.

The easiest way to explain this process is through an example problem. Let's consider the energy changes that occur during the combustion of methane gas:

Example 17.2

Calculate the enthalpy of reaction for the following process:

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

You will need to make use of the following data:

- ΔH_f for $CH_4(g)$ = -74.87 kJ/mol
- ΔH_f for $CO_2(g)$ = -393.5 kJ/mol
- ΔH_f for $H_2O(l)$ = -285.8 kJ/mol

Answer:

We are given ΔH_f values for every reaction component except for $O_2(g)$. Because $O_2(g)$ is the standard form of elemental oxygen, it has a ΔH_f value of zero. Now use the following equation:

$$\begin{aligned}\Delta H_{rxn} &= \Sigma n\Delta H_f(products) - \Sigma n\Delta H_f(reactants)\\ &= (-393.5\text{ kJ/mol} + 2(-285.8\text{ kJ/mol})) - (-74.87\text{ kJ/mol} + 0\text{ kJ/mol})\\ &= -965.1\text{ kJ/mol} - (-74.87\text{ kJ/mol})\\ &= -965.1\text{ kJ/mol} + 74.87\text{ kJ/mol}\\ &= -890.3\text{ kJ/mol}\end{aligned}$$

The enthalpy change that takes course during this reaction is highly negative, indicating a strongly exothermic reaction. This is consistent with what we know about the combustion of methane, the primary component in natural gas.

Lesson Summary

- The first law of thermodynamics tells us that energy can be converted from one form to another but cannot be created or destroyed.
- When discussing energy changes for reactions that are run at a constant pressure, it is generally simpler to measure and tabulate changes in enthalpy (H), which can be thought of as the heat content of a system at constant pressure.
- The standard enthalpy of formation (ΔH_f) for a substance is the enthalpy change that would be necessary to form that substance from its elements in their standard states at 25°C.
- The enthalpy of a reaction can be calculated from ΔH_f values for its various components using the following equation: $\Delta H_{reaction} = \Sigma n\Delta H_{products} - \Sigma n\Delta H_{reactants}$.

Lesson Review Questions

Reviewing Concepts

1. Which of the following situations would violate of the first law of thermodynamics? Explain your answer in each case.
    a. Car brakes heat up when you slow down at a stop sign.
    b. In a warm room, a glass of water spontaneously freezes.
    c. A car parked on a hill rolls upward when the brake is released.
    d. As sun shines on a swimming pool, more water evaporates.
2. How does enthalpy help us determine whether a reaction is exothermic or endothermic?

Problems

1. Use standard enthalpies of formation from the supplemental link below to calculate ΔH_{rxn} for the reaction: $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$.
2. Use standard enthalpies of formation from the supplemental link below to calculate ΔH_{rxn} for the reaction: $4NH_3(g) + 5O_2(g) \rightarrow 6H_2O(g) + 4NO(g)$.
3. Complete combustion of 1.00 mol of acetone (C_3H_6O) liberates 1790 kJ of heat: $C_3H_6O(l) + 4\ O_2(g) \rightarrow 3\ CO_2(g) + 3\ H_2O(l)$; ΔH = -1790 kJ. Using this information and ΔH_f data for CO_2 and H_2O, calculate the standard enthalpy of formation for acetone.
4. Determine ΔH_f for IF, given the following information:

$IF_7 + I_2(s) \rightarrow IF_5 + 2IF$; $\Delta H_f = -89$ kJ
ΔH_f for $IF_7 = -941$ kJ
ΔH_f for $IF_5 = -840$ kJ

5. Write the balanced equation for the complete combustion of C_2H_6, and calculate the heat of combustion per mole of gaseous water formed using standard enthalpies of formation.

Further Reading / Supplemental Links

- Standard enthalpy of formation values: http://chemistry.about.com/od/thermodynamics/a/Heats-Of-Formation.htm
- Video: calculating the heat of reaction: http://www.youtube.com/watch?v=iQuy2mgbV9o

Points to Consider

- How does the state of a material affect enthalpy changes?

17.3 Enthalpy and Phase Transitions

Lesson Objectives

- Explain why enthalpy increases or decreases during a given transition from one physical state to another.
- Calculate enthalpy changes that occur during changes of state.
- Calculate enthalpy changes that occur when materials are dissolved in water.

Lesson Vocabulary

- **molar heat of fusion**: The heat absorbed by one mole of a substance as it is converted from a solid to a liquid.
- **molar heat of vaporization**: The heat absorbed by one mole of a substance as it is converted from a liquid to a gas.
- **heat of solution**: Indicates how much energy is absorbed or released when one mole of a substance is fully dissolved in a specific solvent.

Check Your Understanding

Recalling Prior Knowledge

- What phase transitions can a substance undergo?
- What are the energy requirements for achieving a change of state?

Introduction

When your ice cream melts on a hot day, there is a change in internal energy as well as a change in enthalpy occurring. An enthalpy change also occurs when the moisture in the air condenses onto the cold windshield of a car. These changes of state can be described by the changes in enthalpy that accompany them. In this lesson, you will learn how to calculate and quantify changes of energy as related to changes of state.

Summary of Phase Transition Processes

Figure 17.6 summarizes the basic transitions that a substance may undergo as a result of changes in temperature or pressure. For any phase change, energy will be either released (for exothermic processes) or absorbed from the surroundings (for endothermic processes). Processes in which intermolecular interactions are weakened or broken

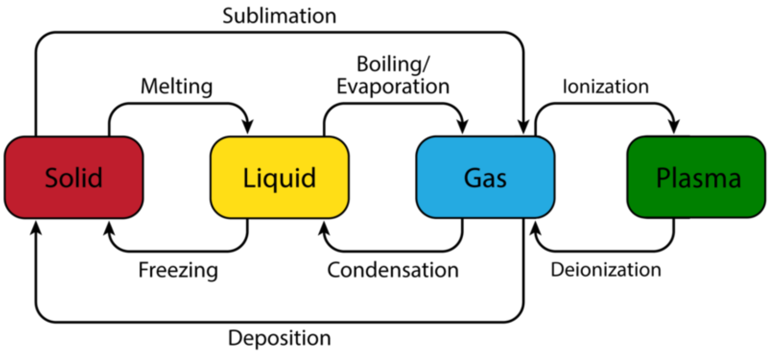

FIGURE 17.6
Phase transitions

(melting, vaporization, and sublimation) require an input of energy; they are endothermic. Processes in which attractive interactions are formed (freezing, condensation, and deposition) release energy, so they are exothermic.

The amount of energy necessary to melt one mole of a substance is known as the **molar heat of fusion**. Similarly, the amount of energy necessary to vaporize one mole of a substance is referred to as the **molar heat of vaporization**. The values of these parameters are given for water in the following table, along with the specific heats exhibited by water in its solid, liquid, and gaseous forms.

TABLE 17.2:

Parameter	Phase Transition	Enthalpy Value
molar heat of fusion (melting)	solid → liquid	+6.0 kJ/mol
molar heat of vaporization	liquid → gas	+40.7 kJ/mol
specific heat of ice		2.09 J/g•°C
specific heat of water		4.18 J/g•°C
specific heat of steam		1.84 J/g•°C

Notice that the process of freezing is the exact reverse of the process of melting, so the enthalpy change has the same magnitude but opposite sign. The same is true for the relationship between condensation and vaporization. Also note that the specific heat of water is dependent on the state of the material. Ice, liquid water, and steam all have different specific heat values. Remember that specific heat refers to the the amount of energy needed to raise the temperature of one gram of liquid water by 1°C.

Energy and Changes of State

We have already learned how to use specific heat to calculate the energy needed to change a material from one temperature to another within a given state. Now let's look at the energy changes required for changes of state.

Example 17.3

How much energy is needed to convert 180 grams of ice at 0°C to liquid water at the same temperature?

Answer:

The heat of fusion for water is 6.0 kJ/mol. First, we need to convert the mass of water to moles:

$$180 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 10. \text{ mol } H_2O$$

We now can calculate the energy needed for the conversion:

$$\Delta H_{fus} = 6.0 \text{ kJ/mol}$$

$$\Delta H = 10 \text{ mol } H_2O \times \frac{6.0 \text{ kJ}}{1 \text{ mol } H_2O} = 60. \text{ kJ}$$

1. Calculation of the energy needed to raise the temperature of the ice from -12°C to 0°C
2. Calculation of the energy needed for the transition from solid ice to liquid water (calculated in the previous example problem)
3. Calculation of the energy needed to raise the temperature of the liquid water from 0°C to 25°C

The portions that require calculating the energy associated with temperature changes will make use of the following equation:

$\Delta H = m \times c \times \Delta T$

First, calculate the energy associated with the temperature change for ice:

$\Delta H = (180 \text{ g})(\frac{2.09 \text{ J}}{\text{g}\cdot{}^\circ\text{C}})(12^\circ\text{C}) = 4514.4 \text{ J}$

Second, recall from the previous problem that melting 180 grams of ice requires 60 kJ (60,000 J) of energy.

Third, calculate the energy needed to change the temperature of the liquid water. Again, note that ice and liquid water have different specific heat values.

$\Delta H = (180 \text{ g})(\frac{4.18 \text{ J}}{\text{g}\cdot{}^\circ\text{C}})(25^\circ\text{C}) = 18810 \text{ J}$

Finally, add all of these energetic requirements together to find the energy needed for the entire change. Make sure that all values have the same units (J or kJ, but not both).

$\Delta H = 4,514.4 \text{ J} + 60,000 \text{ J} + 18,810 \text{ J} = 83,324.4 \text{ J}$

Rounded to the correct number of significant figures, this process would require the input of 83,000 J (83 kJ) of energy.

Note that the enthalpy change is positive, indicating that we need to put energy into the system in order to achieve the desired transition. When going "downhill" from vapor to liquid or liquid to solid, we need to remember to change the sign for ΔH. If we were to do the reverse process, cooling liquid water at 25°C to ice at -12°C, ΔH would be -83 kJ, indicating that 83 kJ of energy would be removed from the system during this transition.

Heat of Solution

If you were to prepare a large solution of sulfuric acid in water, it would be wise to cool the container in which the mixing is taking place. The addition of a strong acid to water releases a great deal of heat (which is why it is better to add the acid to the water and not the water to the acid). The **heat of solution** for a substance tells us how much energy is absorbed or released when one mole of the substance is fully dissolved in a specific solvent. We will only consider heat of solution values for which water is the solvent, but other solvents would have different values for a given solute. The heats of solution for several common solutes are listed in the **Table** 17.3. In each case, assume that the solute is added to a large excess of water, so the solute dissolves completely.

TABLE 17.3:

Material	Heat of Solution (kJ/mol)
H_2SO_4(l)	-96.2
$MgSO_4$(s)	-91.2
$CaCl_2$(s)	-82.9
KOH(s)	-56
NaOH(s)	-44.3
NaCl(s)	3.9
$NaHCO_3$(s)	16.7
KNO_3(s)	35

Some materials have negative heats of solution; the dissolution of one of these solutes in water is an exothermic process. Heat is released, causing a net increase in the temperature of the solution. Conversely, other substances have positive heats of solution. For example, the dissolution of potassium nitrate in water is an endothermic process. The resulting absorption of energy causes the solution to become colder. Calculations involving heats of solutions follow the same basic approach that we have used with other enthalpy problems.

Example 17.5

How much heat would be absorbed or released if we completely dissolved 0.45 moles of sulfuric acid in water?

Answer:

Since the heat of solution for H_2SO_4 is negative, heat will be released during this process. The exact amount can be calculated as follows:

$\Delta H = 0.45 \text{ mol } H_2SO_4 \times \frac{-96.2 \text{ kJ}}{1 \text{ mol } H_2SO_4} = -43 \text{ kJ}$ If we wanted to know the temperature change that this would cause, we would need more information.

Example 17.6

If we dissolved 0.45 moles of sulfuric acid in 1.0 liter of water at 25.0°C, what would be the final temperature of the solution, assuming no heat is lost to the surroundings? Assume that the specific heat of the solution is the same as the specific heat of pure water.

Answer:

To answer this question, we will need to make use of the following equation:

$\Delta H = m \times c \times \Delta T$

Solving for the unknown variable (ΔT), we get the following:

$\Delta T = \frac{\Delta H}{m \times c}$

We already know that 43 kJ of energy will be released into the solution. Because the specific heat is in units of joules, not kilojoules, we will want to use the value 43,000 J instead so that the units cancel out. The specific heat of the solution is assumed to be the same as that of pure water (4.18 J/g•°C). Now, we need to find the mass of the solution. At 25°C, 1.0 L of water has a mass of 1.0 kg (1,000 g). The mass of the sulfuric acid can be calculated as follows:

$0.45 \text{ mol } H_2SO_4 \times \frac{98.08 \text{ g } H_2SO_4}{1 \text{ mol } H_2SO_4} = 44 \text{ g } H_2SO_4$

Therefore, the total mass of the solution would be 1,044 grams. Plugging these values into the above equation, we get the following temperature change:

$\Delta T = \frac{43{,}000 \text{ J}}{1{,}044 \text{ g} \times \frac{4.18 \text{ J}}{\text{g} \cdot {}^\circ\text{C}}} = 9.9^\circ\text{C}$

The final temperature of the solution would be 34.9°C, which is 9.9°C higher than the initial temperature of 25.0°C.

These principles are applied when we use heat packs or cold packs for sore muscles. A heat pack contains water and a solid such as calcium chloride or magnesium sulfate. When the pack is activated, the two materials mix and heat is released. This is because the heats of solution are negative indicating an exothermic reaction. Some packs can get as warm as 90°C. Cold packs use materials such as ammonium nitrate, which has a large positive heat of solution. The endothermic mixing process can cool the solution down to just a few degrees Celsius.

Lesson Summary

- Specific heat and heat capacity provide information about enthalpy changes when the temperature of a substance is altered but no changes of state take place.

- Molar heats of fusion and vaporization allow calculations of energy changes involving a phase transition.
- Combinations of the above parameters can be used to calculate total energy changes for transitions that involve both temperature changes and changes of state.
- Heat of solution data provides information about enthalpy changes that occur when a solute dissolves in a solvent.

Lesson Review Questions

Reviewing Concepts

1. Define the following terms:
    a. heat of fusion
    b. heat of vaporization
    c. heat of solution
2. Indicate whether the following processes are exothermic or endothermic:
    a. melting of water
    b. conversion of liquid bromine to a gas
    c. condensation of chlorine gas
    d. conversion of sodium chloride crystals to molten (liquid) NaCl

Problems

1. Mercury melts at -39°C. How much energy is required to melt 150. grams of mercury if its molar heat of fusion is 2.29 kJ/mol?
2. Sulfur has a boiling point of 444.6°C. If the heat of vaporization for sulfur is 45 kJ/mol, how much heat is released when 42 grams of sulfur vapor is converted to liquid sulfur?
3. Calculate the total enthalpy change when 200. grams of water vapor at 120°C is converted to liquid water at 42°C.
4. How much energy is involved in dissolving 76 grams of NaCl in water? Is this an exothermic or endothermic process?
5. Calculate the total energy involved in converting 50. grams of ice at -10°C to liquid water at 95°C.
6. If the heat of solution for LiBr is -49 kJ/mol, how many grams of LiBr must be dissolved in order to release 3,500 joules of energy?

Further Reading / Supplemental Links

- Specific heat and heat capacity: http://www.iun.edu/~cpanhd/C101webnotes/matter-and-energy/specificheat.html
- Heat of solution: http://sunny.moorparkcollege.edu/~chemistry/chemistry_1B_labs/experiment_one.pdf
- Visual illustration of heats of solution: http://www.youtube.com/watch?v=o7adWQqvDUU

Points to Consider

- How do you determine the enthalpy of formation for a reaction that is not feasible to run in the laboratory?

17.4 Hess's Law

Lesson Objectives

- State Hess's law.
- Use Hess's law to calculate standard enthalpy of formation values.

Lesson Vocabulary

- **Hess's law**: States that the enthalpy change between a set of reactants and a set of products will be the same, regardless of the number of reactions or steps that take place in between the two states.

Check Your Understanding

Recalling Prior Knowledge

The enthalpy of a reaction can be calculated from standard heat of formation values by using the following equation:

$$\Delta H_{rxn} = \Sigma n\Delta H_f(products) - \Sigma n\Delta H_f(reactants)$$

Introduction

If you wished to travel from Memphis, Tennessee (home of the blues) to Nashville, Tennessee (home of country music), there are several available routes. You could take Interstate 40 east to Nashville, which would be a very direct route. You might want to head north on Interstate 55 to visit Cape Girardeau, Missouri before you turn onto U.S 61, and then Interstate 24 would take you to Nashville. Or you may decide to go south to Birmingham, Alabama on Interstate 22 before turning left on Interstate 65 to head back north to Nashville. Whatever the route chosen, all the different alternatives still take you to Nashville. The amount that you have driven depends on your route, but the overall distance between your starting point and your destination is independent of the path that you took. In this lesson, you will see that the energetics of a chemical reaction can be thought of in a similar way.

Hess's Law

In the 19th century, the Swiss-born Russian chemist Germain Hess (1802-1850) developed a law of heat summation, often referred to as **Hess's Law**. This law states that the enthalpy change between a set of reactants and a set of products will be the same, regardless of the number of reactions or steps that take place in between the two states.

In other words, the overall enthalpy change does not depend on how you got from start to finish.

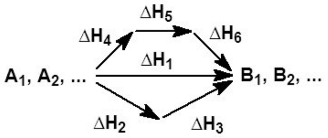

FIGURE 17.7

The specific path leading to the formation of the different B products from A reactants does not influence the overall enthalpy change. $\Delta H_1 = \Delta H_2 + \Delta H_3 = \Delta H_4 + \Delta H_5 + \Delta H_6$

Indirect Method for Determining the Standard Heat of Formation

In the previous lesson, we made use of standard heat of formation values. Although the energy changes can sometimes be measured directly when a compound is generated from its constituent elements in their standard forms, many such reactions are difficult or unfeasible. An alternative way to measure the standard heat of formation is to measure the enthalpy changes for a series of reactions that result in the same net change. The general rules for manipulating thermochemical equations are as follows:

1. When adding two (or more) equations together, their ΔH_{rxn} values should also be added together.
2. Reversing the direction of a chemical equation reverses the sign of the enthalpy change but does not affect its magnitude.
3. If we multiply all components of a chemical reaction by some number, the enthalpy change should be multiplied by the same number.

In general, we are given a set of equations with known ΔH_{rxn} values, and by reversing or multiplying each equation by some factor, we can add them all together to give us the desired transformation. This can be shown most easily through an example.

Example 17.7

We want to determine ΔH_f for $NO_2(g)$, but the formation reaction shown below is difficult to measure directly:

$\frac{1}{2}N_2(g) + O_2(g) \rightarrow NO_2(g) \quad \Delta H_f^\circ = ?\ \text{kJ/mol}$

However, we can measure the enthalpy changes for the following two reactions:

$$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightarrow NO(g) \qquad \Delta H_f^\circ = 90\ \text{kJ/mol}$$
$$NO_2(g) \rightarrow NO(g) + \frac{1}{2}O_2(g) \qquad \Delta H^\circ = 56\ \text{kJ/mol}$$

Use these values to determine the standard heat of formation for $NO_2(g)$.

Answer:

We would like to manipulate the two known reactions so that when they are added together and we cancel the common terms (the compounds that appear on both the reactant and product sides), the net result is our desired transformation. In the desired reaction, nitrogen and oxygen gases are reactants, and $NO_2(g)$ is a product. If we reverse the second known equation, $NO_2(g)$ will be a product. When reversing the direction of a chemical reaction, the magnitude of the enthalpy change stays the same, but the sign is reversed.

$NO(g) + \frac{1}{2}O_2(g) \rightarrow NO_2(g) \quad \Delta H^\circ = -56\ \text{kJ/mol}$

Now we can add the two reactions:

$$\begin{array}{ll} \frac{1}{2}N_2(g)+\frac{1}{2}O_2(g) \rightarrow NO(g) & \Delta H_f^\circ = 90 \text{ kJ/mol} \\ NO(g)+\frac{1}{2}O_2(g) \rightarrow NO_2(g) & \Delta H^\circ = -56 \text{ kJ/mol} \\ \hline \frac{1}{2}N_2(g)+O_2(g)+NO(g) \rightarrow NO(g)+NO_2(g) & \Delta H^\circ = 34 \text{ kJ/mol} \end{array}$$

The ΔH value for this transformation is the sum of the two simpler reactions. The final equation can also be simplified. The NO cancels out, because it is on both sides of the equation, leaving only the desired transformation:

$\frac{1}{2}N_2(g)+O_2(g) \rightarrow NO_2(g) \quad \Delta H_f^\circ = 34 \text{ kJ/mol}$

Note that the enthalpy change for any transformation can be determined in this way; this method can be used for more than just finding heat of formation values.

Example 17.8

What is ΔH_{rxn} for the following reaction?

$CS_2(l)+3O_2(g) \rightarrow CO_2(g)+2SO_2(g)$

The following formation reactions have known ΔH values:

$$\begin{array}{ll} C(s)+2S(s) \rightarrow CS_2(l) & \Delta H_f = 87.9 \text{ kJ/mol} \\ C(s)+O_2(g) \rightarrow CO_2(g) & \Delta H_f = -393.5 \text{ kJ/mol} \\ S(s)+O_2(g) \rightarrow SO_2(g) & \Delta H_f = -296.8 \text{ kJ/mol} \end{array}$$

Answer:

Which components of the first known equation are part of the desired reaction? Carbon and sulfur are not involved in the desired transformation, but one molecule of CS_2 is present as a reactant. If we reverse the first equation, we get the following:

$CS_2(l) \rightarrow C(s)+2S(s) \quad \Delta H = -87.9 \text{ kJ/mol}$

Now, look at the second equation. A single molecule of CO_2 is present as a product, which is what we want for our final equation. Since CO_2 does not show up in any of the other equations, we can assume that this equation will be used as is:

$C(s)+O_2(g) \rightarrow CO_2(g) \quad \Delta H = -393.5 \text{ kJ/mol}$

Finally, look at the third known equation. It has a single molecule of SO_2 as a product. However, we need two molecules of SO_2 on the product side, so we multiply the entire equation, including its ΔH value, by a factor of two:

$2S(s)+2O_2(g) \rightarrow 2SO_2(g) \quad \Delta H = -593.6 \text{ kJ/mol}$

Now, add these three equations together:

$$\begin{array}{ll} CS_2(l) \rightarrow C(s)+2S(s) & \Delta H = -87.9 \text{ kJ/mol} \\ C(s)+O_2(g) \rightarrow CO_2(g) & \Delta H = -393.5 \text{ kJ/mol} \\ 2S(s)+2O_2(g) \rightarrow 2SO_2(g) & \Delta H = -593.6 \text{ kJ/mol} \\ \hline CS_2(l)+3O_2(g)+C(s)+2S(s) \rightarrow CO_2(g)+2SO_2(g)+C(s)+2S(s) & \Delta H = -1075.0 \text{ kJ/mol} \end{array}$$

One mole of carbon and two moles of sulfur appear on both sides of the equation. Cancelling out these terms, we are left with the desired reaction:

$CS_2(l)+3O_2(g) \rightarrow CO_2(g)+2SO_2(g) \quad \Delta H = -1075.0 \text{ kJ/mol}$

Lesson Summary

- Hess's law states that the enthalpy change for a given transformation depends only on the initial and final states, and not on how many stages or steps are taken in between.
- Standard enthalpies of formation can be calculated indirectly using the ΔH_{rxn} values for reactions that are easier to measure directly.

Lesson Review Questions

Reviewing Concepts

1. State Hess's law.
2. Why is this law important?

Problems

1. Calculate the heat released by the burning of sulfur in oxygen: $2S(s) + 3O_2(g) \rightarrow 2SO_3(g)$. ΔH values are known for the following reactions:

$$\begin{aligned} &S(s) + O_2(g) \rightarrow SO_2(g) && \Delta H = -296 \text{ kJ} \\ &2SO_2(g) + O_2(g) \rightarrow 2SO_3(g) && \Delta H = -198 \text{ kJ} \end{aligned}$$

2. Calculate ΔH for the following reaction, which describes the production of syn-gas from carbon: $H_2O(g) + C(s) \rightarrow CO(g) + H_2(g)$. The following enthalpy changes are known:

$$\begin{aligned} &H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g) && \Delta H = -242.0 \text{ kJ} \\ &2CO(g) \rightarrow 2C(s) + O_2(g) && \Delta H = +221.0 \text{ kJ} \end{aligned}$$

3. Calculate the heat of reaction for the following equation: $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$. The following formation reactions have known ΔH values:

$$\begin{aligned} &3C(s) + 4H_2(g) \rightarrow C_3H_8(g) && \Delta H = -103.8 \text{ kJ} \\ &2H_2(g) + O_2(g) \rightarrow 2H_2O(g) && \Delta H = -484 \text{ kJ} \\ &C(s) + O_2(g) \rightarrow CO_2(g) && \Delta H = -393 \text{ kJ} \end{aligned}$$

Further Reading / Supplemental Link

- Hess's Law: http://www.science.uwaterloo.ca/~cchieh/cact/c120/hess.html
- Hess's Law worked example: http://www.utc.edu/Faculty/Gretchen-Potts/chemistryhelp/hess.htm
- Hess's Law video: http://www.khanacademy.org/science/physics/thermodynamics/v/hess-s-law-and-reaction-enthalpy-change

Points to Consider

- How do chemical reactions occur?
- What affects the rate of a chemical reaction?

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CHAPTER 18

Kinetics

Chapter Outline

18.1 RATES OF REACTIONS

18.2 RATE LAWS

18.3 REACTION MECHANISMS

18.4 REFERENCES

The cars roar around the oval track at speeds up to 200 miles/hour. The victor is determined by who crosses the finish line first after a pre-determined number of laps have been driven. Speed is a major factor in winning, but there is also a heavy dose of strategy, driving skill, and some luck in avoiding crashes.

Drag racing involves one basic issue: who can get to the finish line the fastest. The strip is a quarter-mile in length and is straight. Driving skill is important and luck always plays a role. In drag racing the car with the fastest acceleration has an advantage, but top speed is also important. The Top Fuel category (running on nitromethane) record is over 330 miles per hour at the finish line (that's from a standing start and a quarter-mile distance).

Speed is important both on the track and in the chemistry lab. We want to know how fast a reaction occurs for several reasons. The reaction rate can give us useful information about how the reaction occurs. In a manufacturing plant, if the speed of a reaction can be increased, the chemical product can be made in less time, which often means a lower manufacturing cost.

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18.1 Rates of Reactions

Lesson Objectives

- Define “rate.”
- Describe collision theory as it relates to chemical reactions.
- List and describe factors that affect the rate of a chemical reaction.

Lesson Vocabulary

- **reaction rate**: The change in concentration of a reactant or product with time.
- **collision theory**: Molecules need to collide in order for a reaction to take place.
- **activation energy**: The energy that is needed to get reactants close enough together for a reaction to occur.
- **activated complex**: The highest energy state that must be passed through in order for reactants to convert into products.
- **catalyst**: A substance that speeds up the rate of reaction by providing a lower energy pathway but does not undergo any change itself.

Check Your Understanding

What do energy versus reaction progress graphs look like for exothermic and endothermic reactions?

Introduction

In our discussion of car racing, we talked about the speed of the vehicles. Car speed is measured in miles/hour (or kilometers/hour in countries using the metric system). A race car traveling at a speed of 200 miles/hour could go a distance of 200 miles in one hour. A rate indicates the extent of some change in relation to the amount of time that has passed. The rate of travel for a car or other object tells us what distance is traversed in a given unit of time. If we know the total distance traveled and the total time taken, we can calculate the rate as follows:

$Rate = \frac{\Delta distance}{\Delta time}$

Rates can also be expressed for changes in variables other than physical location. In this lesson, you will learn how to use rates to describe chemical reactions.

What is a Rate?

When studying chemical reactions, we are interested in how quickly the amount or concentration of a given reactant or product changes over time. This is known as the **reaction rate**. Mathematically, the reaction rate can be expressed by either of the following equations:

$$Rate = -\frac{\Delta[reactant]}{\Delta time}$$
$$Rate = \frac{\Delta[product]}{\Delta time}$$

Because the concentrations of the reactants decrease over time, the negative sign in the first equation above means that the reaction rate will be a positive value.

Example 18.1

The initial concentration of a given reactant is 0.45 M. After two minutes, its concentration is measured and found to be 0.35 M. What is the rate of this reaction?

Answer:

Use the appropriate rate equation and fill in the given values:

$$\begin{aligned}Rate &= -\frac{\Delta[reactant]}{\Delta time}\\ Rate &= -\frac{c(final)-c(initial)}{t(final)-t(initial)}\\ Rate &= -\frac{0.35\text{ M}-0.45\text{ M}}{2\text{ min}-0\text{ min}}\\ Rate &= -\frac{-0.10\text{ M}}{2\text{ min}}\\ Rate &= 0.05\text{ M/min}\end{aligned}$$

The concentrations of reactants and products are always measured in moles/liter (M) when discussing reaction rates.

For real reactions, we also need to consider the coefficients from the balanced equation. For example, in the reaction 2A → B, the rate of disappearance of A is twice the rate of formation of B, as can be inferred from the stoichiometric coefficients. The rate of product formation can be expressed as follows:

$Rate = \frac{\Delta[B]}{\Delta t}$

However, the rate of disappearance of reactant A is twice the rate of formation of product B. We want to end up with the same reaction rate value regardless of which reaction component is being considered. In order to achieve this, we need to write each rate with respect to the coefficient on the corresponding reaction component.

In the basic reaction formula above, we have determined that the rate of disappearance of reactant A is twice the rate of formation of product B. This means that the rate expression above for the product B is equivalent to the following in terms of the reactant A:

$Rate = -\frac{1}{2}\frac{\Delta[A]}{\Delta t}$

By accounting for the coefficients in the balanced chemical equation, these two rates are equal and we can also say the following:

$\frac{\Delta[B]}{\Delta t} = -\frac{1}{2}\frac{\Delta[A]}{\Delta t}$

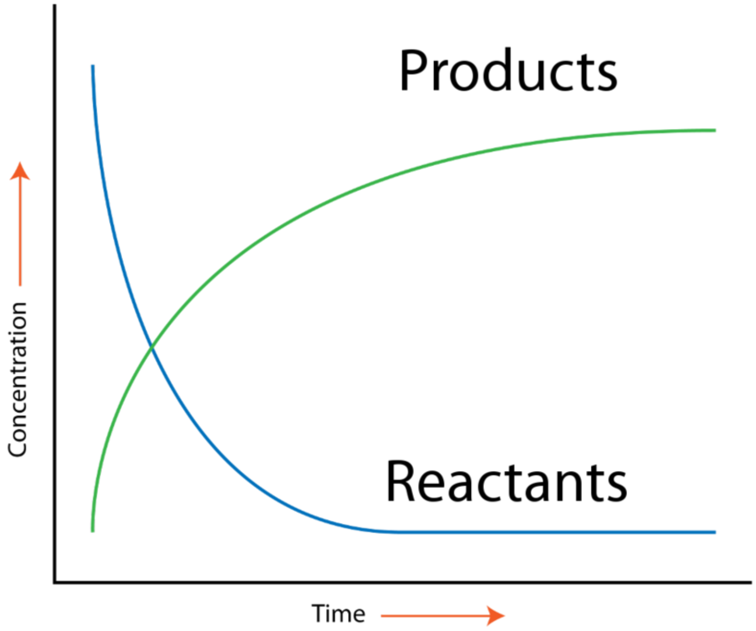

FIGURE 18.1

Collision Theory

Collision theory states that chemical reactions occur when atoms, ions, or molecules collide. In other words, these species need to make contact with one another in order for a reaction to take place. Based on this concept, along with a couple of other key points, collision theory helps to explain why certain factors will influence the rate of a chemical reaction.

We discussed earlier some basic principles about the behavior of gases called the kinetic-molecular theory. Among other things, this theory suggests that gas molecules are in constant motion, and the average speed of the individual gas particles is dependent upon temperature –the higher the temperature, the faster the molecules move. It is not just gas particles that are in constant motion. The molecules and ions that make up liquids and solutions are also continually moving in nearly random directions. As a result, molecules and ions in a solution will collide with one another fairly frequently. As with gases, a temperature increase will produce an increase in the average particle speed.

However, not all collisions between reactant molecules will result in the formation of a product. The colliding particles must possess a minimum amount of energy in order for the reactant-product transition to occur. In the *Thermochemistry* chapter, we saw that simple exothermic reactions have an energy diagram that looks something like **Figure** 18.2.

Although the overall process involves a release of energy (the products are lower energy than the reactants), a certain initial amount of energy needs to be present before the reaction can occur. The amount of energy required to get over the "hump" in the reaction diagram is referred to as the **activation energy** of the reaction. At the top of the peak, the reactants form what is known as an activated complex. The **activated complex** is the highest energy state that must be achieved in order for reactants to convert into products.

In the **Figure** 18.3, the starred compound in the center represents the activated complex. For the indicated transformation, the reactant molecules must come into contact with enough energy to partially break the A-B and C-D bonds that are initially present. If the molecules are simultaneously able to partially form the A-C and B-D bonds in the product, the energetic barrier will not be quite as high, but breaking any chemical bonds requires at least an

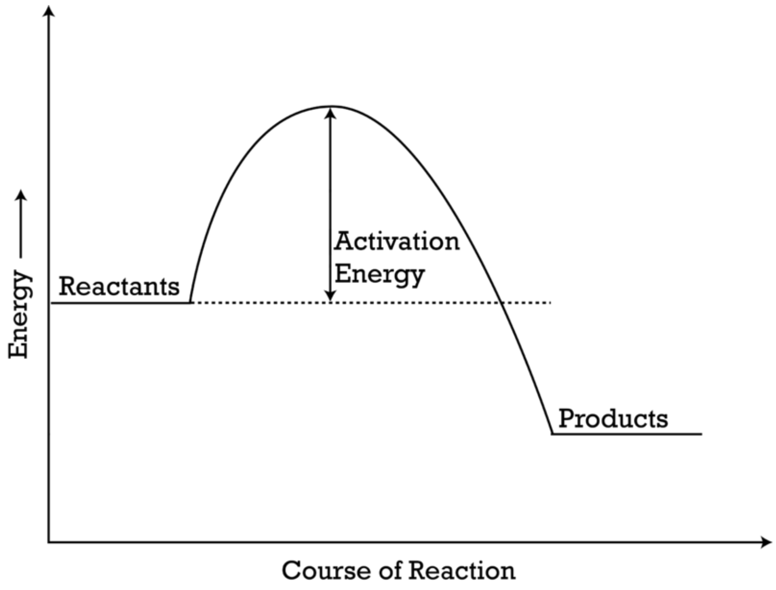

FIGURE 18.2

Activation energy for an exothermic reaction.

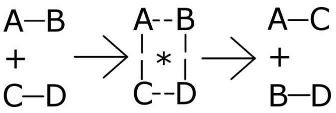

FIGURE 18.3

Formation of activated complex with subsequent release of products.

initial input of energy.

Factors Affecting Reaction Rate

Several factors influence the rate at which a reaction proceeds. Many of these effects can be predicted and rationalized using the basic concepts of collision theory.

Concentration

FIGURE 18.4

Collision theory tells us that molecules need to collide in order for a reaction to take place. All else being equal, anything that increases the frequency of collisions would also increase the rate of reaction. One way to do this is to increase the concentrations of one or more of the reactants. Using a real world example, a busy freeway will experience much more frequent car collisions than a fairly empty neighborhood street. Similarly, forcing more randomly moving molecules into the same amount of space will cause an increased number of collisions over a given length of time, providing the reactants with more opportunities to transform into products.

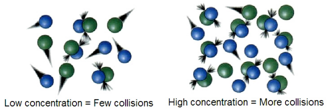

FIGURE 18.5

Pressure

If the pressure of a gaseous mixture is increased by decreasing the available volume, we are effectively pushing the same amount of material into a smaller overall volume. In other words, we are increasing the concentration of the gaseous materials. As we just discussed, an increase in concentration leads to more frequent collisions, thus increasing the rate of reaction.

Note that increasing the external pressure on liquids and solids, which are relatively incompressible, has very little effect on the reaction rate. The volume will be decreased very little, if any, so no significant increase in concentration will result from the pressure change.

Temperature

As the temperature of a system increases, the average speed of its particles also increases. If particles are moving faster, they cover more distance in a shorter amount of time, which increases the frequency of collisions. As a result, the rate of any potential reaction is increased.

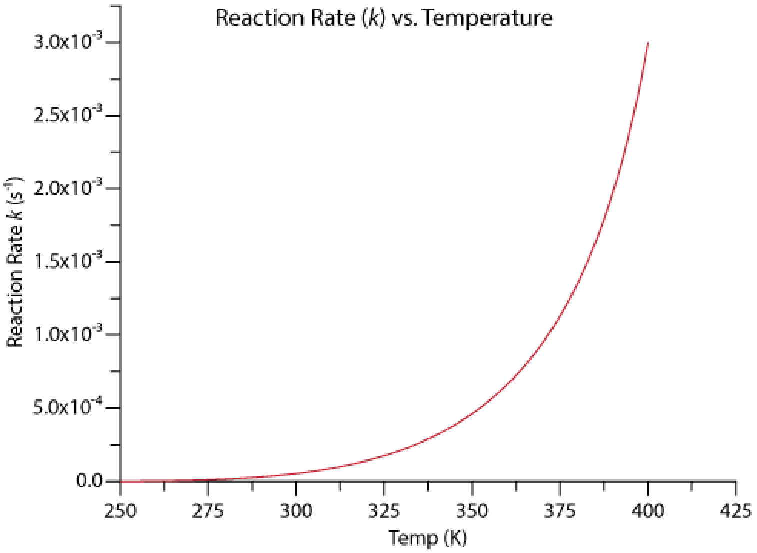

FIGURE 18.6

Effect of temperature on reaction rate.

Additionally, there is another way in which increasing the temperature will increase the rate of a reaction. Fundamentally, the temperature of a substance is a measure of the average kinetic energy of its individual particles. Recall that a collision will only lead to a reaction if the colliding reactants have enough energy to overcome the activation barrier. Increasing the average kinetic energy of the reactants makes it more likely that any given collision will result in a transformation from reactants to products.

For example, the reaction of wood with oxygen to produce carbon dioxide and water is a very exothermic reaction. The excess energy is released as heat and light, which we experience as fire. However, wood can be stored in the air almost indefinitely without bursting into flames. In order for wood to burn, enough energy needs to be added to overcome the initial activation energy barrier. This can be accomplished by increasing the temperature of a small amount of the wood, often by exposing it to another source of flame or the focused rays of the sun. Once the reaction begins, the energy given off by the exothermic combustion process heats the surrounding wood, thus providing the necessary activation energy for continued burning.

Surface Area

Many reactions take place in solution or in the gas phase, where the reactants are evenly dispersed throughout a homogeneous mixture. However, for reactions in which one of the reactants is a pure solid or liquid (meaning that this reactant is not already mixed together with any other reactants), reactivity only occurs at the surface, where particles of the solid or liquid reactant come into contact with particles of the other reactants. All of the molecules or ions in the interior of the pure substance will not be colliding with the other necessary reactants, so they are not really contributing to the overall rate of the reaction. However, increasing the surface area will increase the frequency of potentially reactive collisions, because more reactant particles will be in contact with the other necessary reactants.

For example, if a solid pellet of NaOH is placed into a chamber of HCl gas, a relatively slow acid-base reaction will occur between gaseous HCl molecules and hydroxide ions on the surface of the pellet. If we were to grind the pellet into smaller pieces, it would greatly increase the total surface area, and therefore the overall reaction rate. Once ground up, many hydroxide ions that were on the interior of the pellet, where they were not exposed to any HCl molecules, will now be on the surface, where the necessary collisions can occur.

Catalysts

A **catalyst** is a material that speeds up the rate of a reaction without being consumed by the reaction. For example, the following reaction is very slow, even when heated:

$2KClO_3 \rightarrow 2KCl + 3O_2$

However, adding a tiny amount of manganese dioxide (MnO_2) to a solution of potassium chlorate ($KClO_3$) results in a dramatic increase in the rate at which oxygen gas is produced. At the end of the reaction, the manganese dioxide can be recovered. This is because it is not actually used up in the reaction, but merely facilitates the reaction.

A catalyst works by providing a lower energy pathway from reactants to products. The use of a catalyst involves intermediate reactions which have lower activation complexes than the original reaction. On a simplified reaction energy diagram, this can be thought of as lowering the activation energy for a given transformation. If the activation energy of a reaction is decreased, more collisions will have enough energy to overcome this lower barrier, so the reactant-to-product transformation will occur more frequently. As a result, the overall reaction rate will be higher than for an identical reaction with a larger activation energy barrier.

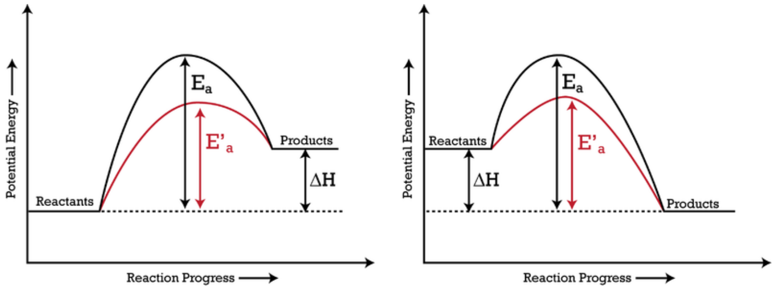

FIGURE 18.7

Another example of a catalytic process is the reaction between an alkene (a carbon-carbon double bond) and hydrogen gas. Due to the details of how covalent bonds are broken and formed, a simple collision between these two molecules will not result in the formation of a product. In the absence of a catalyst, very high energy intermediates, which involve the complete breakage of an H-H single bond, would be required for this process to occur. Because of the very large activation energy required, this uncatalyzed reaction would only occur in extremely high temperatures.

However, the addition of a metal catalyst, such as platinum, provides a lower energy pathway. The energy requirements for breaking the H-H bond are offset somewhat if each hydrogen atom can form a new bond with the metal surface. Then, collisions between the alkene and the metal-hydrogen complex result in the formation of a product. The metal surface is regenerated after the hydrogen atoms are removed, so it is not used up by the reaction, but it increases the rate by stabilizing the high energy hydrogen atoms.

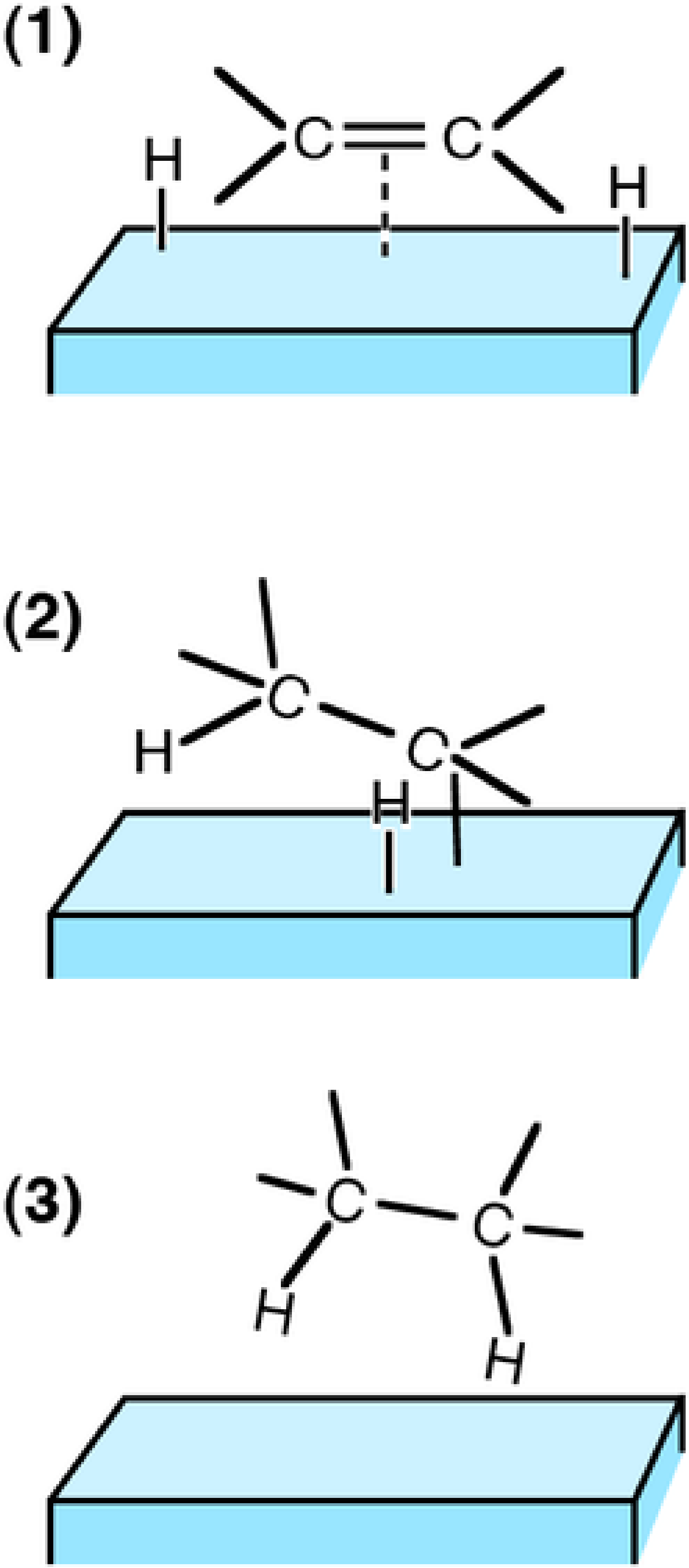

FIGURE 18.8

Catalytic converters in cars increase the rates of several important reactions. Unburned hydrocarbons can more easily be converted to carbon dioxide and water in the presence of a catalyst. Additionally, carbon monoxide (a harmful gas produced by incomplete combustion of fuel) is further oxidized to carbon dioxide, and nitrous oxide compounds (which contribute to smog and acid rain) are transformed back into nitrogen and oxygen gases. By passing car exhaust over these catalysts before their release into the air, the emissions from a combustion engine are made into much less harmful substances, resulting in a much cleaner atmosphere.

Because these catalysts contain expensive metals (rhodium costs about $70.00/gram, platinum about $50.00/gram, and palladium about $15.00/gram), the theft of catalytic converters is a growing problem. A stolen catalytic converter can be sold for over $100.00 at a junk yard.

Lesson Summary

- The rate of a reaction tells us how quickly the reactants are transformed into products. It can be expressed as the change in the concentration of a given reactant or product over a certain length of time.
- Collision theory states that chemical reactions occur when reactants collide with enough energy to overcome the activation energy barrier.
- The activated complex is the highest energy state that must be passed through in order for reactants to be transformed into products.
- The activation energy of a reaction is the amount of energy necessary to form the activated complex from the initial reactants.
- Several factors affect the rate of a chemical reaction, including concentration, pressure (for gases), temperature, surface area (for solids and liquids), and the presence of a catalyst. All of these factors can be rationalized by the basic ideas of collision theory.
- A catalyst increases the rate of a reaction without being consumed. It accomplishes this by providing a lower energy pathway from reactants to products, thus decreasing the activation energy barrier.

Lesson Review Questions

Reviewing Concepts

1. How is the rate of a reaction typically described?
2. Explain the reaction energy graph for an exothermic reaction in terms of collision theory.
3. What is activation energy?
4. For each of the following situations, tell whether the rate of the reaction would increase or decrease, and explain your answer in terms of collision theory.
   a. The concentration of a reactant is doubled.
   b. The reaction is moved from a lab bench at room temperature into an ice bath.
   c. A solid crystalline reactant is broken into smaller pieces with a hammer.

Problems

1. In the reaction A + B $\rightarrow$ C, the initial concentration of A is 0.054 M. After 1.5 minutes, [A] = 0.032 M. Calculate the rate of the reaction in M/sec.
2. If the above reaction is run under different conditions, it might take 0.8 minutes for the concentration of product C to reach 0.029 M. Assuming that no C was present initially, calculate the rate of formation of C in M/sec.

3. Consider the following reaction: $N_2 + 3H_2 \rightarrow 2NH_3$. At a certain point in the reaction, hydrogen gas is being consumed at a rate of 0.096 M/sec. What is the rate at which ammonia is being formed at this point?
4. The decomposition of dinitrogen pentoxide is described by the reaction below: $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$. If O_2 is being formed at a rate of 2.40 mol/min, what is the rate at which N_2O_5 is being used up?

Further Reading/Supplementary Links

- Reaction rates: http://www.chm.davidson.edu/vce/kinetics/ReactionRates.html
- Reaction rate simulation: http://phet.colorado.edu/en/simulation/reactions-and-rates
- Activation energy: http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch22/activate.html
- How a catalytic converter works: http://www.howstuffworks.com/catalytic-converter.htm

Points to Consider

- How do we calculate the rate of a reaction?

18.2 Rate Laws

Lesson Objectives

- Explain why reaction rates are often measured only at the very beginning of a reaction.
- Derive rate laws based on initial rates of reaction.
- Explain what it means for a reaction to be zero-order, first-order, or second-order with respect to a given reactant. Show how this information can be obtained from an experimental rate law.

Lesson Vocabulary

- **initial rate of reaction**: The rate of product formation (or reactant disappearance) that occurs directly after the reactants have been mixed.
- **rate constant**: The proportionality constant "k".
- **second-order**: Indicates an exponent of two; the rate increases twice as fast as the corresponding concentration.
- **first-order**: Indicates an exponent of one; the rate increases directly with the corresponding concentration.
- **zero-order**: Indicates an exponent of zero; the rate does not depend on the corresponding reactant concentration.

Check Your Understanding

Recalling Prior Knowledge

- What do we mean by the “rate” of a reaction?
- How does the concentration of a reactant affect the rate of a reaction?

Introduction

Imagine when you are hungry at the beginning of a meal. A large plate of food is set in front of you, and you start eating quickly. As you become more full, you start eating more slowly. Or, maybe you start off eating slowly and the food is so delicious that you start eating more rapidly. The rate at which you eat may be changing throughout the meal based on your level of satisfaction. The rate of chemical reactions can be thought of in a similar way, as these rates do not necessarily stay constant over time. In this lesson, you will learn how to use initial rates and experimental data to determine rate laws.

Initial Rate of Reaction

If we were to graph the concentration of a reactant over time in a given reaction, we might get a plot that looked something like **Figure** 18.9. For a given portion of the curve, the rate of disappearance is equal to the slope at that point. Because the curve is not linear, it has different slopes at different points. This means that the rate of reaction changes over the course of the reaction. As the reactant is used up, its concentration decreases, resulting in a slower rate for any subsequent reactivity.

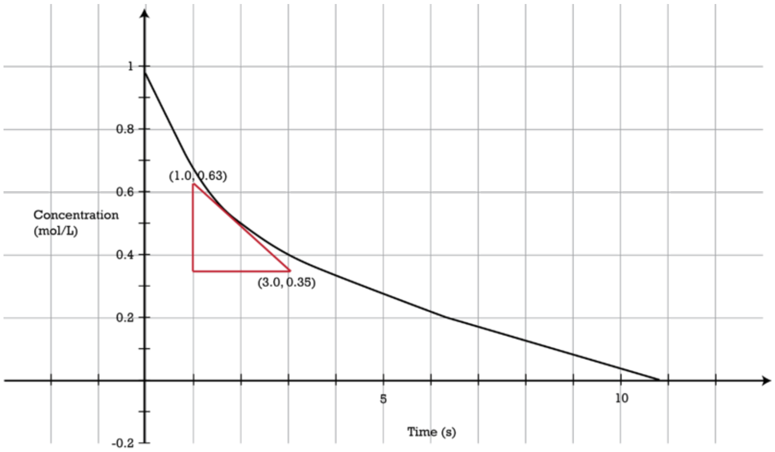

FIGURE 18.9

It is often difficult to monitor the exact concentrations of each reactant in the middle of an ongoing reaction. However, much more precise measurements can be made regarding the concentration of each reactant before they are mixed and the reaction is allowed to proceed. To record more reliable data about the extent to which the rate of a given reaction depends on the concentration of a specific reactant, we often look at the **initial rate of reaction**, which is the rate of product formation (or reactant disappearance) that occurs directly after the reactants have been mixed. In those first few seconds, we can assume that the concentrations of each reactant are essentially equivalent to the amounts that were originally added to the reaction mixture. Additionally, if the presence of the product alters the rate of reaction, this effect is minimized when there is little to no product in the mixture, further simplifying our analysis of the data.

When studying the kinetics of a reaction, what do we measure? The easiest parameter to look at is product formation. If we start at a concentration of zero, we can measure the amount of product present after a short period of time, and the concentration of product divided by the time elapsed gives us the initial rate of reaction. Measuring the disappearance of a reactant is also possible. However, the change in the concentration of the product is often easier to measure, because it is a much larger change based on percentage.

For example, in the generic reaction A $\rightarrow$ B, let's say we start with 1.000 M A and 0 M B. If we allow the reaction to proceed for a very short period of time, we might have 0.998 M A and 0.002 M B. The difference between 0 M and 0.002 M is generally easier to measure accurately than the difference between 1.000 M and 0.998 M.

Rate Laws

So far, we have been assuming that most reactions occur by a very simple process, in which all the necessary reactants collide, and products are formed if the collision is sufficiently energetic. However, most reactions are much more complicated than that. Except for the most basic reactions, several simpler steps, each of which involves a single collision, are required to get from reactants to products. This sequence of steps, known as the reaction mechanism, will be covered in the next lesson.

We have also assumed that increasing the concentration of any reactant will increase the overall rate of reaction. However, the extent to which this is true, and whether it is true for all reactants, depends on the reaction mechanism. What we can say is that the rate of reaction is proportional to the concentration of each reactant raised to some exponent. Mathematically, this can be expressed as follows for the generic reaction A + B → C.

$Rate \propto [A]^x[B]^y$

Alternatively, we can express this as an equation:

$Rate = k[A]^x[B]^y$

where k is a proportionality constant known as the **rate constant**. In general, a larger rate constant is indicative of a faster reaction.

The exponents for an unknown reaction cannot be predicted simply by looking at the chemical equation. Instead, they must be determined experimentally by comparing initial rate data for multiple sets of initial concentrations.

Determining Rate Laws Experimentally

Consider the reaction between nitrogen monoxide gas and hydrogen gas to form nitrogen gas and water vapor.

$$2\text{NO}(g)+2\text{H}_2(g)\rightarrow \text{N}_2(g)+2\text{H}_2\text{O}(g)$$

The rate law for this reaction will have the following form:

$$Rate = k[\text{NO}]^x[\text{H}_2]^y$$

In order to determine the exponents in this equation, the following data were collected at a set temperature and pressure:

TABLE 18.1: **Rate Law example**

Experiment	[NO] (M)	[H_2] (M)	Initial Rate (M/s)
1	0.0050	0.0020	1.25×10^{-5}
2	0.010	0.0020	5.00×10^{-5}
3	0.010	0.0040	1.00×10^{-4}

Notice that the starting concentrations of NO and H_2 were varied in a specific way. In order to compare the rates of reaction and determine the exponent associated with each reactant, the initial concentration of each reactant must be changed while the other is held constant.

Comparing experiments 1 and 2: the concentration of NO was doubled, while the concentration of H_2 was held constant. Doubling the concentration of NO quadrupled the initial reaction rate ($5.00 \times 10^{-5}/1.25 \times 10^{-5} = 4$). Therefore, the exponent associated with the concentration of NO must be 2. In other words, Rate $\propto$ $[\text{NO}]^2$. Because $2^2 = 4$, doubling the value of [NO] increases the rate by a factor of four.

Comparing experiments 2 and 3: the concentration of H_2 was doubled while the concentration of NO was held constant. Doubling the concentration of H_2 doubled the initial rate of the reaction ($1.00 \times 10^{-4}/5.00 \times 10^{-5} = 2$). Therefore, the exponent associated with the concentration of H_2 is 1 (Rate $\propto [\text{H}_2]^1$). Because $2^1 = 2$, doubling the value of [H_2] also doubles the reaction rate.

The overall rate law incorporates both of these results into a single equation:

$$Rate = k[\mathrm{NO}]^2[\mathrm{H_2}]$$

Note that exponents of 1 are generally not included, since $[A]^1 = [A]$. Based on the exponents associated with each concentration, we would say that this reaction is **second-order** with respect to NO and **first-order** with respect to H_2. The overall reaction order is the sum of the individual reaction orders, or the sum of all exponents in the rate law. You can see that this would be a third-order reaction overall.

Additionally, now that we know the form of the rate law, we can plug in data from any of the experiments to determine the value of k for this reaction under the conditions (temperature, pressure, etc.) at which the data was measured. Using the data from experiment 1:

$$\begin{aligned} Rate &= k[\mathrm{NO}]^2[\mathrm{H_2}] \\ 1.25 \times 10^{-5}\,\frac{\mathrm{M}}{\mathrm{s}} &= k[0.0050\ \mathrm{M}]^2[0.0020\ \mathrm{M}] \\ k &= 250\,\frac{1}{\mathrm{M}^2 \cdot \mathrm{s}} \end{aligned}$$

Let's consider another hypothetical reaction of the form A + B → C + D. Under a certain set of conditions, the following data were collected:

TABLE 18.2:

Experiment	[A] (M)	[B] (M)	Initial Rate (M/s)
1	0.015	0.025	0.112
2	0.030	0.025	0.224
3	0.030	0.050	0.224

Comparing experiments 1 and 2, we see that doubling the concentration of A while holding [B] constant doubles the rate. Therefore, this reaction is first-order with respect to A ($\mathrm{Rate} \propto [A]^1$). Plugging this into our generic rate law, we get the following:

$$\begin{aligned} Rate &= k[A]^x[B]^y \\ Rate &= k[A]^1[B]^y \\ Rate &= k[A][B]^y \end{aligned}$$

Next, we can compare experiments 2 and 3, in which [A] is constant but [B] is doubled. This change *does not affect* the overall reaction rate. We can conclude that the rate of the reaction is independent of the concentration of reactant B. How can we express this in terms of the exponents of the rate law? Recall that any value raised to the 0th power is equal to 1 ($x^0 = 1$). To completely remove a concentration from the rate law, we could set its exponent equal to zero:

$$\begin{aligned} Rate &= k[A][B]^0 \\ Rate &= k[A] \times 1 \\ Rate &= k[A] \end{aligned}$$

We say that this reaction is **zero-order** with respect to reactant B. Overall, this is a first-order reaction.

Although other exponents are possible, most reactions are zero-, first-, or second-order with respect to each reactant. Again, the values of the exponents generally cannot be predicted and must be determined experimentally.

Lesson Summary

- The initial rate of reaction is the rate at which the reaction proceeds directly after mixing the reactants. At this point, the concentrations of the reactants have not changed appreciably and the concentrations of the products are negligible.
- The rate law for a given reaction expresses the reaction rate as the product of a rate constant and the concentration of each reactant raised to some exponent.
- The exponents in a rate law, referred to as the order of each reactant, must be determined experimentally, usually by comparing initial rates for multiple combinations of starting concentrations.

Lesson Review Questions

Reviewing Concepts

1. What is the advantage of measuring the initial rate of reaction?
2. What does it mean if a reaction is second-order with respect to a given reactant?
3. What does it mean if a reaction is first-order with respect to a given reactant?
4. What does it mean if a reaction is zero-order with respect to a given reactant?

Problems

1. A generic reaction is found to have the following experimental rate law: $Rate = k[A][B]$. What will happen to the rate of reaction if the concentration of A is tripled?
2. Another reaction has the following rate law: $Rate = k[A][B]^2$. What will happen to the rate of reaction if the concentration of B is doubled?
3. Consider the generic reaction A + B → products. For each set of data given below, determine the reaction order with respect to each reactant and write the experimental rate law.

TABLE 18.3: Table for 3A

Experiment	[A] (M)	[B] (M)	Initial Rate (M/s)
1	0.023	0.014	0.011
2	0.046	0.014	0.044
3	0.023	0.028	0.011

(a)

TABLE 18.4: Table for 3B

Experiment	[A] (M)	[B] (M)	Initial Rate (M/s)
1	0.017	0.021	0.023
2	0.034	0.021	0.023
3	0.017	0.042	0.046

(b)

TABLE 18.5: Table for 3C

Experiment	[A] (M)	[B] (M)	Initial Rate (M/s)
1	0.023	0.017	0.023
2	0.046	0.017	0.046
3	0.023	0.034	0.092

(c)

4. For one reaction of the type A + B → products, the reaction is first-order with respect to A and zero-order with respect to B. Fill in the missing values in the following **Table** 18.6:

TABLE 18.6: Table for 4

Experiment	[A] (M)	[B] (M)	Initial Rate (M/s)
1	0.106	0.012	0.355
2	?	0.012	0.710
3	0.212	0.036	?

5. For another reaction of the type A + B → products, the reaction is second-order with respect to both A and B. Fill in the missing values in the following **Table** 18.7:

TABLE 18.7: Table for 5

Experiment	[A] (M)	[B] (M)	Initial Rate (M/s)
1	0.106	0.012	0.355
2	0.212	0.012	?
3	0.212	0.036	?

Further Reading/Supplementary Links

- Reaction order: http://www.files.chem.vt.edu/RVGS/ACT/notes/rxn_order.html
- Reaction order graphing: http://chem.usm.my/LECTURER/KFT%20131%20sitimariam/Topic_8.pdf

Points to Consider

How would the rate of reaction be calculated for a multiple step process?

18.3 Reaction Mechanisms

Lesson Objectives

- Define and give examples of elementary steps, and be able to identify the molecularity of each step.
- Define and give examples of reaction mechanisms.
- Predict the rate law for a given elementary step.
- Evaluate validity of reaction mechanisms based on rate law data.

Lesson Vocabulary

- **elementary step**: One step in a series of simple reactions that show the progress of a reaction at the molecular level.
- **reaction mechanism**: The sequence of elementary steps that together comprise an entire chemical reaction.
- **intermediate**: A species that appears in the mechanism of a reaction but not in the overall balanced equation.
- **molecularity**: The total number of reactant molecules in an elementary step.
- **bimolecular reaction**: A reaction in which two reacting molecules are present as reactants in an elementary step.
- **unimolecular reaction**: A reaction in which one molecule is present as a reactant in an elementary step.
- **termolecular reaction**: A reaction in which three reacting molecules in an elementary step.
- **rate-determining step**: The slowest elementary step in the reaction mechanism.

Check Your Understanding

Recalling Prior Knowledge

- How do we measure reaction rate?
- What does the order of a reaction tell us?

Elementary Steps

The overall balanced equation for a chemical reaction does not always tell us how a reaction actually proceeds. In many cases, the overall reaction takes place in a series of small steps. An **elementary step** (or elementary reaction) is one step in a series of simple reactions that show the progress of a reaction at the molecular level. In terms of collision theory, each elementary step corresponds to a single collision. A **reaction mechanism** is the sequence of elementary steps that together comprise an entire chemical reaction. As an analogy, consider the route that you might take while driving to the grocery store. That route may consist of several turns, similar to the elementary steps. The overall reaction specifies only the beginning point (your house) and the final destination (the store), with no information about the specifics in between.

Understanding the mechanism of a reaction can be very useful, because this knowledge often gives us insights into how to improve the reaction, get better yields, or make the reaction proceed more rapidly. Additionally, many seemingly different reactions often have very similar reaction mechanisms. Understanding the types of elementary steps that are common to many different chemical species allows us to make predictions about the reactivity patterns of unknown compounds.

The reaction mechanism concept can be illustrated by the reaction between nitrogen monoxide and oxygen to form nitrogen dioxide:

$$2NO(g)+O_2(g)\rightarrow 2NO_2(g)$$

It may seem as though this reaction would occur as the result of a collision between two NO molecules and one O_2 molecule. However, a careful analysis of the reaction has detected the presence of N_2O_2 during the reaction. A proposed mechanism for this reaction consists of two elementary steps:

$$\text{Step 1: } 2NO(g)\rightarrow N_2O_2(g)$$
$$\text{Step 2: } N_2O_2(g)+O_2(g)\rightarrow 2NO_2(g)$$

In the first step, two molecules of NO collide to form a molecule of N_2O_2. In the second step, that molecule of N_2O_2 collides with a molecule of O_2 to produce two molecules of NO_2. The overall chemical reaction is the sum of the two elementary steps:

$$\begin{array}{r} 2NO(g) \rightarrow \cancel{N_2O_2(g)} \\ \cancel{N_2O_2(g)} + O_2(g) \rightarrow 2NO_2(g) \\ \hline 2NO(g) + O_2(g) \rightarrow 2NO_2(g) \end{array}$$

The N_2O_2 molecule is not part of the overall reaction. It was produced in the first elementary step, then reacts in the second elementary step. An **intermediate** is a species that appears in the mechanism of a reaction but not in the overall balanced equation. An intermediate is always formed in an earlier step of the mechanism and then consumed in a later step.

Molecularity

The **molecularity** of an elementary step is the total number of reactant molecules in that step. In both steps of the reaction mechanism shown above, two reactant molecules collide with one another. These are both **bimolecular reactions**. Notice that the colliding molecules may be the same (as in step 1 above) or different (as in step 2 above).

A **unimolecular reaction** is one in which only one molecule is present as a reactant. If we think about this in terms of collision theory, we would expect a unimolecular reaction to take place when the reactant molecule collides with either the wall of the container or molecules of solvent. The substance with which the reactant collides does not participate in the reaction, but it provides the necessary energy to cause whatever rearrangement or bond breakage is required for the given step.

A **termolecular reaction** involves three reacting molecules in one elementary step. Termolecular steps are relatively rare, because they require the simultaneous collision of three molecules with sufficient energy and the correct orientation to form an activated complex, which is an extremely unlikely event. When termolecular reactions do occur, they tend to be very slow. The vast majority of elementary steps are either unimolecular or bimolecular.

Rate Laws and Mechanisms

In general, we cannot predict the rate law for a chemical reaction by looking at its balanced equation, because the rate law for a multi-step reaction depends on the reaction mechanism. In contrast, we *can* predict the rate law for an elementary step. Consider the following unimolecular step:

$$\mathrm{A} \rightarrow products$$

Because it occurs in a single elementary step, the rate of product formation will increase linearly with the concentration of A, making the rate of this reaction first-order with respect to A.

$$Rate = k[\mathrm{A}]$$

A bimolecular elementary step could be one of two types. Either a molecule of A could react with a molecule of B or two molecules of A could react with each other. In either case, the rate of reaction depends on how frequently the collisions between reactant molecules occur.

$$\begin{aligned} \mathrm{A+B \rightarrow products} \qquad & \mathrm{rate = k[A][B]} \\ \mathrm{2A \rightarrow products} \qquad & \mathrm{rate = k[A]^2} \end{aligned}$$

The reaction order for each reactant in an elementary step is equal to its stoichiometric coefficient in the equation for that step. In the first equation above, each coefficient is a 1, and so the reaction is first-order with respect to A and first-order with respect to B. In the second equation, the coefficient of 2 means the reaction is second-order with respect to A.

Rate-Determining Steps

The determination of a reaction mechanism can only be made in the laboratory. When a reaction occurs in a sequence of elementary steps, the overall reaction rate is governed by whichever one of those steps is the slowest. The **rate-determining step** is the slowest step in the reaction mechanism. To get an idea of how one step is rate-determining, imagine driving on a one-lane road where it is not possible to pass another vehicle. The rate of flow of traffic on such a road would be dictated by whatever car is traveling at the lowest speed.

Consider the reaction mechanism presented in the previous section:

Step 1: $2\mathrm{NO}(g) \rightarrow \mathrm{N_2O_2}(g)$
Step 2: $\mathrm{N_2O_2}(g) + \mathrm{O_2}(g) \rightarrow 2\mathrm{NO_2}(g)$

Let's say that the first step is much slower than the second step. If this is true, the rate of the overall reaction would be completely determined by the speed at which the first elementary step proceeds. As soon as it is formed, the $\mathrm{N_2O_2}$ intermediate would immediately be consumed by the (much faster) second step.

What is the rate of the first step? Because it is an elementary step, we can predict its rate law based on the balanced equation. An elementary step in which the reactants consist of two molecules of NO(g) would have the following rate law:

$$Rate = k[\mathrm{NO}]^2$$

If we have correctly identified the mechanism of this reaction and chosen the correct rate-determining step, this will also be the rate of the overall reaction:

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

If the experimentally determined rate law for this reaction does not match the one predicted by the proposed mechanism, then the mechanism (or the choice of rate-determining step) is incorrect. However, if the two rate laws do match, we cannot necessarily say that we have found the correct mechanism, because there is always more than one mechanism that can be proposed for any given rate law. Thus, the experimentally determined rate law can invalidate or provide support for a proposed mechanism, but it cannot prove that the mechanism is correct.

In general, the rate law for a mechanism can be predicted based on the form of the rate-determining step. However, the analysis gets more complicated when a step other than the first step is rate-determining. This is due to the fact that intermediates in a reaction are not directly included in the rate law. For the purposes of this book, you will not be required to predict the rate law for any multi-step reactions unless the first step is the rate-determining step.

Lesson Summary

- A reaction mechanism describes the series of elementary steps by which the reactants are transformed into the products.
- The number of reactant molecules in an elementary step is referred to as its molecularity. The vast majority of elementary steps are unimolecular or bimolecular.
- Unlike the rate law for a multi-step reaction, the rate law of an elementary step can be predicted from its balanced equation.
- The rate-limiting step is the slowest step in a mechanism. The rate of the overall reaction is directly dependent on the speed of the rate-determining step.
- The experimentally determined rate law can rule out incorrect mechanisms but cannot prove that a mechanism is correct.

Lesson Review Questions

1. Describe an elementary step as it relates to collision theory.
2. How can the molecularity of an elementary step be determined?
3. Why must all reactions contain a rate-determining step?
4. Which of the following elementary steps is bimolecular?
   (a) $A \rightarrow C + D$
   (b) $A + B \rightarrow 2C + D$
   (c) $2A + B \rightarrow 2C$
5. The rate law for the reaction 2A + B → Products is: $Rate = k[A][B]$. Which reaction mechanism is consistent with this information?
   (a)

$$\begin{aligned} A + B &\rightarrow AB && (slow) \\ AB + A &\rightarrow Products && (fast) \end{aligned}$$

   (b)

$$\begin{aligned} A + A &\rightarrow A_2 && (slow) \\ A_2 + B &\rightarrow Products && (fast) \end{aligned}$$

(c)

$$\begin{aligned} A + B &\rightarrow AB && (fast) \\ AB + A &\rightarrow Products && (slow) \end{aligned}$$

(d)

$$\begin{aligned} A + A &\rightarrow A_2 && (fast) \\ A_2 + B &\rightarrow Products && (slow) \end{aligned}$$

6. The following three-step mechanism is proposed for the reaction between NO and H_2:

$$\begin{aligned} &\mathrm{NO + NO \rightarrow N_2O_2} && (fast) \\ &\mathrm{N_2O_2 + H_2 \rightarrow N_2O + H_2O} && (slow) \\ &\mathrm{N_2O + H_2 \rightarrow N_2 + H_2O} && (fast) \end{aligned}$$

   (a) What is the rate determining step?
   (b) Write the balanced equation for the overall reaction.
   (c) Are there any intermediates? if so, state what they are.

Further Reading/Supplementary Links

- Reaction mechanisms: http://www.sparknotes.com/chemistry/kinetics/mechanisms/section1.html
- More reaction mechanisms: http://chemwiki.ucdavis.edu/Physical_Chemistry/Kinetics/Rate_Laws/Reactions/Reaction_Mechanisms
- Reaction mechanism video: http://chemwiki.ucdavis.edu/Physical_Chemistry/Kinetics/Rate_Laws/Reactions/Reaction_Mechanisms

Points to Consider

Do reactions only go in one direction? Can reverse reactions occur?

18.4 References

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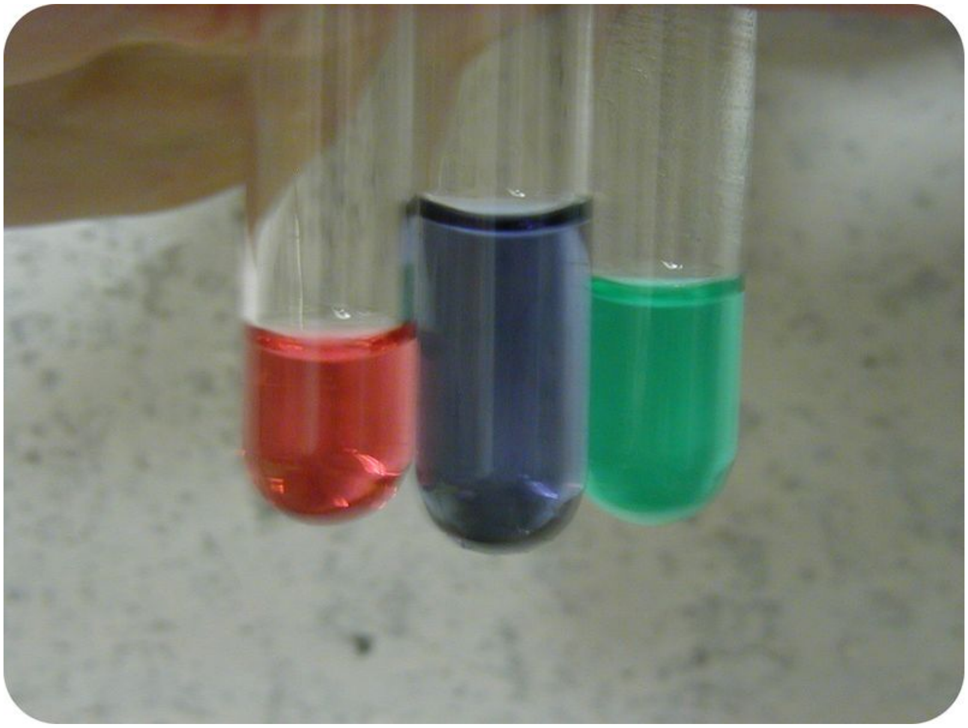
CHAPTER 19

Chemical Equilibrium

Chapter Outline

19.1 THE NATURE OF CHEMICAL EQUILIBRIUM
19.2 APPLICATIONS OF EQUILIBRIUM CONSTANTS
19.3 FACTORS AFFECTING CHEMICAL EQUILIBRIA
19.4 REFERENCES



When dissolved in water, cobalt chloride produces a reddish-pink solution. The introduction of additional chloride ions causes a shift from a fully hydrated cobalt cation ($[Co(H_2O)_6]^{2+}$(aq)) to a new complex ($[CoCl_4]^{2ˇ}$ (aq)). This is accompanied by a change in color, from reddish-pink to blue. The green solution shown in the figure above is a third type of cobalt complex. The equilibrium between the two complexes is sensitive not only to the concentration of the chloride ion, but also to the temperature. Increasing the temperature causes a shift from the pink to the blue species, and lowering the temperature reverses this color change.

So far, we have generally assumed that the reactants in a chemical reaction are irreversibly transformed into products. However, many chemical reactions are reversible, meaning that it is also possible for the reaction to go "backwards". When both the forward and reverse reactions can proceed at a reasonable rate, a state of equilibrium is eventually reached, in which both reactions are occurring at the same rate and no net change is made to the amounts of reactants or products. In this chapter, we will look at the factors that govern chemical equilibria.

User:Chemicalinterest/Wikimedia Commons. commons.wikimedia.org/wiki/File:Cobalt_chloride_equilibrium.JPG. Public Domain.

19.1 The Nature of Chemical Equilibrium

Lesson Objectives

- Define chemical equilibrium in terms of reaction rates.
- Define equilibrium constant.
- Be able to write an equilibrium constant expression for a chemical reaction using the law of mass action.

Lesson Vocabulary

- **irreversible process**: A chemical reaction that can only be run in the forward direction; that is, the products do not react to form the reactants.
- **chemical equilibrium**: The state in which the rate of the forward reaction is equal to the rate of the reverse reaction.
- **equilibrium constant**: The ratio of the rate constant of the forward reaction and the rate constant of the reverse reaction.
- **equilibrium constant expression**: The ratio of the product concentrations and the reactant concentrations, raised to their respective exponents.
- **law of mass action**: States that for any reaction at equilibrium, the ratio of product concentrations to reactant concentrations (along with the appropriate exponents) is equal to a constant.

Check Your Understanding

1. Can you give an example of a chemical process that is reversible?
2. Can you think of a chemical process that is not reversible, or that would be very difficult to reverse?

Introduction

We have not always known that some chemical processes are reversible. In fact, not long ago, it was widely thought that chemical processes were irreversible. For instance, the dissolving of table salt into water was viewed as a unidirectional process; once the salt dissolved, it could not be undissolved from the solution. Dissolution reactions were therefore viewed as **irreversible processes**. However, in the early 1800s, the Frenchman Claude Lois Berthollet (1748-1822) observed a dissolution reaction that appeared to be reversible.

FIGURE 19.1

Berthollet was a chemist hired by Napoleon to travel to Egypt during what later became known as the Battle of the Pyramids (1798). One day, Berthollet observed crystals of sodium carbonate (also known as trona) that had formed along one of the ponds he was visiting.

FIGURE 19.2

Trona is a mineral composed of hydrated sodium carbonate, $Na_2CO_3 \bullet 10H_2O$, that is often found crystallized with other salts. Berthollet was struck by this occurrence, because the double displacement reaction that often occurred in the salt-rich natron ponds was expected to produce only calcium carbonate and sodium chloride, not sodium carbonate.

$$Na_2CO_{3(aq)} + CaCl_{2(aq)} \rightarrow CaCO_{3(s)} + 2NaCl_{(aq)}$$

Berthollet suggested that the presence of Na_2CO_3 meant that this double displacement reaction was actually reversible.

$$Na_2CO_{3(aq)} + CaCl_{2(aq)} \rightleftarrows CaCO_{3(s)} + 2NaCl_{(aq)}$$

The reversibility of this reaction would explain how the reactants and products could all be present at the same time.

Reversible Reactions

Equilibrium in Chemical Reactions

Consider the following generic chemical equation:

$A + B \rightleftarrows C + D$

At the beginning of the reaction, only the reactants A and B are present. Recall that over the course of a reaction, the reaction rate slows down. This is because the rate depends on the concentrations of one or more reactants. As the reactants are used up, their concentrations drop, thus decreasing the reaction rate.

At the same time, the concentrations of the products, C and D, are increasing from their initial concentrations of zero. For the reverse reaction, C and D are the reactants, so the rate of the reverse reaction will increase as more C and D are present. As the reaction progresses, the rate of the forward reaction decreases, and the rate of the reverse reaction increases. Eventually, these two rates will be equal. In other words, the rate at which the products are formed is equal to the rate at which they are consumed, so no net change is taking place. A reaction has reached **chemical equilibrium** when the rate of the forward reaction is equal to the rate of the reverse reaction.

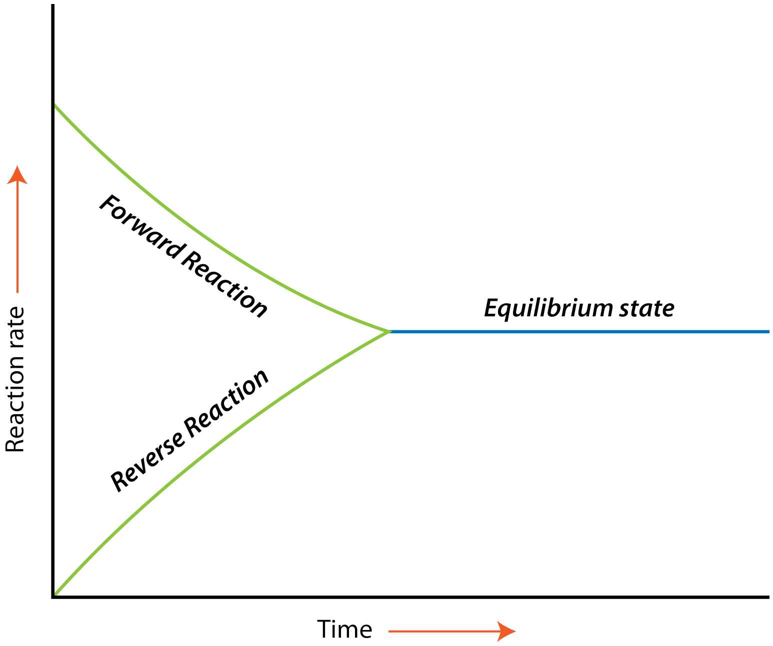


FIGURE 19.3

After equilibrium has been reached, the concentrations of all reaction components will remain constant unless a change is made to the system. Because the concentrations are no longer changing, it may appear that the reaction has "stopped." This is incorrect; both the forward and reverse reactions are still going on, even at equilibrium. However, because the two reactions are proceeding at the same rate, no net change is observed.

The Equilibrium Constant (K

The Law of Mass Action

Consider again a generic reversible reaction in which reactants A and B react to form products C and D. This equilibrium is shown below, where the lower case letters represent the coefficients of each substance.

$aA + bB \rightleftarrows cC + dD$

Let's assume that this reaction occurs by a single elementary step. If that were the case, the rate law for the forward reaction would have the following form:

$Rate_{forward} = k_f[A]^a[B]^b$

where the concentrations of each reactant, indicated by the square brackets around the formula, are measured in molarity units (mol/L).

Similarly, the rate law for the reverse reaction can be written using the concentrations of C and D (the reactants for the reverse process):

$Rate_{reverse} = k_r[C]^c[D]^d$

In a reaction at equilibrium, the rate of the forward reaction equals the rate of the reverse reaction. Mathematically, this means the following:

$$\begin{aligned} Rate_{forward} &= Rate_{reverse} \\ k_f[A]^a[B]^b &= k_r[C]^c[D]^d \\ \frac{k_f}{k_r} &= \frac{[C]^c[D]^d}{[A]^a[B]^b} \end{aligned}$$

The ratio of the two rate constants would just be another constant. This new constant, written as K_{eq}, K_c, or simply K, is known as the **equilibrium constant** for this reaction. The **equilibrium constant expression** has the following form:

$K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$

We derived this expression based on reactions that occur by a single elementary step. However, it turns out that the equilibrium constant expression is valid for any reaction, even those that occur by a multi-step mechanism. For any reaction at equilibrium, the ratio of product concentrations to reactant concentrations (along with the appropriate exponents) is equal to a constant. This is known as the **law of mass action**.

Example 19.1

Write the equilibrium constant expression for the following reaction:

$2SO_3(g) \rightleftarrows 2SO_2(g) + O_2(g)$

Answer:

The products go in the numerator, and the reactant goes in the denominator. Any component that has a coefficient in the balanced equation is raised to that power in the equilibrium constant expression.

$K_{eq} = \frac{[SO_2]^2[O_2]}{[SO_3]^2}$

Heterogeneous Equilibria

So far, we have been assuming that a decrease in the amount of a reactant or product also decreases its concentration. This is true for gases, where the concentration is equal to the number of moles divided by the volume of the container. Because the container generally does not change size over the course of the reaction, fewer moles of gas means a lower concentration. This is also true for substances that are dissolved in water or another solvent. Assuming the volume of the solvent does not change appreciably during the reaction, fewer moles of solute in the same amount of solvent results in a lower concentration.

However, for solid or liquid reaction components, this is not necessarily true. Consider the following reaction:

$NH_4CO_2NH_2(s) \rightleftarrows 2NH_3(g) + CO_2(g)$

The "concentration" of a solid is essentially another way of measuring its density. A certain number of moles are present for a given volume of the solid, and this value does not depend on how much of the solid is present. As the reaction proceeds, the amount of solid reactant will decrease, but so will the volume it occupies. A similar argument can be made for liquids. As a result, the concentrations of solids and liquids are essentially constant over the course of a reaction.

Now, let's look at the equilibrium constant expression that could be generated for this reaction. Following the rules that we have given so far, it would take the following form:

$K_{eq} = \frac{[NH_3]^2[CO_2]}{[NH_4CO_2NH_2]}$

However, because the concentration of solid ammonium carbamate is constant during the reaction, we could potentially simplify this expression as follows:

$$(K_{eq})[NH_4CO_2NH_2] = [NH_3]^2[CO_2]$$
$$K'_{eq} = [NH_3]^2[CO_2]$$

where K'$_{eq}$ is the product of the original equilibrium constant and the constant concentration of the solid reactant. By convention, the simpler form is used by chemists. Whenever solid or liquid reactants or products are part of a chemical reaction, their concentrations are *not* included in the equilibrium constant expression, and it is understood that the constant concentration of the missing reaction components is incorporated into the value of any measured equilibrium constants.

Example 19.2

Write the equilibrium constant expression for the following reaction:

$2Mg(s) + O_2(g) \rightleftarrows 2MgO(s)$

Answer:

Because both Mg and MgO are present as solids, they are not included in the equilibrium constant expression. The only remaining component is oxygen gas. Because oxygen is a reactant, it will appear in the denominator.

$K_{eq} = \frac{1}{[O_2]}$

Concentration vs. Partial Pressure

Let's take a look at one way in which the ideal gas law can be rearranged. We are most familiar with the following form:

$PV = nRT$

Dividing both sides by volume and rearranging the variables, we could also write this law as follows:

$P = (RT)(\frac{n}{V})$

What is the significance of this? Take a look at the fraction on the right. We are dividing the amount of gas (in moles) by the volume (in liters). The fraction n/V is simply the concentration of the gas. At a given temperature, the partial pressure of any gas is directly proportional to its concentration. Because of this, we can write an alternate equilibrium constant expression in which partial pressures are used in place of concentrations. The pressure-based equilibrium constant, indicated by the abbreviation K$_p$, can be written as follows for a generic reaction in which all components are present in the gas state:

$$aA(g) + bB(g) \rightleftarrows cC(g) + dD(g)$$
$$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$$

For reactions that include solids or liquids in addition to gases, those components are left out of the equilibrium constant expression, just as they are for a concentration-based equilibrium constant. For reactions that include both gases and aqueous components, the K$_p$ form of the equilibrium constant is generally not used.

Example Problem 19.3

Write the pressure-based equilibrium constant expression (K$_p$) for the following reaction:

$2O_3(g) \rightleftarrows 3O_2(g)$

Answer:

The process here is exactly the same as for a normal equilibrium constant expression, except that we are using partial pressures instead of concentrations. Reactants go in the denominator, and products go in the numerator. Each component is raised to an exponent that is equal to its coefficient in the balanced equation.

$K_p = \frac{(P_{O_2})^3}{(P_{O_3})^2}$

Converting Between K

For a gaseous substance, the conversion factor between concentration and partial pressure can be derived from the ideal gas law:

$$P_AV = n_ART$$
$$P_A = (\frac{n_A}{V})(RT)$$
$$P_A = [A](RT)$$

where [A] is the molar concentration of A. Let's look again at the generic expression for K$_p$:

$$aA(g) + bB(g) \rightleftarrows cC(g) + dD(g)$$
$$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$$

If we substitute in concentrations for each of the partial pressures, we would get the following:

$$K_p = \frac{([C](RT))^c([D](RT))^d}{([A](RT))^a([B](RT))^b}$$
$$K_p = \frac{[C]^c[D]^d}{[A]^a[B]^b} \times \frac{(RT)^c(RT)^d}{(RT)^a(RT)^b}$$

The fraction on the left is simply the generic expression for K_c. Additionally, the exponents in the fraction on the right can be manipulated as follows:

$K_p = K_c(RT)^{(c+d)-(a+b)}$

The exponent $(c+d)-(a+b)$ is the sum of the stoichiometric coefficients for the gaseous products minus the sum of the coefficients for the gaseous reactants. This value is sometimes abbreviated as Δn. Note that Δn can be a negative or positive number. Using this abbreviation, the conversion factor between K_p and K_c can be written as follows:

$K_p = K_c(RT)^{\Delta n}$

Lesson Summary

- At equilibrium, the rate of the forward reaction is equal to the rate of the reverse reaction.
- The ratio between the concentrations of the products and the concentrations of the reactants, each raised to the appropriate exponent, is constant at a given temperature. This is referred to as the equilibrium constant.
- By convention, only gaseous and aqueous reaction components are included in the equilibrium constant expression, since solids and liquids do not change concentration when they are consumed or formed.
- The partial pressure of an ideal gas is proportional to its concentration. K_p is an alternate way to express the equilibrium of a reaction that includes gaseous components.

Review Questions

1. At chemical equilibrium, what is the relationship between the rate of the forward reaction and the rate of the reverse reaction?
2. What does the law of mass action say about any reaction at equilibrium?
3. Why are solids and liquids left out of the equilibrium constant expression?
4. Explain why the equilibrium constant expression as derived from concentrations can be converted to the equilibrium constant expression as derived from partial pressures.
5. Construct balanced chemical equations and write the equilibrium constant expression (either K_p or K_c) for each of the following processes.
   a. Sodium metal reacts vigorously with oxygen gas to produce sodium oxide.
   b. Aluminum oxide decomposes to form aluminum metal and oxygen gas.
   c. Nitrogen gas and oxygen gas react to form nitrogen monoxide gas.
6. Give an example of a chemical equilibrium that exists in our daily lives.
7. Write a K_{eq} expression for each of the following processes.
   a. Solid calcium carbonate is heated and decomposes into solid calcium oxide and carbon dioxide gas.
   b. Hydrogen gas (H_2) and solid iodine (I_2) are combined to form hydrogen iodide gas (HI).

Further Reading / Supplemental Links

- Equilibrium constants: http://www.chemguide.co.uk/physical/equilibria/kc.html
- More equilibrium constants: http://chemistry.twu.edu/tutorial/DetEqConstantSum.html

Points to Consider

- How do you suppose the forward and reverse processes are related for a given chemical equilibrium?

19.2 Applications of Equilibrium Constants

Lesson Objectives

- Use experimental data to determine an equilibrium constant.
- Be able to interpret the value of an equilibrium constant to say whether the equilibrium for a particular reaction is product-favored or reactant-favored.

Lesson Vocabulary

- **ICE table**: A mathematical method that can be used to determine equilibrium constants for chemical reactions based on the Initial, Change in, and Equilibrium amounts of reactants and products.

Check Your Understanding

- Write the equilibrium constant expression for the reaction in which carbon monoxide gas decomposes into solid carbon and oxygen gas. Write the expressions for both K_c and K_p.

Introduction

Figure 19.4 shows a brown cloud over a major U.S. city. The brown color comes from nitrogen dioxide, a highly toxic gas that exists in equilibrium with other atmospheric gases. These materials are harmful to health and contribute to other detrimental processes, such as the formation of acid rain. The phenomenon is observed primarily in large urban areas where there is a large amount of automobile traffic in a concentrated area. Urban locations where air circulation is poor, such as valleys, may see an especially high amount of these gases.

Under normal conditions, NO_2 is in equilibrium with its dimeric form, N_2O_4. N_2O_4 is also quite toxic, but it is colorless. This equilibrium can be written as the following chemical equation:

$$2NO_2(g) \rightleftarrows N_2O_4(g)$$

Once this reaction reaches equilibrium, will the material exist mostly as NO_2, mostly as N_2O_4, or as an approximately even mixture? To answer this question, we would need to determine the equilibrium constant for this reaction at the temperature of interest.

FIGURE 19.4

The brown color is from nitrogen dioxide gas. Nitrogen dioxide is a byproduct from the combustion of fossil fuels like coal and gasoline.

Calculating Equilibrium Constants

Experiments are very useful for determining equilibrium constants for various reactions. We are going to give a simple example of an experiment that could be done to determine the equilibrium constant for this reaction.

The equilibrium constant expression for the reaction above has the following form:

$$K_c = \frac{[N_2O_4]}{[NO_2]^2}$$

In order to calculate the value of K_c, we need to determine the concentrations of both the reactant and the product for any system that has reached equilibrium. One possible method for achieving this is as follows:

- First, we would put a known amount of our reactant (NO_2) into a rigid container of fixed volume.

Remember: The equilibrium constant expression only applies for a specific constant temperature, so we want to keep the temperature consistent throughout course of the reaction. Most equilibrium constants are given for a standard temperature of 25°C.

- After putting our reactant into the container, we would allow the system to reach equilibrium. We know that the system is at equilibrium once the concentrations of each component are no longer changing over time. Because N_2O_4 is colorless but NO_2 is brown, the concentration of NO_2 can be determined by colorimetry, which relates the amount of visible light absorbed by a given sample to its concentration.
- Once at equilibrium, we will determine the concentration of the remaining NO_2, and the concentration of N_2O_4 can be calculated by knowing the total amount of material present in our reaction vessel.
- Finally, these values can then be plugged into the equilibrium constant expression to determine the value of the equilibrium constant.

Example 19.4

0.2000 moles of pure NO_2 is placed in a rigid 1-liter container at a fixed temperature. The system is allowed to reach equilibrium, at which point the concentration of NO_2 is found to be 0.0204 M. Calculate the equilibrium constant for the following reaction:

$2NO_2(g) \rightleftarrows N_2O_4(g)$

Answer:

First, write the equilibrium constant expression for the given equation:

$K_c = \frac{[N_2O_4]}{[NO_2]^2}$

We are given the equilibrium concentration of NO_2, so now we need to find the concentration of N_2O_4. This can be accomplished by setting up a table that compares the initial and equilibrium amounts of each reaction component. This type of table is often called an **ICE table**, where ICE stands for initial, change, equilibrium. Start by drawing out a blank table for the given reaction:

TABLE 19.1: **Example 19.4 ICE Table Initial Setup**

	$2NO_2(g)$	$\rightleftarrows$	$N_2O_4(g)$
Initial amount			
Change			
Equilibrium amount			

Then, fill in the known information:

TABLE 19.2: **Example 19.4 ICE Table I**

	$2NO_2(g)$	$\rightleftarrows$	$N_2O_4(g)$
Initial amount	0.2000 mol		0 mol
Change			
Equilibrium amount	0.0204 mol		

ICE tables are often written in units of concentration. The values that we are using in this table have units of moles. We are able to use moles rather than concentration because the reaction vessel is a rigid 1-L container, so the number of moles is actually equal to the concentration (*0.200* mol = *0.200*mol/ 1-L = *0.200* M). As long as the total volume of the container does not change over the course of the reaction, using either moles or concentration is an acceptable way to set up this type of problem.

Because we are starting with no product, we know that the amount of product will increase and the amount of reactant will decrease before an equilibrium is reached. Therefore, we can add the following information:

TABLE 19.3: **Example 19.4 ICE Table II**

	$2NO_2(g)$	$\rightleftarrows$	$N_2O_4(g)$
Initial amount	0.2000 mol		0 mol
Change	-2x mol		+x mol
Equilibrium amount	0.0204 mol		x mol

These numbers are related to the coefficients from the balanced equation. If the amount of N_2O_4 increases by x moles, the amount of NO_2 must decrease by $2x$ moles. Because we know the initial and equilibrium amounts of NO_2, we can solve for x:

$$\begin{aligned} 0.2000 \text{ mol} - 2x &= 0.0204 \text{ mol} \\ x &= 0.0898 \text{ mol} \end{aligned}$$

At equilibrium, our reaction mixture contains 0.0204 moles of NO_2 and 0.0898 moles of N_2O_4. Because the reaction is taking place in a 1-L container, the concentrations of these two components will be 0.0204 M and 0.0898 M, respectively. Plugging these values into the equilibrium constant expression, we get the following:

$$K_c = \frac{[N_2O_4]}{[NO_2]^2}$$

$$K_c = \frac{[0.0898]}{[0.0204]^2}$$

$$K_c = 2.16 \times 10^3$$

The equilibrium constant for this reaction has a value of 2.16×10^3 for the temperature at which these data were collected.

Now we will consider a different experiment in which we start with the product of this reaction (as written above), but no reactant:

Example 19.5

0.8450 moles of pure N_2O_4 is placed in a rigid 1-liter container at a fixed temperature (the same temperature as in the previous example problem). The system is allowed to reach equilibrium, at which point the concentration of NO_2 is found to be 0.01966 M. Calculate the equilibrium constant for the following reaction:

$2NO_2(g) \rightleftarrows N_2O_4(g)$

Answer:

Again, we are given the equilibrium concentration of NO_2, so now we need to find the concentration of N_2O_4. Start by setting up an ICE table, including any known information:

TABLE 19.4: **Example 19.5 ICE Table Initial Setup**

	$2NO_2(g)$	$\rightleftarrows$	$N_2O_4(g)$
Initial amount	0 mol		0.8450 mol
Change			
Equilibrium amount	0.01966 mol		

Because we are starting with no reactant, we know that the amount of reactant will increase and the amount of product will decrease before an equilibrium is reached. Therefore, we can add the following information:

TABLE 19.5: **Example 19.5 ICE Table I**

	$2NO_2(g)$	$\rightleftarrows$	$N_2O_4(g)$
Initial amount	0 mol		0.8450 mol
Change	+2x mol		-x mol
Equilibrium amount	0.01966 mol		0.8450-x mol

Using the information given for the final amount of NO_2, solve for x:

$$\begin{aligned} 0 \text{ mol} + 2x &= 0.01966 \text{ mol} \\ x &= 0.00983 \text{ mol} \end{aligned}$$

Then, use the value of x to determine how much N_2O_4 is present at equilibrium:

$0.8450 \text{ mol} - x = 0.8450 \text{ mol} - 0.00983 \text{ mol} = 0.83517 \text{ mol}$

At equilibrium, our reaction mixture contains 0.01966 moles of NO_2 and 0.83517 moles of N_2O_4. Because the reaction is taking place in a 1-L container, the concentrations of these two components will be 0.01966 M and 0.83517 M, respectively. Plugging these values into the equilibrium constant expression, we get the following:

$$\begin{aligned} K_c &= \frac{[N_2O_4]}{[NO_2]^2} \\ K_c &= \frac{[0.83517]}{[0.01966]^2} \\ K_c &= 2.16 \times 10^3 \end{aligned}$$

Again, the equilibrium constant for this reaction has a value of 2.16×10^3. The measured equilibrium constant for a given reaction at a set temperature is always the same, regardless of whether we start with all reactants, all products, or some combination of the two. Even though the final concentrations depend on the initial conditions (the final concentrations are different in the previous two example problems), the ratio defined by the equilibrium constant expression will have the same value once the system reaches equilibrium. This shows that the equilibrium constant is the same for any given chemical reaction at a specified temperature, regardless of the initial amounts of reactants and products.

Interpreting the Value of an Equilibrium Constant

What does the value of K_c tell us about the relative position of the equilibrium? Let's look at the results of the previous example problem. At equilibrium, we had a product concentration of 0.83517 M and a reactant concentration of 0.01966 M. Because there are more products than reactants at equilibrium, we say that this reaction is *product-favored* at the given temperature. Similarly, reactions in which the reactants are more prevalent than the products at equilibrium are said to be *reactant-favored*.

How can we tell whether a reaction is product-favored or reactant-favored without actually calculating equilibrium amounts? Remember that in the equilibrium constant expression, the product concentrations are in the numerator, whereas the reactant concentrations are in the denominator. In a product-favored equilibrium, the value of the numerator would be much larger than the value of the denominator, so $K_{eq} > 1$ means that the products are favored over the reactants. Conversely, a $K_{eq} < 1$ would suggest that the reactants are favored over the products. Finally, a K_{eq} value that is approximately equal to 1 means that significant amounts of both the reactants and the products are present at equilibrium.

Lesson Summary

- The equilibrium constant is a ratio that describes the relative equilibrium concentrations of products and reactants for a given chemical process.
- An equilibrium constant can be determined from experimental data.

- Equilibrium constants allow us to predict the relative amounts of reactants and products for a given chemical process.
- The equilibrium constant depends on the temperature at which the reaction is taking place, but it does not depend on the initial (pre-equilibrium) concentrations of the reactants and products.

Review Questions

1. Write the equilibrium constant expression (K_c) for each of the following processes:
    (a) $2O_3(g) \rightleftarrows 3O_2(g)$
    (b) $3O_2(g) \rightleftarrows 2O_3(g)$
    (c) $2NO(g) + Cl_2(g) \rightleftarrows 2NOCl(g)$
2. The equilibrium constants for three different reactions are shown below. Are these reactions reactant-favored or product-favored?
    (a) 4.64×10^{-3} at 25°C
    (b) 2.2×10^{-10} at 100°C
    (c) 150 at 25°C
3. Write the pressure-based equilibrium constant expression (K_p) for the following reaction: $N_2(g) + 3H_2(g) \rightleftarrows 2NH_3(g)$. If K_p=4.3×10^{-3} for the forward reaction, calculate K_p for the reverse reaction. (*Hint*: Write the equilibrium constant expression for the reverse reaction. How is it related to the expression for the forward reaction?)
4. The equilibrium constant for the following reaction is equal to 1.74×10^{-5}: $CH_3CO_2H(aq) + H_2O(l) \rightleftarrows CH_3CO_2^-(aq) + H_3O^+(aq)$. Would you expect there to be more CH_3CO_2H or more $CH_3CO_2{}^-$ present after this reaction reaches equilibrium?
5. What is the value of K_c for the following reaction: $2A + B \rightleftarrows C$? The equilibrium concentrations of A, B, and C are [A]=1.64 M, [B]=1.84 M, and [C]=0.45 M.
6. 2.34 moles of A and 1.17 moles of B are introduced into a 3.8 L vessel. They are allowed to react until the following process reaches equilibrium: $2A + B \rightleftarrows C$. At equilibrium, 0.52 moles of A are present. What is the value of K_c for this reaction?

Further Reading / Supplemental Links

1. Chemical equilibria simulation: http://group.chem.iastate.edu/Greenbowe/sections/projectfolder/animationsindex.htm
2. NO_2/N_2O_4 equilibrium experiment: Teresa Anderson Curtin, Darryl Wahlstrom, McCormick James Journal of Chemical Education 1991 68 (9), 781

Points to Consider

- Given that the chemical equilibrium for all chemical reactions is temperature dependent, how do you suppose temperature influences a given chemical equilibrium?
- Can you think of chemical processes that may be reactant-favored at one temperature and product-favored at another?
- Can you think of other factors that may influence whether or not a given chemical process is reactant-favored or product-favored?

- What is the relationship between the equilibrium constant and the stoichiometric coefficients?

19.3 Factors Affecting Chemical Equilibria

Lesson Objectives

- Determine whether various changes would alter the position of an equilibrium.
- Describe Le Châtelier's Principle, and use it to predict the direction that a reaction would shift in response to various changes.

Lesson Vocabulary

- **Le Châtelier's Principle**: States that when a chemical system is at equilibrium and is disturbed by a stress, the system will respond by attempting to counteract that stress until a new equilibrium is established.

Check Your Understanding

- Write the equilibrium constant expression for the following chemical reaction: $2\text{NOBr}(g) \rightleftarrows 2\text{NO}(s) + \text{Br}_2(g)$
- If K_c for this process is 0.0142, would you expect the reaction to be reactant-favored or product-favored?

Introduction

So far you have learned about what chemical equilibrium means and how to calculate an equilibrium constant for a reaction based on reaction rate and reactant component concentrations. In order to establish chemical equilibrium, the rates of the forward and reverse reactions change until they become equal. In this lesson, you will learn how a chemical reaction maintains equilibrium when a stress is put on the system.

Le Châtelier's Principle

Equilibrium represents a balance between the reactants and the products of a chemical reaction. Changes to the conditions of the system can disturb that equilibrium. When this occurs, the system reacts in such a way as to restore the equilibrium. However, the position of equilibrium will be changed following the disturbance. In other words, the response of the system involves a change in the amounts of the reactants and products. Some will increase and some will decrease until equilibrium is reestablished.

Chemical equilibrium was studied by French chemist Henri Le Châtelier (1850-1936), and his description of how a system at equilibrium responds to a change in conditions has become known as **Le Châtelier's principle**. This principle states that when a chemical system is at equilibrium and is disturbed by a stress, the system will respond by attempting to counteract that stress until a new equilibrium is established. Stresses to a chemical system include changes in the concentrations of reactants or products, changes in the temperature of the system, or changes in the pressure of the system. We will discuss each of these stresses separately. In each case, the change to the equilibrium position will cause either the forward or reverse reaction to be favored over the opposite process. When the forward reaction is favored, the concentrations of the products increase, and the concentrations of the reactants decrease. When the reverse reaction is favored, the concentrations of the products decrease, and the concentrations of the reactants increase.

TABLE 19.6: Reaction to Stresses

Original Equilibrium	Favored Reaction	Result
$A \rightleftharpoons B$	forward: $A \rightarrow B$	[A] decreases; [B] increases
$A \rightleftharpoons B$	reverse: $A \leftarrow B$	[A] increases; [B] decreases

Concentration

A change in the concentration of one of the substances in an equilibrium system typically involves either the addition or the removal of one of the reactants or products. Consider the Haber-Bosch process for the industrial production of ammonia from nitrogen and hydrogen gases:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

If the concentration of one substance in a system is increased, the system will respond by favoring the reaction that consumes that substance. When more N_2 is added, the forward reaction will be favored because the forward reaction uses up N_2 and converts it to NH_3. Initially, the forward reaction speeds up because one of the reactants is present at a higher concentration, but the rate of the reverse reaction is unaffected. Since the two rates are no longer equal, the system is no longer at equilibrium, and there will be a net shift to the right (producing more NH_3) until the two rates are once again balanced. The concentration of NH_3 increases, while the concentrations of N_2 and H_2 decrease. After some time passes, equilibrium is reestablished with new concentrations of all three substances. As can be seen in **Figure** 19.5, the new concentration of NH_3 is higher than it was originally, because the forward reaction became temporarily favored due to the stress. The new concentration of H_2 is lower. The final concentration of N_2 is higher than it was in the original equilibrium, but lower than it was immediately after the addition of N_2 that disturbed the original equilibrium. By responding in this way, the value of the equilibrium constant for the reaction, K_{eq}, does not change as a result of the stress to the system.

Conversely, if more NH_3 were added, the reverse reaction would be favored. This "favoring" of a reaction means temporarily speeding up the reaction in that direction until equilibrium is reestablished. Recall that once equilibrium is reestablished, the rates of the forward and reverse reactions are again equal. The addition of NH_3 would result in a net increase in the formation of the reactants, N_2 and H_2.

An equilibrium can also be disrupted by the full or partial removal of a reactant or product. If the concentration of a substance is decreased, the system will respond by favoring the reaction that replaces that substance. In the industrial Haber-Bosch process, NH_3 is removed from the equilibrium system as the reaction proceeds. As a result, the forward reaction is favored so that more NH_3 will be produced. The concentrations of N_2 and H_2 decrease. Continued removal of NH_3 will eventually force the reaction to go to completion until all of the reactants are used up. If either N_2 or H_2 were removed from the equilibrium system, the reverse reaction would be favored, and the concentration of NH_3 would decrease.

The effects of changes in concentration on a system at equilibrium are summarized in **Table** 19.7.

TABLE 19.7: Stresses and Responses

Stress	Response
addition of reactant	forward reaction favored

TABLE 19.7: (continued)

Stress	Response
addition of product	reverse reaction favored
removal of reactant	reverse reaction favored
removal of product	forward reaction favored

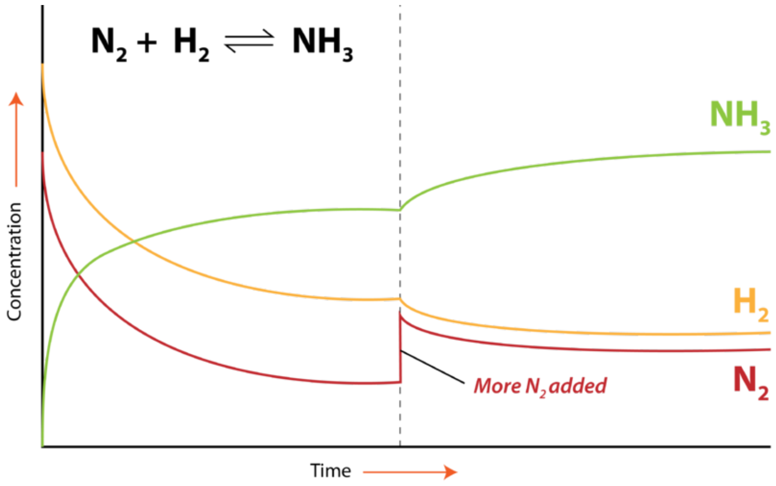


FIGURE 19.5
The Haber-Bosch process is an equilibrium between the reactants (N_2 and H_2) and the product (NH_3). When more N_2 is added, the system favors the forward reaction until equilibrium is reestablished.

Temperature

Increasing or decreasing the temperature of a system at equilibrium is also a stress to the system. The equation for the Haber-Bosch process is written again below, this time as a thermochemical equation.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 91 \text{ kJ}$$

The forward reaction is the exothermic direction; the formation of NH_3 releases heat. The reverse reaction is the endothermic direction; as NH_3 decomposes to N_2 and H_2, heat is absorbed. An increase in the temperature of a system favors the direction of the reaction that absorbs heat, or the endothermic direction. Absorption of heat in this case is a relief of the stress provided by the temperature increase. For the Haber-Bosch process, an increase in temperature favors the reverse reaction. The concentration of NH_3 in the system decreases, while the concentrations of N_2 and H_2 increase.

Conversely, a decrease in the temperature of a system favors the direction of the reaction that releases heat, or the exothermic direction. For the Haber-Bosch process, a decrease in temperature favors the forward reaction. Therefore the concentration of NH_3 in the system increases, while the concentrations of N_2 and H_2 decrease.

For changes in concentration, the system responds in such a way that the value of the equilibrium constant, K_{eq}, is unchanged. However, a change in temperature shifts the equilibrium and changes the value of K_{eq}. As discussed in the previous section, values of K_{eq} are dependent on the temperature. When the temperature of the system for the Haber-Bosch process is increased, the resultant shift in equilibrium towards the reactants means that the K_{eq} value decreases. When the temperature is decreased, the shift in equilibrium towards the products means that the K_{eq} value increases.

Le Châtelier's principle as related to temperature changes can be illustrated easily by the equilibrium between dinitrogen tetroxide and nitrogen dioxide.

$$N_2O_4(g) + \text{heat} \rightleftharpoons 2NO_2(g)$$

Dinitrogen tetroxide (N_2O_4) is colorless, while nitrogen dioxide (NO_2) is dark brown in color. When N_2O_4 breaks down into NO_2, heat is absorbed according to the forward reaction above. Therefore, an increase in the temperature of the system will favor the forward reaction, while a decrease in temperature will favor the reverse reaction. By changing the temperature, the equilibrium between colorless N_2O_4 and brown NO_2 can be manipulated, resulting in a visible color change.

The video below shows three sealed glass tubes containing N_2O_4 and NO_2. When one tube is placed in hot water, the equilibrium favors the brown NO_2. When another tube is placed in ice cold water, the equilibrium lies in favor of the colorless N_2O_4.

http://www.youtube.com/watch?v=tlGrBcgANSY (0:55)

MEDIA

Click image to the left for more content.

Pressure

Changing the pressure of an equilibrium system in which gases are involved is also a stress to the system. A change in the pressure on a liquid or a solid has a negligible effect. We will return again to the equilibrium for the Haber-Bosch process. Imagine the gases are contained in a closed system in which the volume of the system is controlled by an adjustable piston as shown in **Figure** 19.6.

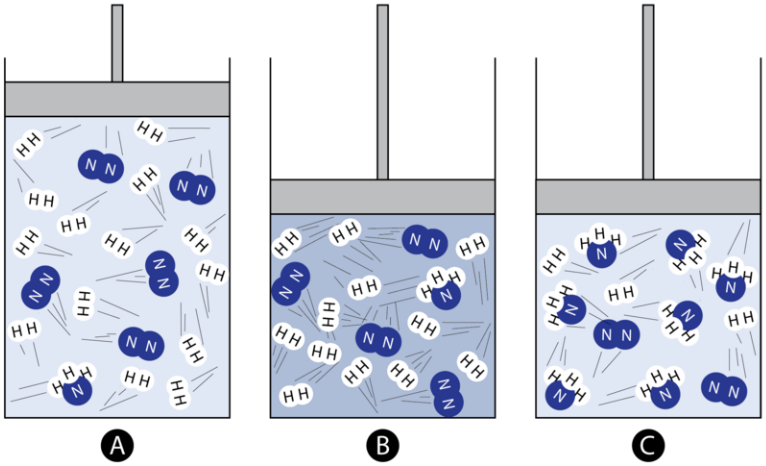


FIGURE 19.6

(A) A mixture of nitrogen, hydrogen, and ammonia in equilibrium. (B) When the pressure is increased on the equilibrium mixture, the forward reaction is favored because that results in a reduction of the total moles of gas present. (C) Fewer moles of gas will exert a lower total pressure, so the stress is partially relieved by such a shift.

On the far left, the reaction system contains primarily N_2 and H_2, with only one molecule of NH_3 present. As the piston is pushed inwards, the pressure of the system increases according to Boyle's Law. This is a stress to the equilibrium. In the middle image, the same number of molecules are now confined to a smaller space, so the pressure has increased. According to Le Châtelier's principle, the system responds in order to relieve the stress. In the image on the right, the forward reaction has been favored, in which each one molecule of N_2 combines with three molecules of H_2 to form one molecule of NH_3. The overall result is a decrease in the number of gas molecules in the entire system. This decreases the pressure and counteracts the original stress of a pressure increase. When the pressure is increased by decreasing the available volume, system responds by favoring the reaction direction that produces fewer gas molecules. In this case, it is the forward reaction that is favored.

A decrease in pressure on the above system could be achieved by pulling the piston outward, increasing the container volume. The equilibrium would respond by favoring the reverse reaction, in which NH_3 decomposes to N_2 and H_2. This is because the overall number of gas molecules would increase, and so would the pressure. When the pressure of a system at equilibrium is decreased by providing more total volume, the reaction that produces more total moles of gas becomes favored. This is summarized in the **Table** 19.8.

TABLE 19.8: **Stresses and Responses to Pressure Changes**

Stress	Response
pressure increase	reaction produces fewer gas molecules
pressure decrease	reaction produces more gas molecules

Like changes in concentration, the K_{eq} value for a given reaction is unchanged by a change in pressure.

It is important to remember when analyzing the effect of a pressure change on equilibrium that only gases are affected. If a certain reaction involves liquids or solids, they should be ignored. Calcium carbonate decomposes according to the equilibrium reaction:

$$CaCO_3(s) \rightleftharpoons CaO(s) + O_2(g)$$

Oxygen is the only gas in the system. An increase in the pressure of the system has no effect on the rate of decomposition of $CaCO_3$, but it speeds the reverse reaction by forcing the oxygen molecules closer together, causing a net shift to the left. When a system contains equal moles of gas on both sides of the equation, pressure has no effect on the equilibrium position, as in the formation of HCl from H_2 and Cl_2.

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

It should also be noted that increasing the pressure by the addition of an inert gas (nonreactive gas) has *no effect* on the equilibrium. This can be thought of in terms of the pressure-dependent equilibrium constant (K_p). Unlike an increase or decrease in the volume of the container, the addition of an inert gas does not affect the partial pressures of any reaction components. Because the ratio of partial pressures is still equal to the equilibrium constant, no change is necessary to maintain equilibrium.

Use of a Catalyst

Since a catalyst speeds up the rate of a reaction, you might think that it would have an effect on the equilibrium position. However, catalysts have equal effects on the forward and reverse rates, so for a system that is already at equilibrium, these two rates remain equal. A system will reach equilibrium more quickly in the presence of a catalyst, but the equilibrium position itself is unaffected.

Lesson Summary

- Le Chatelier's principle describes how a chemical system responds to stresses in order to reestablish equilibrium.
- Changes in the concentrations of reactants or products will cause a reaction to shift left or right in order to reestablish an equilibrium position. These changes do not change the value of K_{eq}.
- Changes in temperature will change the value of K_{eq}. The direction of the change depends on whether the reaction is endothermic or exothermic.
- When the pressure of a system is changed by changing the volume of the container, reactions in which some components are in the gas phase may shift to reestablish equilibrium. Changing the pressure by adding an inert gas does not affect a system at equilibrium.
- Adding a catalyst speeds up the progression of the reaction towards equilibrium, but does not change the equilibrium position itself.

Review Questions

1. Describe the basis of Le Chatlier's principle.
2. Is the value of the equilibrium constant changed with the addition or removal of reactant or product? If so, how? If not, why not?
3. Is the value of the equilibrium constant changed when the temperature is increased or decreased? If so, how? If not, why not?
4. How does the addition of an inert gas affect the equilibrium of a system?
5. Why does the addition of a catalyst have no effect on the equilibrium position?

6. The following reaction is allowed to reach equilibrium: $\mathrm{CaCO_3}(s) + \text{heat} \rightleftarrows \mathrm{CaO}(s) + \mathrm{CO_2}(g)$. Would the reaction shift left, shift right, or remain unchanged in response to each of the following changes:
   (a) Increasing the pressure by decreasing the volume at a constant temperature
   (b) Increasing the pressure by adding an inert gas at a constant temperature and volume
   (c) Increasing the temperature at a constant pressure
   (d) Adding a catalyst
7. The following reaction is allowed to reach equilibrium: $\mathrm{CO}(g) + \mathrm{H_2O}(g) + \text{heat} \rightarrow \mathrm{CO_2}(g) + \mathrm{H_2}(g)$. Would the reaction shift left, shift right, or remain unchanged in response to each of the following changes:
   (a) Increasing [CO]
   (b) Decreasing [H_2]
   (c) Decreasing [H_2O]
   (d) Increasing [CO_2]

Further Reading / Supplemental Links

- Chemical equilibria simulation: http://group.chem.iastate.edu/Greenbowe/sections/projectfolder/animationsindex.htm
- (Curtin, Wahlstron and McCormick, 1991). NO2/N2O4 equilibrium experiment. Journal of Chemical Education 1991 68 (9), 781

Points to Consider

- When chemical equilibrium is achieved for a given chemical process, the rate at which the forward process occurs is the same as the rate at which the reverse process occurs. What factors do you suppose affect the rate at which equilibrium is achieved?
- Some chemical processes are spontaneous, while others are not. How do you suppose chemical equilibrium is related to whether or not a chemical process is spontaneous or not?
- Can you think of examples where a particular process is spontaneous under certain conditions (say temperature) and nonspontaneous under other conditions?

19.4 References

1. Photogravure by H. Liffart, Berlin; scanned, image processed, and uploaded by Armin Kübelbeck. http://commons.wikimedia.org/wiki/File:Claude_Louis_Berthollet_01.jpg . Public Domain
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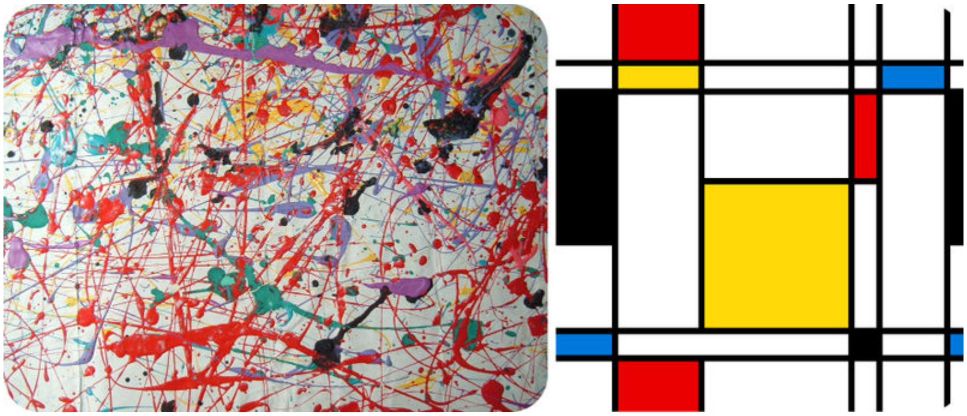
CHAPTER 20 Entropy and Free Energy

Chapter Outline

20.1 ENTROPY
20.2 SPONTANEOUS REACTIONS AND FREE ENERGY
20.3 FREE ENERGY AND EQUILIBRIUM
20.4 REFERENCES



The two paintings above represent two distinct movements in twentieth-century abstract art. Pollock was a proponent of abstract expressionism, mainly a post-World War II development. He was well-known for his drip paintings, where paint is dripped or poured on the canvas. Mondrian was strongly influenced by the earlier Cubist movement, which was characterized by extensive use of geometric forms. We can see the high level of disorder in Pollock's work, generated by random activity. On the other hand, the paintings by Mondrian represent a high level of structure and order.

The world we live in has aspects of order and disorder. We see order in the regular crystalline structure of solid sodium chloride and disorder in the random spattering of raindrops on a sidewalk. We also can observe changes in the amount of random movement exhibited by a single substance. For example, ice is highly ordered; each molecule of water is held rigidly in place by a network of hydrogen bonds. As the ice melts, the molecules gain more freedom of movement. They still cluster together into a liquid, but the individual molecules are free to move past one another and exchange hydrogen bonding partners. As the water vaporizes, its movement becomes even less restricted. No longer bound by intermolecular interactions, each molecule of water is free to move in essentially any direction. In this chapter, we will be discussing the concept of entropy, which quantifies order and disorder as pertains to chemical processes.

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20.1 Entropy

Lesson Objectives

- Describe what it means to call a process spontaneous, and give examples.
- Define entropy.
- Be able to predict whether the entropy of a system is increasing or decreasing.
- Calculate ΔS°_{rxn} from appropriate data.

Lesson Vocabulary

- **spontaneous**: Describes a reaction in which the given conditions favor the formation of the products.
- **entropy (S)**: A measure of probability or the degree of order.
- **standard entropy**: A measure of the entropy of a substance at 25°C and 1 atm of pressure.
- **second law of thermodynamics**: States that the entropy of the universe will increase for any spontaneous process.
- **third law of thermodynamics**: States that a perfectly regular crystal at a temperature of 0 K (absolute zero) would have an entropy value of 0.

Check Your Understanding

- How can we tell whether a reaction is exothermic or endothermic?
- What does the value of an equilibrium constant tell us about a reversible reaction?
- What information is needed to calculate the enthalpy change for a given reaction?

Introduction

Have you ever wondered why its easy to let your bedroom get messy, but much more difficult to keep it neat? When your bedroom is neat and orderly, everything is in a place where it belongs. When it's messy, everything seems to be out of order. It's as if you're bedroom naturally becomes messy, but you have to make an effort to keep it neat. Physical and chemical processes can be thought of in a similar way. There is a natural tendency for a physical or chemical process to progress in a certain direction. In this lesson, you will learn about the quantity used describe orderliness and how to predict the reaction direction in physical and chemical processes.

What is a Spontaneous Process?

Chemists want to be able to predict the outcome of reactions. They would like it to be possible to predict what will happen when reactants are added together under a given set of conditions. The conditions of a reaction might include things like temperature, pressure, and concentrations of various reaction components. If the given conditions favor the formation of products, the reaction is said to be **spontaneous**.

It should be noted that just because a process is spontaneous does not mean that it occurs quickly. The rusting of iron is a spontaneous process that takes place over a long period of time. The combustion of gasoline in oxygen (also a spontaneous process) is extremely fast when provided with a spark, but gasoline can be stored in air for quite a while without spontaneously combusting. Thermodynamics predicts the direction in which a reaction will eventually proceed, but it does not tell us anything about the rate at which the reaction occurs. The rate of a reaction depends on many factors, including activation energy, temperature, concentration, and the presence or absence of a catalyst. Chemical kinetics focuses on the pathway between reactants and products, while thermodynamics considers only the difference between the initial and final states.

We know of many examples of processes that occur spontaneously. If the temperature is below 0°C, a glass of liquid water will freeze. If the temperature is above 0°C, a cube of ice will melt. A hot object will gradually lose heat to its surroundings. Many chemical reactions also occur spontaneously. Two molecules of hydrogen will react with one molecule of oxygen to form water, releasing a significant amount of energy in the process. The spontaneous reaction between aluminum and bromine to form aluminum bromide also releases energy.

FIGURE 20.1

Melting ice in the Beaufort Sea off the North Slope of Alaska.

However, a process does not need to be exothermic in order to be spontaneous. For example, the melting of ice is an endothermic process, but it is still spontaneous at high enough temperatures. If we add ammonium nitrate to water, it will spontaneously dissolve, but the resulting solution will be cooler, indicating that energy in the form of heat was consumed in the process. To determine whether a process is spontaneous, we need to look not only at the change in enthalpy, but also the change in a factor called entropy.

What Is Entropy?

At its most basic level, **entropy** (S) is a measure of probability. States that have a high probability of occurring by random chance have a high entropy value, and states that are unlikely to occur by random chance have a low entropy value. There is a natural tendency for things to increase in entropy over time. An equivalent statement is that nature will spontaneously move toward the states that have the highest probability of existing.

Entropy can also be thought of as the number of possible arrangements that lead to a certain state. The more ways that a given state can be achieved, the greater the probability of finding that state, and the higher its entropy value. For example, think about the objects in your bedroom. Imagine every item being randomly placed at some location within the room. Now imagine this happening again and again. How many of the resulting arrangements would lead you to classify your room as "messy?" How many would qualify as a "clean" room? In this hypothetical example, every state has an equal possibility of happening, but because there are so many more ways to arrange items to make a messy room than a clean room, the "messy" state would have a higher entropy value than the "clean" state.

There are many examples in the chemical world of changes in entropy. Phase transitions are one obvious example. When a substance makes a transition from the liquid state to the gaseous state, the particles have many more possible arrangements, because they are no longer confined to a specified volume in which they are close to each other; gas particles can move freely throughout their container. Vaporization represents an increase in entropy. In the opposite direction, a liquid loses entropy when it freezes to a solid. Because solids have very ordered structures, there are fewer possible arrangements of particles that would result in the properties associated with a solid.

The Second Law of Thermodynamics

Recall that, according to the first law of thermodynamics, the total amount of energy in the universe is conserved for any given process. Entropy is not conserved; in fact, it is always increasing. Nature is constantly moving from less probable states to more probable ones. The **second law of thermodynamics** states that the entropy of the universe will increase for any spontaneous process.

To determine whether a given process is spontaneous, it is often helpful to break down the total entropy change as follows:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

where ΔS_{sys} and ΔS_{surr} represent the changes in entropy that occur in the system and in the surroundings, respectively.

To predict whether a given reaction will be spontaneous, we need to know the sign of ΔS_{univ}. If ΔS_{univ} is positive, the entropy of the universe increases, and the reaction is spontaneous in the direction that it is written. If ΔS_{univ} is negative, the reaction is spontaneous in the reverse direction. If ΔS_{univ} is equal to zero, the system is at equilibrium. To predict whether a reaction is spontaneous, we need to determine the entropy changes in the system and in the surroundings.

Entropy of a System (ΔS

Let's consider the change of state for one mole of water from liquid to gas:

$$H_2O_{(l)} \rightarrow H_2O_{(g)}$$

In this case, the water is the system, and the surrounding are everything else. How does the entropy of the water change in this process? As we saw earlier, the vaporization process leads to an increase in entropy, because there are many more possible ways to arrange the individual water molecules when they are allowed to move freely about their container. The entropy of the system increases, so ΔS_{sys} will be a positive value.

FIGURE 20.2

Phase changes are one type of process for which we can reliably predict the sign of the change in entropy. Not all transformations are quite so obvious, but the direction of the change in entropy can be easily predicted for certain types of chemical reactions.

1. If there is a difference in the number of gaseous components between the reactants and the products, the side with more moles of gas will most likely have a higher entropy value. This is because a greater number of moles indicates a greater number of gas particles and a greater number of arrangements of the gas particles.

For example, consider the following reaction:

$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(g)$

Three moles of gaseous reactants combine to make two moles of gaseous products. Therefore, we would expect this process to result in a decrease in entropy. ΔS_{sys} will have a negative value for this reaction.

2. Dissolved substances have a higher entropy value than their corresponding precipitate.

For example, if we mix silver nitrate with sodium chloride, we have the following reaction:

$AgNO_3(aq) + NaCl(aq) \rightarrow NaNO_3(aq) + AgCl(s)$

The ions from the aqueous components are free to move around the entire solution, but the silver and chloride ions in the solid AgCl are all clustered together into a precipitate, ordered into a specific pattern of alternating cations and anions. Overall, this transformation represents a decrease in the entropy of the system.

3. All else being equal, more separate particles corresponds to a higher degree of entropy.

This makes sense when we think about the arrangements available. Consider the following reaction:

$C(s) + O_2(g) \rightarrow CO_2(g)$

Each side of this equation contains one mole of gas particles, so that will not be a deciding factor. However, there are more total particles on the reactants side than on the products side. Because there are more ways to arrange two moles of particles than one mole of particles, this process represents an overall decrease in entropy.

4. If there is an increase in temperature, entropy will increase.

So far, we have been thinking about entropy in terms of the ways in which particles can be distributed over a certain amount of space. However, other factors that are subject to random distributions also make contributions to the entropy of a system. As you know, an increase in temperature means that there is more overall kinetic energy available to the individual particles. This energy is distributed randomly through enormous amounts of collisions between particles. Having more energy available means that there are more ways that it can be distributed, so an increase in temperature also corresponds to an increase in entropy.

Entropy of the Surroundings (ΔS

In general, the process of interest is taking place in the system, and there are no changes in the composition of the surroundings. However, the temperature of the surroundings does generally change. Entropy changes in the surroundings are determined primarily by the flow of heat into or out of the system. In an exothermic process, heat flows into the surroundings, increasing the kinetic energy of the nearby particles. For an exothermic reaction, ΔS_{surr} is positive. Conversely, heat flows from the surroundings into the system during an endothermic process, lowering the kinetic energy available to the surroundings and resulting in a negative value for ΔS_{surr}.

As it turns out, the amount of entropy change for a given amount of heat transfer also depends on the absolute temperature. We will not go into the exact derivation, but it turns out that the entropy change of the surroundings can be defined in terms of the enthalpy change of the system:

$$\Delta S_{surr} = -\frac{\Delta H_{sys}}{T}$$

where T is the temperature in Kelvin. For an exothermic reaction, ΔH_{sys} is negative, so ΔS_{surr} would be a positive value. This makes sense, because heat is being released into the surroundings, increasing the amount of kinetic energy available to the surrounding particles. For an endothermic reaction, ΔH_{sys} is positive, so ΔS_{surr} would be a negative value.

Entropy of the Universe (ΔS

Substituting this into our earlier equation for ΔS_{univ}, we get the following:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$
$$\Delta S_{univ} = \Delta S_{sys} - \frac{\Delta H_{sys}}{T}$$

This is a particularly useful equation, because it allows us to determine whether a process is spontaneous by looking only at the system of interest. It also helps to explain why not all exothermic reactions are spontaneous, and not all reactions that increase the entropy of the system are spontaneous. The enthalpy change, entropy change, and overall temperature all factor into whether a given transformation will proceed spontaneously.

The Third Law of Thermodynamics

When we discussed enthalpy, we always talked about changes in enthalpy, never about the absolute enthalpy of a substance. Even the standard enthalpy of formation value ($\Delta H°_f$) is a measure of the change in enthalpy between a compound and its elements in their standard states. There is no absolute zero for enthalpy, but this is not true for entropy. The **third law of thermodynamics** says that a perfectly regular crystal at a temperature of 0 K (absolute zero) would have an entropy value of 0.

As the temperature of a perfect crystal increases, its particles start to vibrate slightly around their optimal positions, thus increasing the entropy of the system. The dependence of entropy on temperature varies by substance, so the only temperature at which all crystals have the same entropy is absolute zero. The **standard entropy** of a substance is a measure of its entropy at 25°C and 1 atm of pressure. Like standard enthalpy of formation values, standard entropies are tabulated for a wide range of substances. However, unlike enthalpy of formation values, all standard entropy values are positive, because the absolute zero for entropy is the most ordered possible state. Additionally, this means that pure elements in their standard states do *not* have a standard entropy of zero.

Because entropy changes are generally small compared to enthalpy changes, we generally express their units in terms of joules instead of kilojoules. Standard entropy values are most commonly given in units of J/K•mol. A few representative values are given in the following table:

TABLE 20.1: Selected standard entropy values

Substance	Standard Entropy S° J/K•mol
$H_2O_{(l)}$	69.95
$H_2O_{(g)}$	188.84
carbon (graphite)	5.6
carbon (diamond)	2.377
carbon (vapor)	158.1
methane - $CH_4(g)$	186.26
ethane - $C_2H_6(g)$	229.2
propane - $C_3H_8(g)$	270.3

Note: When referring to standard entropy, standard enthalpy of formation, and standard heat of formation, we use the notation with the degree symbol to indicate the standard conditions of 25°C and 1 atm. Without the degree symbol these values are not necessarily from the standard state.

As expected, the entropy values for solids are low, the values for gases are high, and the ones for liquids are intermediate. Another observation can be made by looking at the three hydrocarbon gases at the end of the table. For similar molecules, a higher molecular weight generally leads to a larger standard entropy value. Although this is a drastic oversimplification, we can think of this in terms of the electrons that make up each molecule. A larger molecular weight generally means more protons, which also means more electrons. There are more ways to arrange a large number of electrons within a molecule than there are to arrange a smaller number. Although these arrangements are heavily constrained by the positions of the various nuclei, there is still an overall trend for larger molecules to have higher entropy values.

Calculating ΔS

Calculations of the change in entropy for a given reaction are analogous to those used to determine ΔH_{rxn}. The entropy change for a reaction can be calculated by taking the difference between the total of the standard entropy values of the products and those of the reactants:

$$\Delta S^{\circ}_{\text{rxn}} = \Sigma n S^{\circ}(\text{products}) - \Sigma n S^{\circ}(\text{reactants})$$

As with our enthalpy calculations, each standard entropy value is multiplied by the coefficient of the corresponding substance in the balanced equation. Extensive tables of standard entropy values can be found on the internet.

Example 20.1

Calculate ΔS_{rxn} for the following reaction:

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

The standard entropy values for N_2, H_2, and NH_3 are 191.6, 130.7, and 192.5 J/K•mol, respectively.

Answer:

Multiply the standard entropy value of each component by its coefficient from the balanced equation, and subtract the values of the reactants from those of the products.

$$\begin{aligned}
\Delta S^{\circ}_{\text{rxn}} &= \Sigma n S^{\circ}(\text{products}) - \Sigma n S^{\circ}(\text{reactants}) \\
\Delta S^{\circ}_{\text{rxn}} &= 2S^{\circ}(\text{NH}_3) - [S^{\circ}(\text{N}_2) + 3S^{\circ}(\text{H}_2)] \\
\Delta S^{\circ}_{\text{rxn}} &= 2(192.5\ \text{J/K}\cdot\text{mol}) - [191.6\ \text{J/K}\cdot\text{mol} + 3(130.7\ \text{J/K}\cdot\text{mol})] \\
\Delta S^{\circ}_{\text{rxn}} &= -198.7\ \text{J/K}\cdot\text{mol}
\end{aligned}$$

There is a substantial decrease in entropy over the course of this reaction. This could have been predicted simply by looking at the balanced equation. There are four moles of gaseous reactants and just two moles of gaseous products. In general, the side of the equation with more moles of gas has a higher total entropy.

Example 20.2

Predict whether the change in entropy would be positive or negative for the following reaction:

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

Then, use the standard entropy values for each substance to calculate the exact change in entropy.

Answer:

A single solid reactant is splitting into two products, one of which is a gas. We would expect the entropy of the system to increase over the course of this reaction. The exact change can be calculated as follows:

$$\begin{aligned}
\Delta S^{\circ}_{\text{rxn}} &= \Sigma n S^{\circ}(\text{products}) - \Sigma n S^{\circ}(\text{reactants}) \\
\Delta S^{\circ}_{\text{rxn}} &= [S^{\circ}(\text{CaO}) + S^{\circ}(\text{CO}_2)] - S^{\circ}(\text{CaCO}_3) \\
\Delta S^{\circ}_{\text{rxn}} &= [39.8\ \text{J/K}\cdot\text{mol} + 213.6\ \text{J/K}\cdot\text{mol}] - 92.9\ \text{J/K}\cdot\text{mol} \\
\Delta S^{\circ}_{\text{rxn}} &= 160.5\ \text{J/K}\cdot\text{mol}
\end{aligned}$$

As predicted, ΔS_{rxn} is a positive value, indicating that entropy increases upon going from reactants to products.

Lesson Summary

- A process is spontaneous if the formation of products is favored under the given conditions. Spontaneous processes may be fast or slow.

- Entropy (S) measures the probability of attaining a given state. Things naturally progress towards more probable states, so entropy has a tendency to increase.
- The second law of thermodynamics states that the entropy of the universe will increase during any spontaneous process.
- The change in the entropy of the universe can be broken down into the following components:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

- The sign of ΔS_{univ} tells us whether or not a process is spontaneous in the direction that it is written. If ΔS_{univ} is positive, then the forward reaction is spontaneous.
- The third law of thermodynamics states that the entropy of a perfect crystal at 0 K is zero.
- Standard entropy is the entropy of a substance at 25°C and 1 atm of pressure.
- The entropy change for a reaction can be calculated using standard entropy values.

Lesson Review Questions

1. Define entropy.
2. State the second law of thermodynamics.
3. For each of the following situations, state whether there is an increase or decrease in entropy. Explain your reasoning in each case.
    a. liquid water freezes.
    b. a car is in a collision that completely demolishes it.
    c. wood burns.
    d. $I_2(s) \rightarrow I_2(g)$.
    e. $2\ Mg(s) + O_2(g) \rightarrow 2\ MgO(s)$.

Use the entropy values from http://chemed.chem.wisc.edu/chempaths/Table-of-Standard-Molar-Entropies-1184.html for the following calculations:

4. Calculate $\Delta S°_{rxn}$ for the reaction $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$.
5. Calculate $\Delta S°_{rxn}$ for reactions d and e of question 3, and comment on how well your predictions matched the actual entropy changes.
6. Which form of carbon has a higher degree of organization: diamond or graphite? Explain your answer.
7. Compare the S° of ethane with that of ethanol (159.9 J/K•mol). Explain why ethane has a higher standard entropy value than ethanol. (Hint: the boiling point of ethane is -89°C, and the boiling point of ethanol is 78°C. At what temperature are standard entropy values tabulated?

Further Reading/Supplementary Links

- Some basic ideas about entropy: http://entropysimple.oxy.edu/content.htm
- Entropy values: http://boomeria.org/chemtextbook/cch20.html
- Table of standard molar entropies: http://chemed.chem.wisc.edu/chempaths/Table-of-Standard-Molar-Entropies-1184.html

Points to Consider

- Can we reliably predict under what conditions a reaction will be spontaneous?

20.2 Spontaneous Reactions and Free Energy

Lesson Objectives

- Define Gibbs free energy, and be able to calculate the change in Gibbs free energy for a given process when provided with the appropriate data.
- Use the value for Gibbs free energy to predict whether a reaction will occur spontaneously.

Vocabulary

- **Gibbs free energy**: A thermodynamic quantity that combines enthalpy and entropy into a single value in order to predict whether or not a process is spontaneous.

Check Your Understanding

- What must be true for a reaction to be considered spontaneous?

Gibbs Free Energy

We have learned that a spontaneous reaction must increase the total entropy in the universe: $\Delta S_{univ} > 0$. To analyze the entropic effects of a given process, we generally break this quantity down into two separate components. This is expressed with the following equation:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0$$

In general, the entropy change for a chemical reaction or phase change can be easily determined from standard entropy values. Additionally, we saw in the previous lesson that the following relationship is true:

$$\Delta S_{surr} = -\frac{\Delta H_{sys}}{T}.$$

Substituting this into the above equation, we get the following:

$$\Delta S_{univ} = \Delta S_{sys} - \frac{\Delta H_{sys}}{T} > 0$$

This equation can then be rearranged as follows:

$$\begin{aligned} T\Delta S_{univ} &= -\Delta H_{sys} + T\Delta S_{sys} > 0 \\ -T\Delta S_{univ} &= \Delta H_{sys} - T\Delta S_{sys} < 0 \end{aligned}$$

Now we can talk about the entropy changes in the universe simply by looking at data about the system of interest. If the results of the equation are less than zero, the reaction will be spontaneous. The American physicist Josiah Gibbs took this idea and introduced a thermodynamic quantity that combines enthalpy and entropy into a single value that has been named after him. **Gibbs free energy** is defined by the following equation:

$$\Delta G = \Delta H_{sys} - T\Delta S_{sys}$$

where ΔG is the change in free energy, ΔH is the change in enthalpy, T is the temperature (in Kelvin), and ΔS is the change in entropy. As we can see by comparing this to the derived equations above, the value of ΔG must be less than zero for a spontaneous process. Stated another way, systems have a natural tendency to move towards a minimum amount of free energy.

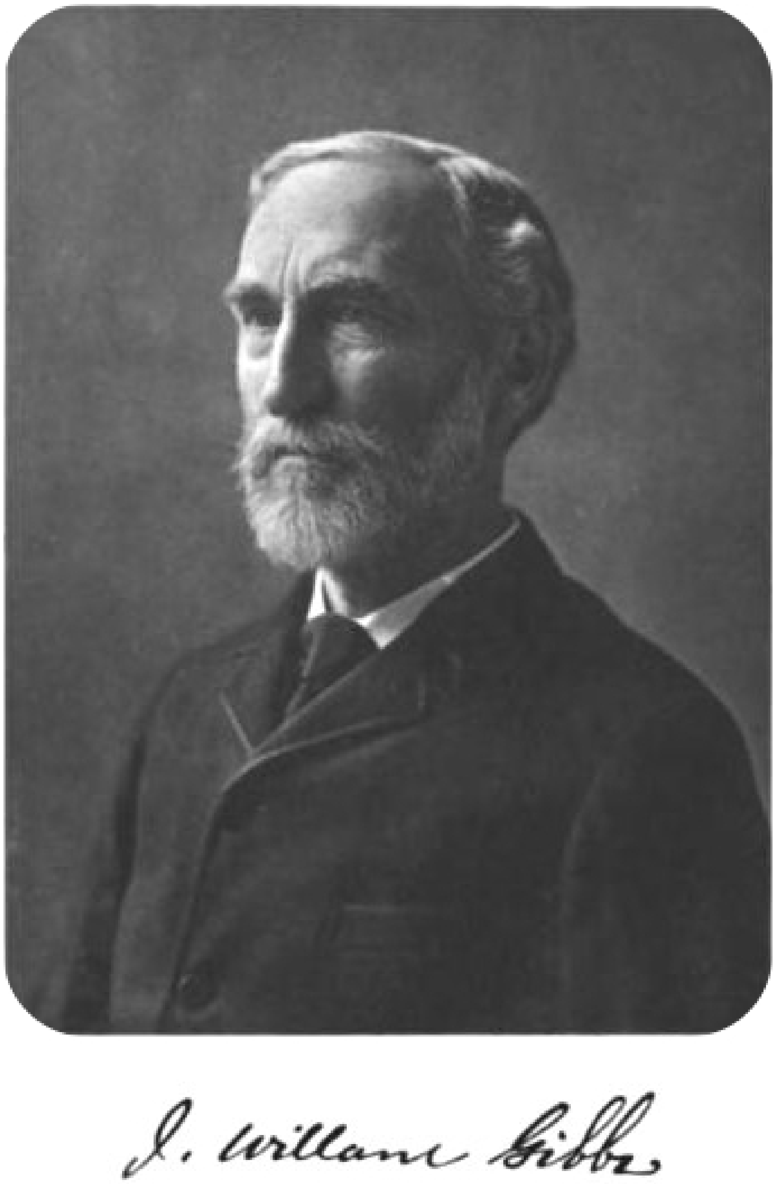

FIGURE 20.3

Gibbs postulated that a system progressed towards the equilibrium direction which exhibited the highest entropy.

Standard Free Energy Change

Much like the corresponding equations for $\Delta H°_{rxn}$ and $\Delta S°_{rxn}$, $\Delta G°_{rxn}$ for a given reaction can be calculated from the corresponding $\Delta G°_f$ values, which are tabulated for a wide variety of substances.

$$\Delta G°_{rxn} = \Sigma n \Delta G°_f(\text{products}) - \Sigma n \Delta G°_f(\text{reactants})$$

As with the standard enthalpy of formation values, there is no absolute zero for Gibbs free energy, so each $\Delta G°_f$ value is the change in free energy for a compound when prepared from its constituent elements in their standard states. Also like the enthalpy of formation values, $\Delta G°_f$ for any element in its most stable form at 25°C is zero.

Example 20.3

Calculate the value of $\Delta G°_{rxn}$ for the combustion of methane:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

$\Delta G°_f$ values can be found at the following website: http://chemed.chem.wisc.edu/chempaths/GenChem-Textbook/The-Free-Energy-629.html

Answer:

Multiply each $\Delta G°_f$ value by the coefficient from the balanced equation, and subtract the free energy of the reactants from that of the products. Note that water is present as a liquid, so make sure to use the $\Delta G°_f$ value for the correct state. Because $O_2(g)$ is the standard form of oxygen, it has a $\Delta G°_f$ value of zero.

$$\Delta G°_{rxn} = \Sigma n \Delta G°_f(\text{products}) - \Sigma n \Delta G°_f(\text{reactants})$$
$$\Delta G°_{rxn} = [(-394.36 \text{ kJ/mol}) + 2(-237.13 \text{ kJ/mol})] - [(-50.72 \text{ kJ/mol} + 2(0 \text{ kJ/mol})]$$
$$\Delta G°_{rxn} = -868.62 \text{ kJ/mol} - (-50.72 \text{ kJ/mol})$$
$$\Delta G°_{rxn} = -817.90 \text{ kJ/mol}$$

The large negative value for $\Delta G°_{rxn}$ indicates that the forward reaction is heavily favored under standard conditions. This reaction proceeds spontaneously in the forward direction.

Gibbs Free Energy and Non-Standard Conditions

The sign of $\Delta G°$ predicts the behavior of a chemical reaction at the standard conditions of 25°C and 1 atm of pressure. If $\Delta G°$ is negative, the reaction will proceed spontaneously, if $\Delta G°$ is zero, the reaction is at equilibrium, and if $\Delta G°$ is positive, the reaction will proceed spontaneously in the *reverse* direction. However, this does not tell us what will happen with a given reaction under non-standard conditions.

Consider the following reaction between ammonia and hydrogen chloride gas:

$$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$$

We could calculate $\Delta G°_{rxn}$ for this reaction using $\Delta G°_f$ values, as we did in the previous example problem, but that would only tell us the value of ΔG at 25°C. Alternatively, we could calculate ΔG at other temperatures using the following equation:

$$\Delta G_{rxn} = \Delta H_{rxn} - T\Delta S_{rxn}$$

Unlike ΔG, ΔH and ΔS do not vary much with changes in temperature. For simplicity, we will assume that for a specified reaction the ΔH_{rxn} and ΔS_{rxn} values are the same at any temperature. By calculating ΔH_{rxn} and ΔS_{rxn} from the relevant standard enthalpy and entropy values, we can calculate the value of ΔG at any temperature. Let's start by finding ΔH_{rxn}:

$$\Delta H^\circ_{rxn} = \Sigma n\Delta H^\circ_f(\text{products}) - \Sigma n\Delta H^\circ_f(\text{reactants})$$
$$\Delta H^\circ_{rxn} = -315.39\text{ kJ/mol} - [(-46.3\text{ kJ/mol}) + (-92.3\text{ kJ/mol})]$$
$$\Delta H^\circ_{rxn} = -176.70\text{ kJ/mol}$$

The large negative value indicates that this is a highly exothermic reaction. Then, find ΔS_{rxn}:

$$\Delta S^\circ_{rxn} = \Sigma nS^\circ_f(\text{products}) - \Sigma nS^\circ_f(\text{reactants})$$
$$\Delta S^\circ_{rxn} = 94.6\text{ J/K}\bullet\text{mol} - [193.0\text{ J/K}\bullet\text{mol} + 187.0\text{ J/K}\bullet\text{mol}]$$
$$\Delta S^\circ_{rxn} = -285.4\text{ J/K}\bullet\text{mol}$$

A negative value here indicates a decrease in entropy over the course of the reaction. This is consistent with what we might expect for a reaction in which two gases combine to make a single solid product.

Now, let's calculate the value of ΔG_{rxn} for this reaction at a couple of different temperatures. First, let's look at what we would get using the standard temperature of 25°C (298 K). Before plugging any values into our equation, we first need to make sure that our units match. Our enthalpy value is written in terms of kilojoules (kJ), but the value for entropy is written in terms of joules. One of these must be changed in order to add the two quantities together. Because free energy changes are usually written in units of kJ/mol, like enthalpy changes, we should convert the value of ΔS°_{rxn} from -285.4 J/K•mol to -0.2854 kJ/K•mol by dividing by 1,000. Now, we can plug values into the following equation:

$$\Delta G_{rxn} = \Delta H_{rxn} - T\Delta S_{rxn}$$
$$\Delta G_{rxn} = -176.70\text{ kJ/mol} - (298\text{ K})(-0.2854\text{ kJ/K}\bullet\text{mol})$$
$$\Delta G_{rxn} = -176.70\text{ kJ/mol} - (-85.05\text{ kJ/mol})$$
$$\Delta G_{rxn} = -91.65\text{ kJ/mol}$$

$\Delta G_{rxn} < 0$, so this reaction would proceed spontaneously at a temperature of 25°C. It should also be noted that, because we are using the standard temperature at which thermodynamic data is generally measured, this would be the approximate value obtained if we had calculated ΔG_{rxn} using ΔG°_f values.

What if we increase the reaction temperature to 500°C (773 K)? The same calculation can be performed at the new temperature:

$$\Delta G_{rxn} = \Delta H_{rxn} - T\Delta S_{rxn}$$
$$\Delta G_{rxn} = -176.70\text{ kJ/mol} - (773\text{ K})(-0.2854\text{ kJ/K}\bullet\text{mol})$$
$$\Delta G_{rxn} = -176.70\text{ kJ/mol} - (-220.61\text{ kJ/mol})$$
$$\Delta G_{rxn} = 43.91\text{ kJ/mol}$$

At this temperature, the reaction would *not* be spontaneous in the forward direction. However, the reverse reaction in which $\Delta G_{rxn} = -43.91$ kJ/mol would be spontaneous at 500°C.

Lesson Summary

- Gibbs free energy combines enthalpy and entropy into a single thermodynamic variable that can be used to predict whether a given reaction will occur spontaneously.

- The sign of ΔG predicts the behavior of a chemical reaction at a constant temperature and pressure. If ΔG is negative, the forward reaction will proceed spontaneously, if ΔG is zero, the reaction is at equilibrium, and if ΔG is positive, the *reverse* reaction will be spontaneous.
- ΔG_{rxn} can be calculated at 25°C using $\Delta G°_f$ values.
- ΔG_{rxn} can be calculated at other temperatures from the values of ΔH_{rxn} and ΔS_{rxn}.

Lesson Review Questions

1. What thermodynamic quantities are used to define Gibbs free energy?
2. Define each component of the equation describing Gibbs free energy.
3. What is true for all spontaneous processes regarding Gibbs free energy equation?
4. What is the change in Gibbs free energy for the formation of any element in its most stable state at 25degC?
5. What can be inferred from a very large ΔG_{rxn}? From a very small ΔG_{rxn}?
6. What does a ΔG value of zero imply?
7. Describe how it is possible that a reaction is spontaneous at some temperatures but not at others.
8. Use the table at http://chemed.chem.wisc.edu/chempaths/GenChem-Textbook/The-Free-Energy-629.html to calculate $\Delta G°_{rxn}$ for the following reactions at 25°C:
    a. $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
    b. $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$
    c. $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$
    d. $2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(l)$

Further Reading/Supplementary Links

- Gibbs free energy: http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch21/gibbs.php
- ΔG values: http://chemed.chem.wisc.edu/chempaths/GenChem-Textbook/The-Free-Energy-629.html

Points to Consider

- How does the equilibrium of a reaction affect the free energy?
- Can we use free energy calculations to determine equilibrium constants?
- Can we use equilibrium constants to determine free energy changes?

20.3 Free Energy and Equilibrium

Lesson Objectives

- Use the reaction quotient to determine which direction a reaction must run in order to reach equilibrium.
- Use the equilibrium constant of a reaction to calculate the change in Gibbs free energy.
- Use changes in Gibbs free energy to calculate equilibrium constants.
- Predict whether the reactants or products of a reaction are favored under a given set of conditions by looking at either the equilibrium constant or the change in Gibbs free energy.

Lesson Vocabulary

- **reaction quotient (Q)**: The ratio of the reactant and product concentrations in their non-equilibrium states, raised to their respective exponents.

Check Your Understanding

- What data is needed to calculate the change in Gibbs free energy for a reaction?
- What information is needed to calculate an equilibrium constant?

The Reaction Quotient

In the previous chapter, we learned how to set up an equilibrium constant expression. For the generic reaction shown below, the equilibrium constant expression is constructed as follows:

$$aA + bB \rightleftarrows cC + dD$$

$$K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

It should be emphasized that the equation above is only true when the reaction is at equilibrium. Given enough time, the indicated ratio of concentrations will eventually converge on the equilibrium constant, but for any reaction in which net changes are still occurring, this equation is not true. For a reaction that is still in progress, it is often useful to calculate the same ratio of concentrations, but in a non-equilibrium state. This value is called the **reaction quotient** (Q), and comparing the value of Q to the value of K_{eq} tells us which direction the reaction needs to shift in order to reach equilibrium.

$K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ (Only if the reaction is at equilibrium)

$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ (Always)

If Q >K$_{eq}$, then the concentrations of the products (in the numerator) are too large compared to the concentrations of the reactants. Therefore, the reverse reaction must be favored (reducing the products and generating more reactants) in order for the reaction to achieve equilibrium. If Q <K$_{eq}$, the situation is reversed. There are too many reactants and not enough products, so the reaction quotient is a small number compared to K$_{eq}$, and the forward reaction will be favored until equilibrium is reached. When Q = K$_{eq}$, the reaction is at equilibrium.

Free Energy at Non-Standard Concentrations

In the previous section, we looked at values for ΔG°, which tells us the free energy change for a reaction being run at standard conditions. In addition to the requirements for temperature and pressure (25°C and 1 atm), standard conditions also specify the concentrations of each reaction component. Under standard conditions, the concentration of each reaction component in the aqueous or gaseous states is exactly 1 M.

Plugging a value of 1 M in for every concentration in the reaction quotient expression will give us a value of Q = 1. Unless K$_{eq}$ happens to be exactly 1, reaction mixtures are not at equilibrium under standard conditions. However, we can calculate the value of ΔG for any combination of concentrations if we know the values of ΔG° and Q. The following equation (which we will not derive) shows the relationships between these quantities:

$\Delta G = \Delta G^\circ + RT \ln Q$

- ΔG = free energy change of the reaction under existing conditions
- ΔG° = free energy change of the reaction under standard-state conditions
- R = universal gas constant (8.314 J/K•mol)
- T = absolute temperature (in Kelvin)
- Q = reaction quotient

Although ΔG° is going to be a fixed value for a given temperature, ΔG will vary depending on the value of RT ln Q.

Free Energy and the Equilibrium Constant

At equilibrium, the forward and reverse reactions proceed at equal rates. The driving force in each direction is equal, because the free energy of the reactants and products under equilibrium conditions is equivalent (ΔG = 0). We also know that, at equilibrium, Q = K$_{eq}$. For a reaction that has reached equilibrium, the equation above becomes the following:

$$\Delta G = \Delta G^\circ + RT \ln Q$$
$$0 = \Delta G^\circ + RT \ln K$$
$$\Delta G^\circ = - RT \ln K$$

This equation provides us with a way to convert between ΔG° and the equilibrium constant for a given reaction. Knowing either ΔG° or K$_{eq}$ tells us whether the reactants or products are favored at equilibrium. This relationship is summarized in the following table:

TABLE 20.2: **Relationship between equilibrium constant and ΔG°**

K	ln K	ΔG°	Comments

TABLE 20.2: (continued)

K	ln K	ΔG°	Comments
<1	negative	positive	reactants favored over products at equilibrium
1	0	0	equilibrium situation; products and reactants equally favored
>1	positive	negative	products favored over reactants at equilibrium

Example 20.4

The standard free energy of formation (ΔG°_f) for ammonia is -16.6 kJ/mol. Calculate the equilibrium constant for the following reaction at 25°C (298 K):

$N_2(g) + 3H_2(g) \rightleftarrows 2NH_3(g)$

Answer:

If we know the value of ΔG° for this reaction, we can calculate the equilibrium constant using the equation above. ΔG° can be calculated from ΔG°_f values using the following equation:

$$\Delta G^\circ_{rxn} = \Sigma n\Delta G^\circ_f(\text{products}) - \Sigma n\Delta G^\circ_f(\text{reactants})$$

Because nitrogen and hydrogen are both in their standard elemental states, they have ΔG°_f values of zero.

$$\Delta G^\circ_{rxn} = \Sigma n\Delta G^\circ_f(\text{products}) - \Sigma n\Delta G^\circ_f(\text{reactants})$$
$$\Delta G^\circ_{rxn} = 2(-16.6\text{ kJ/mol}) - [(0\text{ kJ/mol}) + 3(0\text{ kJ/mol})]$$
$$\Delta G^\circ_{rxn} = -33.2\text{ kJ/mol}$$

Then solve $\Delta G^\circ = -RT\ln K_{eq}$ for K_{eq}:

$$\Delta G^\circ = -RT\ln K_{eq}$$
$$\ln K_{eq} = -\frac{\Delta G^\circ}{RT}$$
$$K_{eq} = e^{-\frac{\Delta G^\circ}{RT}}$$

Before plugging values into this equation, note that we are using a value of 8.314 J/K•mol for R, but our value for ΔG° is -33.2 kJ/mol. In order for our units to cancel correctly, we need to convert -33.2 kJ/mol to -33,200 J/mol. Then, K_{eq} can be calculated as follows:

$$K_{eq} = e^{-\frac{\Delta G^\circ}{RT}}$$
$$K_{eq} = e^{-\frac{-33{,}200\text{ J/mol}}{(8.314\text{ J/K}\cdot\text{mol})(298\text{ K})}}$$
$$K_{eq} = e^{13.4}$$
$$K_{eq} = 6.6 \times 10^5$$

K_{eq} is very large, indicating that the products are heavily favored at 25°C.

Looking at the equation above, we see that increasing the temperature for any reaction makes the fraction in the exponent smaller, thus moving the equilibrium constant closer to 1. If we were to run the ammonia formation reaction above, known as the Haber process, at a higher temperature, the equilibrium constant would be smaller,

FIGURE 20.4

and the desired products would be less favored. However, the industrial manufacture of ammonia uses this reaction at temperatures of 400-450°C. Why are elevated temperatures used? Knowing whether reactants or products are energetically favored is one important factor for optimizing production of a desired product, but it is not the only relevant variable. As it turns out, this reaction is quite slow, so even if the products are heavily favored at equilibrium, it takes a long time to reach that equilibrium. Increasing the temperature speeds up the reaction, and this advantage makes up for the slightly less favorable equilibrium constant.

Example 20.5

The equilibrium constant for the following reaction is 1.6×10^{-10} at 25°C:

$$AgCl(s) \rightleftarrows Ag^+(aq) + Cl^-(aq)$$

Calculate $\Delta G°$.

Answer:

Simply plug the relevant values into the following equation:

$$\Delta G° = -RT \ln K_{eq}$$
$$\Delta G° = -(8.314\ \mathrm{J/K \cdot mol})(298\ \mathrm{K}) \ln(1.6 \times 10^{-10})$$
$$\Delta G° = -55,884\ \mathrm{J/mol}$$

Note that the answer will be in J/mol (not kJ/mol) if we cancel the units correctly. Rounding the correct number of significant figures and converting to the usual units for free energy values, $\Delta G°$ = 56 kJ/mol for this reaction. This is a very large number, indicating that the reactants are highly favored, as would be expected for a relatively insoluble ionic compound.

One type of equilibrium that we will be studying extensively in the following chapter is the ionization of an acid in water:

$$HA(aq) + H_2O(l) \rightleftarrows A^-(aq) + H_3O^+(aq)$$

where HA is a generic acid, and A^- is its conjugate base.

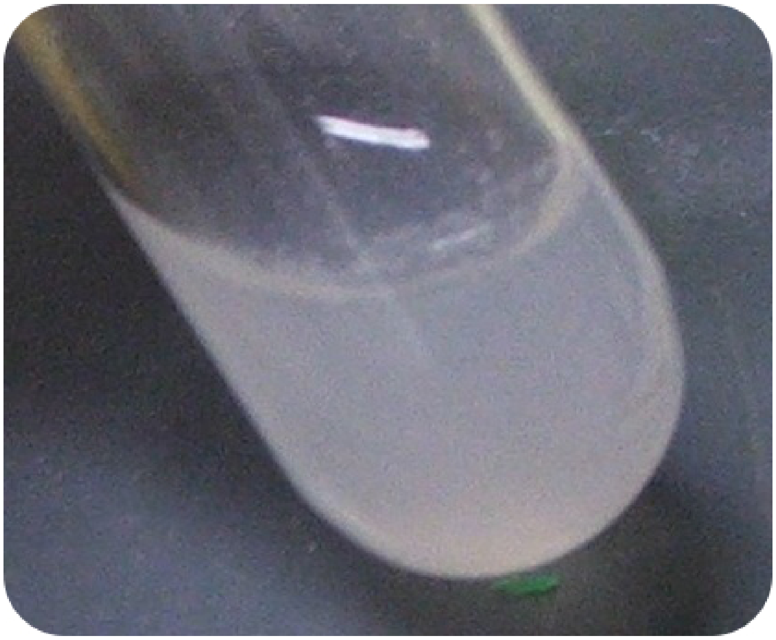

FIGURE 20.5

Lesson Summary

- The reaction quotient can be compared to the equilibrium constant to determine which direction a reaction will shift in order to reach equilibrium.
- Gibbs free energy values can be used to determine equilibrium constants.
- Equilibrium constants can be used to calculate changes in Gibbs free energy.
- Equilibrium constants and Gibbs free energy values allow us to predict the extent to which reactants or products will be favored once a reaction reaches equilibrium.

Lesson Review Questions

1. What is the difference between the equilibrium constant and the reaction quotient?
2. In which direction will the reaction proceed based on the three following conditions?
    a. $Q>K_{eq}$
    b. $Q<K_{eq}$
    c. $Q=K_{eq}$
3. What conditions does the notation ΔG° imply? Explain the difference between ΔG° and ΔG.
4. Define each value in the equation that relates ΔG° and ΔG.
5. How can ΔG° or K_{eq}be used to tell whether reactants or products are favored at equilibrium?
6. Calculate ΔG° for the process $2H_2O(l) \rightleftarrows H_3O^+(aq) + OH^-(aq)$ if the equilibrium constant at 25°C is 1×10^{-14}.
7. Calculate ΔG° and K_{eq} for the following reaction at 25°C: $2H_2O(g) \rightleftarrows 2H_2(g) + O_2(g)$
8. Calculate the equilibrium constant for the following reaction at 25°C: $2O_3(g) \rightleftarrows 3O_2(g)$
9. Calculate ΔG° for the ionization of acetic acid (CH_3CO_2H). The equilibrium constant for the following reaction is 1.8×10^{-5}:

$$CH_3CO_2H(aq) + H_2O(l) \rightleftarrows CH_3CO_2^-(aq) + H_3O^+(aq)$$

Further Reading/Supplementary Links

- Gibbs free energy and equilibrium: http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch21/gibbs.php#relation
- More equilibrium material: http://www.science.uwaterloo.ca/~cchieh/cact/applychem/gibbsenergy.html

Points to Consider

- How do equilibrium processes influence the behavior of acids and bases?

20.4 References

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CHAPTER 21 Acids and Bases

Chapter Outline

21.1 ACID-BASE DEFINITIONS

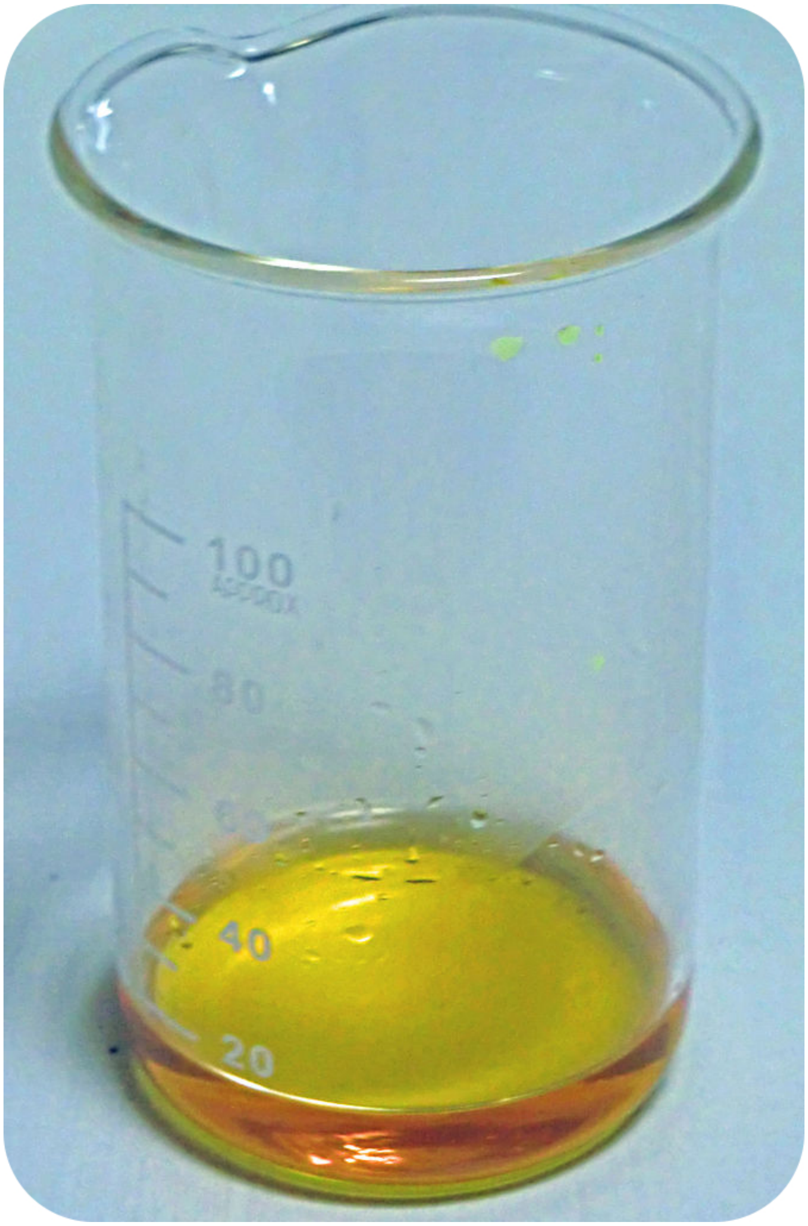
21.2 THE pH CONCEPT

21.3 ACID AND BASE STRENGTH

21.4 ACID-BASE NEUTRALIZATION REACTIONS AND TITRATIONS

21.5 SALT SOLUTIONS

21.6 REFERENCES



Aqua regia, a mixture of nitric acid and hydrochloric acid, is one of the few materials that will dissolve gold. This material, translated to "royal water" in English, was named so because it could dissolve the royal metal gold. First noted in the fourteenth century, aqua regia could be used to help ascertain whether a particular material was actually gold or was some trickery of the alchemist. Nitric acid by itself will not dissolve gold, but will in combination with hydrochloric acid. The chemistry of the process is rather complex, with both acids reacting with the metal to form soluble gold compounds. The gold can be recovered from the solution, making the process useful for purification purposes.

Acids and bases have had many uses throughout history. In this chapter we want to explore the properties of acids and bases and the reactions in which they take part.

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21.1 Acid-Base Definitions

Lesson Objectives

- List some common properties of acids and bases.
- Describe how acids and bases are defined based on the Arrhenius, Bronsted-Lowry, and Lewis definitions. Understand the differences between these three systems.

Lesson Vocabulary

- **Arrhenius acid**: A compound that releases H^+ ions when dissolved in water.
- **Arrhenius base**: A compound that generates hydroxide ions (OH^-) when dissolved in water.
- **Brønsted-Lowry acid**: A compound that can donate a proton (an H^+ ion) to an appropriate acceptor.
- **Brønsted-Lowry base**: A compound that can remove a proton from a relatively strong Brønsted-Lowry acid.
- **Lewis acid**: A chemical species that accepts a pair of electrons.
- **Lewis base**: A chemical species that donates a pair of electrons.
- **monoprotic acid**: A compound with only one acidic hydrogen atom that can be transferred to a strong base.
- **polyprotic acid**: A compound with two or more acidic hydrogen atoms that can be transferred to a strong base.

Check Your Understanding

- What comes to mind when you think of acids? How does a base differ from an acid?

Introduction

When you think of acids, "sour" is likely to come to mind. For the ancient Greeks, "sour-tasting" is in fact what defined a category of substances which later became known as acids. Bases were first categorized by their uses in soaps, as well as their ability to counteract properties of acids. In this lesson, you will learn about a few definitions for acids and bases as well as some of their properties.

Properties of Acids and Bases

Acids and bases are versatile and useful materials in many chemical reactions. Some properties that are common to aqueous solutions of acids and bases are listed in **Table** 21.1.

TABLE 21.1: properties of acids and bases

Acids	Bases
conduct electricity in solution	conduct electricity in solution
turn blue litmus paper red	turn red litmus paper blue
have a sour taste	have a slippery feeling
react with bases to create a neutral solution	react with acids to create a neutral solution
react with active metals to produce hydrogen gas	

Note: Litmus paper is a type of treated paper that changes color based on the acidity of the solution it comes in contact with.

Defining Acids and Bases

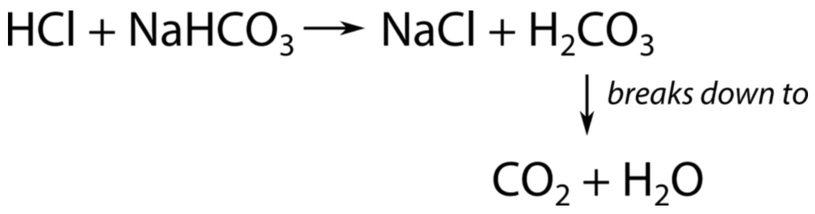
An early way of classifying acids and bases was proposed by Svante Arrhenius, a Swedish chemist, in 1894. An **Arrhenius acid** is any compound that releases H^+ ions when dissolved in water. An **Arrhenius base** is a compound that generates hydroxide ions (OH^-) when dissolved in water. Some representative examples are given in the **Table** 21.2.

TABLE 21.2: Arrhenius acids and bases

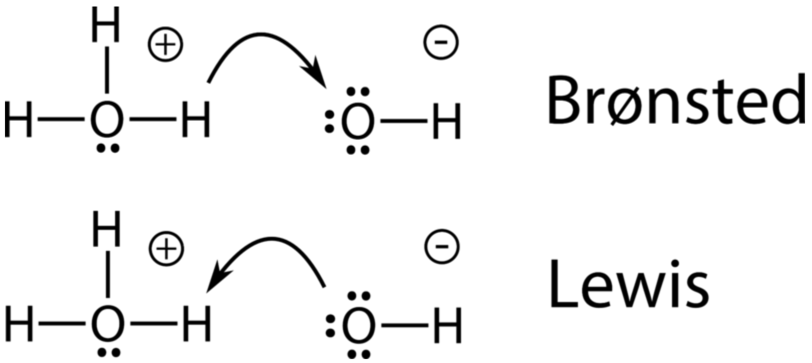
Acids	Bases
hydrochloric acid: $HCl \rightarrow H^+ + Cl^-$	sodium hydroxide: $NaOH \rightarrow Na^+ + OH^-$
nitric acid: $HNO^{3 \rightarrow H} + + NO_3{}^-$	potassium hydroxide: $KOH \rightarrow K^+ + OH^-$
hydrobromic acid: $HBr \rightarrow H^+ + Br^-$	calcium hydroxide: $Ca(OH)_2 \rightarrow Ca^{2+} + 2\ OH^-$

Many strong acids and bases can be identified based on the Arrhenius model. However, there are many compounds that share a number of common characteristics with acids and bases but do not fit the Arrhenius definitions. In the early 1920s, the Danish scientist Johannes Brønsted and the English researcher Thomas Lowry each published ideas that expanded the Arrhenius concept. According to this newer definition, a **Brønsted-Lowry acid** is any compound that can donate a proton (an H^+ ion) to an appropriate acceptor. A **Brønsted-Lowry base** is a compound that can remove (or accept) a proton from a relatively Brønsted-Lowry acid.

Overall, the Brønsted-Lowry model suggested that any acid-base reaction could be reduced to the transfer of a proton from an acid to a base. For example, the reaction between hydrochloric acid (HCl) and sodium bicarbonate ($NaHCO_3$) involves the transfer of an H^+ ion from the acid (HCl) to the base (the bicarbonate ion). The resulting carbonic acid (H_2CO_3) is unstable and breaks down to form carbon dioxide and water:



Another more general definition of acids and bases was offered by the American chemist G.N. Lewis. A **Lewis acid** is any chemical species that accepts a pair of electrons, and a **Lewis base** is a chemical species that donates a pair of electrons. This is the broadest most commonly used definition, and all compounds that qualify as an acid or base under the previous definitions are also Lewis acids and bases.



In the diagram above, we see the same process illustrated multiple times, highlighting the ways in which the compounds are acting as an acid or a base according to each definition. According to the Brønsted-Lowry model, the protonated water molecule (the acid) is donating a proton to the OH^- ion (the base). According to the Lewis model, the hydroxide ion has a pair of electrons (indicated by the black bar) that it donates to the protonated water molecule. "Pronated" refers to the extra hydrogen atom in the molecule, which increases its charge from neutral to +1. In both instances, the hydroxide ion serves as a base and the protonated water molecule is the acid.

An example of a Lewis acid-base reaction that would not fit the other definitions of acid and base is the formation of an adduct between boron trifluoride and ammonia:

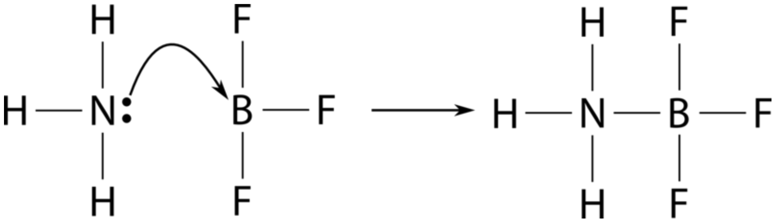


FIGURE 21.1

The ammonia serves as a Lewis base by donating its lone pair of electrons to make a new bond with boron (the Lewis acid), which has an empty orbital (indicated by ○) that can accept two electrons.

Unless otherwise indicated, we will be using the Brønsted-Lowry model of acids and bases for the remainder of the chapter.

Monoprotic and Polyprotic Acids

Acids can further be categorized based on how many acidic hydrogen atoms they contain. Acidic hydrogen atoms are those which will be transferred to a base. A **monoprotic acid** has only one acidic hydrogen that would be transferred to a strong base, whereas a **polyprotic acid** has two or more. Common monoprotic acids include HCl, HBr, and HNO_3. A common diprotic acid is sulfuric acid (H_2SO_4), and phosphoric acid (H_3PO_4) provides an example of a triprotic acid. In each case, all hydrogens are available to participate in acid-base reactions. However, that is not the case for all acidic molecules. For example, in acetic acid (CH_3COOH), only the hydrogen bonded to the oxygen atom is acidic. The other three hydrogens are covalently bonded to carbon and cannot be removed by any of the bases that we will consider in this chapter.

TABLE 21.3: **Acids**

Name	Structure
hydrobromic acid	HBr

TABLE 21.3: (continued)

Name	Structure
hydrochloric acid	HCl
hydrofluoric acid	HF
hydroiodic acid	HI
nitric acid	HNO_3
perchloric acid	$HClO_4$
acetic acid	CH_3COOH

TABLE 21.4:

Name	Structure
carbonic acid	H_2CO_3
sulfuric acid	H_2SO_4
sulfurous acid	H_2SO_3

TABLE 21.5:

Name	Structure
phosphoric acid	H_3PO_4

Lesson Summary

- Acids and bases were originally identified based on their physical and chemical properties.
- According to the Arrhenius model, acids and bases are compounds that release H^+ or OH^- ions when dissolved in water.
- In the Brønsted-Lowry model, an acid is a compound that can donate a proton (H^+ ion), and a base is a compound that can accept a proton.
- A Lewis base is an electron-pair donor, whereas a Lewis acid is an electron-pair acceptor. This is the broadest of the three definitions.
- Acids can be classified as monoprotic or polyprotic based on the number of acidic hydrogens they contain.

Lesson Review Questions

1. List three characteristics exhibited by acids and three exhibited by bases.
2. Based on the given acid and base characteristics, can you think of a few substances that might be classified as acids and a few that might be classified as bases?
3. Based on Arrhenius' definitions, how can you tell the difference between an acidic substance and a basic substance?
4. Why were Arrhenius' definitions expanded upon?
5. Based on Brønsted-Lowry definitions, how can you tell the difference between an acidic substance and a basic substance?
6. What definition is most widely applicable in defining acids and bases?
7. Describe the difference between a monoprotic acid and a polyprotic acid.

8. The formula for propanoic acid is CH_3CH_2COOH. Is this acid monoprotic or polyprotic? Explain your answer.

Further Reading/Supplementary Links

- Summary of acid and base properties: http://www.chemtutor.com/acid.htm
- Strong and weak acids and bases: http://www.highlands.edu/academics/divisions/scipe/chemistry/Site/GHandouts_files/Strong%20and%20Weak%20Acids%20and%20Bases.pdf

Points to Consider

- How can we tell how acidic or basic a solution is?

21.2 The pH Concept

Lesson Objectives

- Describe the self-ionization of water, and calculate the equilibrium constant for this reaction.
- Define pH.
- List the pH values of some common materials.
- Calculate pH when given the concentration of hydrogen ions.
- Calculate the concentration of hydrogen ions when given the pH of a solution.
- Describe ways of measuring the pH of a solution.

Lesson Vocabulary

- **amphoteric**: A substance that can act as both an acid and a base.
- **neutral solution**: An aqueous solution in which $[H_3O^+] = [OH^-]$.
- **acidic solution**: An aqueous solution in which $[H_3O^+] > [OH^-]$.
- **basic solution**: An aqueous solution in which $[H_3O^+] < [OH^-]$.
- **pH**: A measure of the concentration of hydrogen atoms in solution; $pH = -log[H^+]$.
- **acid-base indicator**: A substance which changes color based on the relative acidity of the solution.

Check Your Understanding

- Based on what you know about acids and bases, would you expect an acidic solution to have a high or low concentration of H^+ ions?

Self-Ionization of Water

Water is an example of what is known as an **amphoteric** substance, which means that it can act as both an acid and a base. In the presence of a strong acid, water can be a proton acceptor (a base), producing the hydronium ion (H_3O^+):

$$HCl(aq) + H_2O(l) \rightarrow Cl^-(aq) + H_3O^+(aq)$$

However, water can also donate a proton (acting as an acid) when combined with a strong enough base, producing the hydroxide ion (OH^-):

$$CH_3O^-(aq) + H_2O(l) \rightleftarrows CH_3OH(aq) + OH^-(aq)$$

Overall, water is a weak acid and a weak base. Because it has both of these properties, any sample of liquid water undergoes the following acid-based reaction in which both hydronium and hydroxide ions are produced to a very small extent:

$$H_2O(l) + H_2O(l) \rightleftarrows H_3O^+(aq) + OH^-(aq)$$

Because the reactants are in the liquid phase, they are not included in the equilibrium constant expression. As a result, the value of K_{eq} for this reaction can be calculated as follows:

$$\mathrm{K_{eq}} = [\mathrm{H_3O^+}][\mathrm{OH^-}]$$

Water's ability to act as an acid or a base is relatively weak, so we would expect the reactants to be heavily favored in this equilibrium. Indeed, at 25°C, this equilibrium constant has a value of only 1.0×10^{-14}. However, despite the minimal extent of self-ionization, this is a fundamentally important equilibrium for any reactions that take place in water, which includes essentially all biochemical reactions that occur inside any living organism. Because of its particular importance, this equilibrium constant is given the special symbol K_w.

In a pure sample of water, there are no external sources of H_3O^+ or OH^- (no additional acids or bases), so for each H_3O^+ ion that is formed by the self-ionization of water, an OH^- ion will be formed as well. As a result, $[H_3O^+] = [OH^-]$ in pure water. Because both of these concentrations are the same, we can solve for the equilibrium concentrations using the value of K_w. Let x be the concentration of H_3O^+ (and therefore also the concentration of OH^-):

$$\begin{aligned}\mathrm{K_w} &= [\mathrm{H_3O^+}][\mathrm{OH^-}]\\ 1.0 \times 10^{-14} &= [\mathrm{x}][\mathrm{x}]\\ 1.0 \times 10^{-14} &= \mathrm{x}^2\\ 1.0 \times 10^{-7} &= \mathrm{x}\end{aligned}$$

At equilibrium, $[H_3O^+] = [OH^-] = 1.0 \times 10^{-7}$ in a sample of pure water. An aqueous solution in which $[H_3O^+] = [OH^-]$ is referred to as a **neutral solution**. However, the addition of an external acid or base will shift the relative amounts of these two ions. Adding an acid will increase the amount of H_3O^+. As a consequence, the amount of OH^- will need to decrease in order to reestablish equilibrium (at which point the equilibrium expression for K_w will once again have the correct value). In an **acidic solution**, $[H_3O^+] > [OH^-]$. Similarly, in a **basic solution**, the amount of OH^- will increase and the amount of H_3O^+ will decrease, so $[H_3O^+] < [OH^-]$.

Shorthand Notation for Aqueous Acids

It is very common for chemists to write H^+ instead of H_3O^+ when talking about aqueous solutions of acids and bases. However, H^+ will not exist as an isolated ion if dissolved in water. Instead, it will be closely associated with (at least) one molecule of the solvent. It is generally acceptable to use H^+, but it should be understood that this is just a shorthand notation for H_3O^+. Consequently, the expression for K_w is often written as follows:

$$\mathrm{K_w} = [\mathrm{H^+}][\mathrm{OH^-}]$$

Acid-base reactions are also sometimes written in a way that makes use of this shorthand. For example, you might see the following acid-dissociation reaction:

$$HNO_3(aq) \rightarrow H^+(aq) + NO_3^-(aq)$$

However, a better description of this process would be the following:

$$HNO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$$

H^+ is not just "falling off" of nitric acid. Instead, it is being pulled off by water, which is a better base than the resulting nitrate anion. Again, the shorthand version is acceptable to use, but keep in mind that a more accurate description would include water as a base whenever "H^+" is being generated in an aqueous solution.

pH of Aqueous Solutions

Because we are dealing with such small concentrations of H^+ and OH^-, a system was invented in order to talk about the acidity or basicity of a solution that uses more manageable numbers. The Danish chemist Søren Sørenson proposed a new quantity that he called **pH**, which is defined as follows:

$$pH = -log[H^+]$$

One of the confusing consequences of pH values as defined by this equation is that the higher the hydrogen ion concentration, the lower the pH. A solution with a hydrogen ion concentration of 1×10^{-3} would have a pH of 3, and a solution with a hydrogen ion concentration of 1×10^{-5} would have a pH value of 5.

Example 21.1

What is the pH of a neutral solution (at 25°C)?

Answer:

As we saw in the previous section, a neutral solution has a hydrogen ion concentration of 1.0×10^{-7}.

$$\begin{aligned} pH &= -log[H^+] \\ pH &= -log[1.0 \times 10^{-7}] \\ pH &= 7.00 \end{aligned}$$

A neutral solution has a pH of 7. Acidic solutions have higher concentrations of H^+, so they have pH values that are less than 7. Conversely, basic solutions have lower concentrations of H^+ and pH values greater than 7.

Here is a list of the pH values for some common acidic and basic solutions:

Example 21.2

What is the concentration of hydrogen ions in a solution that has a pH value of 4.67?

Answer:

Start with the definition of pH and plug in the known value:

$$\begin{aligned} pH &= -log[H^+] \\ 4.67 &= -log[H^+] \end{aligned}$$

The logarithm function can be inverted as follows:

$$\begin{aligned} -log[H^+] &= 4.67 \\ log[H^+] &= -4.67 \\ 10^{log[H^+]} &= 10^{-4.67} \\ [H^+] &= 10^{-4.67} \\ [H^+] &= 2.1 \times 10^{-5} \end{aligned}$$

The hydrogen ion concentration in this solution is 2.1×10^{-5} M.

How to Measure pH

There are two common ways to measure pH. When only an approximate pH value is needed, an inexpensive test involves the use of **acid-base indicators**, which change color based on the relative acidity of the solution. One type

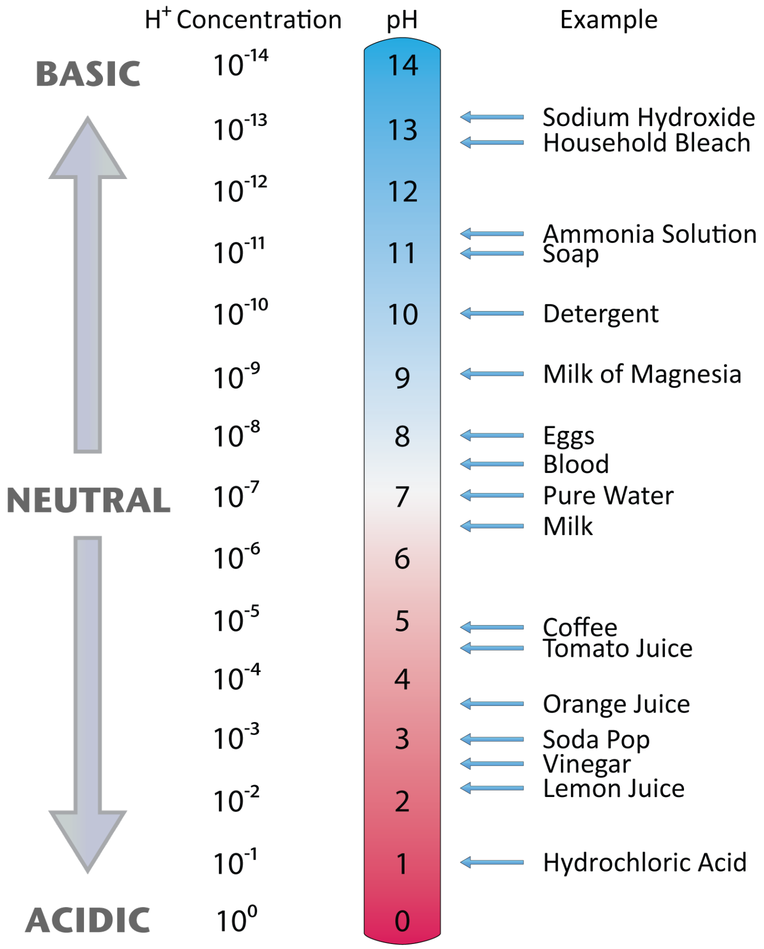


FIGURE 21.2

of common indicator is litmus paper. For example, if a piece of litmus paper is dipped into an acidic solution (pH below ~4.5), it will turn red, and dipping it into a basic solution (pH above ~8.5) will turn it blue. Solutions of intermediate pH will result in various shades of purple. Because different indicators change color at different pH values, the use of multiple indicators can generally narrow down the possible pH of a solution to a range of about 0.5-1 pH units. **Figure** 21.3 shows the colors exhibited by various indicators at different pH values.

More precise measurements can be obtained by using a digital pH meter, which can detect the concentration of H^+ based on small changes in electrical potential. Although a bit more expensive and cumbersome to use, such a device is essential for determining the exact pH of a solution.

Lesson Summary

- Water can react with itself to produce H_3O^+ and OH^-. The equilibrium constant for this reaction (K_w) is equal to 1.0×10^{-14} at 25°C.
- When talking about acids in an aqueous solution, H^+ is often used as a shorthand for H_3O^+.
- pH provides a way to talk about the acidity of a solution (the relative concentration of H^+) using more manageable numbers. It is defined by the equation pH = -log [H^+].
- A neutral solution has a pH value of 7 ([H^+] = 1.0×10^{-7}). Acidic solutions have lower pH values (higher concentrations of H^+), and basic solutions have higher pH values (lower concentrations of H^+).

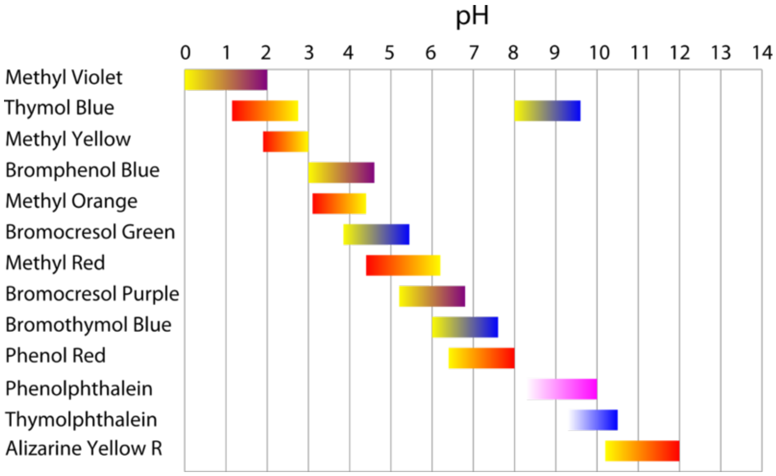


FIGURE 21.3

FIGURE 21.4

- The pH of a solution can be approximated by using indicators or measured more precisely by using a pH meter.

Lesson Review Questions

1. Describe the characteristics of water which make it an amphoteric substance.
2. How do the concentrations of H_3O^+ and OH^- compare in pure water?

3. How do the concentrations of H_3O^+ and OH^- compare in an acid? In a base?
4. As the concentration of H_3O^+ increases, does pH increase or decrease? Explain.
5. As the concentration of OH^- increases, does pH increase or decrease? Explain.
6. What structural feature do Brønsted-Lowry bases and Lewis bases have in common?
7. How can acid-base indicators be used to approximate the pH of a solution?
8. How does litmus paper behave in an acidic solution versus in a basic solution?
9. Calculate the pH of the following solutions. Assume complete dissociation of each strong acid ([Acid] = $[H^+]$):
   a. 4.5×10^{-3} M HBr
   b. 1.34×10^{-4} M HCl
   c. 7.98×10^{-2} M HNO_3
10. Calculate the hydrogen ion concentrations in each of the following solutions:
    a. pH = 1.05
    b. pH = 5.65
    c. pH = 2.42
11. If the approximate pH of a solution is known, the indicators that will give you the most information are those for which the color change occurs near that pH value. Which indicator would you choose to check the approximate pH of the following solutions?
    a. pH ~ 4.1
    b. pH ~ 7.0
    c. pH ~ 2.4

Further Reading/Supplementary Links

- The pH scale: http://www.elmhurst.edu/~chm/vchembook/184ph.html
- How to calculate pH: http://www.csun.edu/~jeloranta/CHEM102/discussion7.pdf
- pH calculator: http://www.webqc.org/phsolver.php

Points to Consider

- How do we classify an acid as strong or weak?
- For a given concentration of acid, would you expect the pH to be lower for a strong acid or a weak acid?
- How can the relative strengths of various acids be quantified?

21.3 Acid and Base Strength

Lesson Objectives

- Explain the difference between a strong acid and a weak acid.
- Explain the difference between a strong base and a weak base.
- Calculate the pH values of acidic or basic solutions based on the original concentration of the acid or base.

Lesson Vocabulary

- **strong acid**: An acid which when dissolved in water will completely transfer its proton to the solvent.
- **weak acid**: An acid whose dissociation favors the reactants at equilibrium; only a small number of the acidic molecules dissociate to form H^+.
- **strong base**: A base whose dissociation favors the products at equilibrium; most molecules *do* remove a proton from water.
- **weak base**: A base whose dissociation favors the reactants at equilibrium; most molecules do *not*' remove a proton from water.

Check Your Understanding

- How are equilibrium constants calculated from data about the concentrations of each reacting species?

Strong vs. Weak Acids

So far, we have primarily been defining acids by their ability to donate an H^+ ion and bases by their ability to accept an H^+ ion. However, acids and bases vary in their relative ability to undergo these processes.

In general, acids can be classified as strong or weak based on the extent to which they produce H_3O^+ when dissolved in water. For a generic acid, we can write the following equilibrium reaction:

$$\mathrm{HA(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + A^-(aq)}$$

Using the usual shorthand notation, this equation can also be written as follows:

$$\mathrm{HA(aq) \rightleftarrows H^+(aq) + A^-(aq)}$$

This type of equilibrium, in which a proton is being transferred to water, is often indicated by writing the equilibrium constant as K_a. The relative position of this equilibrium for a given acid determines whether it will be considered strong or weak. When dissolved in water, a **strong acid** will completely transfer its proton to the solvent. In terms of the equilibrium above, the products will be heavily favored (K_a »1). In fact, the products are so heavily favored that the reverse reaction is often not even considered, and the proton transfer is written as unidirectional. For example, the strong acid HCl can dissociate in water according to the following reaction:

$$\begin{aligned}&\mathrm{HCl(aq)+H_2O(l)\rightarrow H_3O^+(aq)+Cl^-(aq)}\\&\qquad\mathrm{(HCl(aq)\rightarrow H^+(aq)+Cl^-(aq))}\end{aligned}$$

At equilibrium, essentially no intact HCl molecules are still present in solution.

In contrast, the equilibrium for a **weak acid** favors the reactants. A particularly common type of weak acid is an organic molecule that contains a carboxyl group (CO_2H, sometimes written as COOH). For example, acetic acid (the acidic component of vinegar) has the formula CH_3CO_2H. Its dissociation equation can be written as follows:

$$\begin{aligned}&\mathrm{CH_3CO_2H(aq)+H_2O(l)\rightleftarrows H_3O^+(aq)+CH_3CO_2^-(aq)}\\&\qquad\mathrm{(CH_3CO_2H(aq)\rightleftarrows H^+(aq)+CH_3CO_2^-(aq))}\end{aligned}$$

Because we are dealing with a weak acid, K_a for this equilibrium is much less than 1. At equilibrium, most of the acetic acid molecules are still intact, and only a small percentage have transferred their protons to the solvent. The K_a values for some weak acids are listed below:

TABLE 21.6: Ka

Acid Name	Structure	K_a
hydrofluoric acid	H-F	7.1×10^{-4}
nitrous acid	O=N-O-H	4.5×10^{-4}
formic acid	HCOOH	1.7×10^{-4}
acetic acid	CH_3COOH	1.8×10^{-5}
hydrocyanic acid	H-CN	4.9×10^{-10}

In more advanced textbooks, you can learn how to tell whether a particular acid is strong or weak. For now, be able to recognize the following as strong acids: HCl, HBr, HI, HNO_3, H_2SO_4, and $HClO_4$. All of these strong acids ionize completely when dissolved in water. Most other acids that you encounter in general chemistry courses are weak acids.

Strong vs. Weak Bases

Analogous to the acid dissociation reaction from the previous section, we can write the reaction between a generic base and water as follows:

$$\mathrm{B(aq)+H_2O(l)\rightleftarrows BH^+(aq)+OH^-(aq)}$$

The equilibrium constant for a reaction in which a base is deprotonating water (taking water's hydrogen atom) is often given the symbol K_b. Strong bases and weak bases can then be defined based on the position of this equilibrium. A **weak base** would have a very small K_b value (much less than 1), indicating that most molecules of the base do *not* remove a proton from water. Conversely, a **strong base** would have a K_b value greater than or equal to 1.

Nitrogen-containing compounds are a common type of weak base. The lone pair on the nitrogen atom can accept a proton from water as follows:

$$\mathrm{NH_3(aq)+H_2O(l)\rightleftarrows NH_4^+(aq)+OH^-(aq)}$$

The equilibrium constant for this reaction is quite low, so most of the NH_3 molecules will not remove a proton from water. K_b values for a few nitrogen-containing bases are listed below:

TABLE 21.7: **Kb**

Base	K_b
ethylamine ($CH_3CH_2NH_2$)	5.6×10^{-4}
methylamine (CH_3NH_2)	4.4×10^{-4}
ammonia (NH_3)	1.8×10^{-5}

The only strong bases that are commonly used in general chemistry courses are ionic compounds composed of metal cations and hydroxide anions, such as NaOH, KOH, or $Ba(OH)_2$.

Calculating pH for Acidic and Basic Solutions

Strong Acids and Bases

In the case of strong acids and bases, the pH for a solution of known concentration is relatively easy to calculate. For example, the strong acid HCl will dissociate completely, so we assume that the amount of acid added to the solution is equal to the amount of H^+ present at equilibrium.

Example 21.3

What is the pH of a 0.150 M aqueous solution of HCl?

Answer:

Because HCl is a strong acid, we can assume that all of its acidic hydrogens are transferred to the solvent molecules. Therefore, $[H^+] = 0.150$ M, so pH can be calculated as follows:

$$\text{pH} = -\log[H^+]$$
$$\text{pH} = -\log[0.150]$$
$$\text{pH} = 0.82$$

As expected for an acidic solution, the pH is much lower than 7.

Because the strong bases that you will encounter are all ionic compounds that contain the hydroxide anion, you can assume complete dissociation in water, which would tell you the concentration of hydroxide. Then, the concentration of H^+ can be calculated using the expression for K_w.

Example 21.4

What is the pH of a 0.245 M aqueous solution of NaOH?

Answer:

Because NaOH is a soluble ionic compound, we can assume that it fully dissociates in water. After dissociation, $[OH^-] = 0.245$ M. We can then use the value of K_w to determine $[H^+]$.

$$K_w = [H^+][OH^-]$$
$$1.0 \times 10^{-14} = [H^+][0.245]$$
$$[H^+] = 4.08 \times 10^{-14}$$

Then, use the definition of pH to determine the pH of this solution:

pH = - log [H$^+$]
pH = - log [4.08 × 10^{-14}]
pH =13.39

As expected for a basic solution, this value is significantly larger than 7.

Weak Acids and Bases

Because only a small portion of any available weak acid or base molecules undergo a proton transfer to form either H$^+$ or OH$^-$ ions, calculating the pH of one of these solutions is slightly more complicated. The following example problem outlines the general strategy for answering this type of question.

Example Problem 21.5

The K$_a$ of acetic acid (CH_3CO_2H) is 1.8×10^{-5}. Calculate the pH of a 0.50 M solution of acetic acid.

Answer:

First, set up an ICE table for the acid dissociation equation. Before any proton transfers occur, we have acetic acid at a concentration of 0.50 M, no acetate anion, and an H$^+$ concentration of 1.0×10^{-7} M. Once the reaction begins, some of the acetic acid will be converted to acetate as it transfers an H$^+$ ion to the solvent. The amount of acetic acid that dissociates in order to reach equilibrium (the quantity you are trying to find) is represented by *x*. A corresponding increase then occurs in the concentrations of the products. The equilibrium concentrations of each species can then be written in terms of *x*.

TABLE 21.8: **Ionization**

	CH_3CO_2H	$\rightleftarrows$	H$^+$	+	$CH_3CO_2{}^-$
Initial concentration (M)	0.50		1.0×10^{-7}		0.00
Change (M)	-x		+x		+x
At equilibrium (M)	0.50 –x		1.0×10^{-7} + x		x

Then, write the equilibrium constant expression and plug in the equilibrium values from the ICE table.

$$K_a = \frac{[H^+][CH_3CO_2^-]}{[CH_3CO_2H]}$$

$$1.8 \times 10^{-5} = \frac{[1.0\times10^{-7}+x][x]}{[0.50-x]}$$

Solving this equation by hand would be quite difficult. Fortunately, for essentially all of the weak acid problems that you will be expected to solve, we can make two simplifying assumptions. First, we assume that only a very small percentage of the acetic acid molecules will be ionized, which means that the drop in concentration (x) is much smaller than the original concentration (0.50 M). This is reasonable based on the small value of K$_a$. Mathematically, this assumption means that (0.50 - x) is approximately equal to 0.50. For example, say we found that x had a value of 0.0012. If we subtract this value from 0.50, we get 0.4988, and rounding to the correct number of significant figures would give us 0.50. Based on this assumption, we can simplify the above equation as follows:

$$1.8 \times 10^{-5} = \frac{[1.0\times10^{-7}+x][x]}{[0.50]}$$

The second assumption is that the amount of H$^+$ produced by this reaction is much larger than the amount already present. This is reasonable because even a weak acid tends to be much more acidic than pure water (unless it is present in extremely low concentrations). Mathematically, this means that we can ignore the 1.0×10^{-7} M H^+ already present. For example, if x has a value of 0.0012, the quantity (1.0×10^{-7} + x) is equal to x after rounding to the correct number of significant figures. This second assumption further simplifies the equation above, and we can now solve for x:

$$1.8 \times 10^{-5} = \frac{[x][x]}{[0.50]}$$
$$9.0 \times 10^{-6} = x^2$$
$$x = 0.0030$$

The concentration of H^+ at equilibrium is equal to 1.0×10^{-7} + 0.0030 M, which after rounding is simply 0.0030 M. Then, find the pH as usual:

$$pH = -\log[H^+]$$
$$pH = -\log[0.0030]$$
$$pH = 2.52$$

A 0.50 M solution of acetic acid would have a pH of 2.52.

As long as we can make the two simplifying assumptions shown above, determining the pH of a weak acid solution becomes much simpler. As we saw in the example problem,

$$K_a = \frac{[x]^2}{[C]}$$

where x is the equilibrium concentration of H^+ and C is the original concentration of the weak acid. Overall, this reduces to a much simpler expression for finding $[H^+]$:

$$[H^+] = \sqrt{C \times K_a}$$

Calculations involving weak bases can be carried out in the same fashion.

Lesson Summary

- Strong acids completely transfer their acidic protons to the solvent when dissolved in water. When a weak acid is dissolved in water, most of the molecules will retain their acidic protons, and only a small percentage will dissociate.
- Strong bases completely dissociate in water, releasing all hydroxide anions into the solution. The most common strong bases are soluble metal hydroxides. Weak bases partially deprotonate water to form small amounts of hydroxide and the protonated base.
- The pH of an acidic solution can be calculated from the original concentration of the acid and the value of K_a. Only the original concentration is required for strong acids.
- The pH of a basic solution can be calculated from the original concentration of the base and the value of K_b. Only the original concentration is required for strong bases.

Lesson Review Questions

1. Describe the difference between a strong and a weak acid. How does the K_a value for a given acid correspond to acid strength?

2. Describe the difference between a weak acid and a weak base. How does the K_b value for a given base correspond to base strength?
3. Identify each of the following compounds as a strong acid, strong base, weak acid, or weak base:
    a. HCl
    b. KOH
    c. HF
    d. $(CH_3)_2NH$
    e. CH_3CH_2COOH
4. Calculate the pH of a 0.65 M solution of HF (K_a = 7.1 x 10^{-4}).
5. Calculate the pH of a 0.25 M solution of acetic acid (K_a = 1.8 x 10^{-5}).
6. A 0.10 M solution of a weak acid gave a pH reading of 4.2. Calculate the hydrogen ion concentration, then determine K_a for the unknown acid.
7. Give a few examples of strong and weak acids, and a few examples of strong and weak bases.

Further Reading/Supplementary Links

- Strong and weak acids and bases: http://www.chemteam.info/AcidBase/Strong-Weak-AcidBase.html
- Calculating K_a values: http://www.chemteam.info/AcidBase/Calc-Ka-from-data.html

Points to Consider

What would happen if you combined a strong acid and a strong base?

21.4 Acid-Base Neutralization Reactions and Titrations

Lesson Objectives

- Define and give examples of acid-base neutralization reactions. Be able to write both molecular and net ionic equations for these reactions.
- Describe how antacids deal with stomach acidity.
- Describe the titration process when using an indicator.
- Describe the titration process when using a pH meter.
- Describe titration curves for both monoprotic and polyprotic acids.

Lesson Vocabulary

- **neutralization**: The reaction between an acid and a base in which neutral water is produced.
- **titration**: A laboratory technique that very accurately measures the concentration of a solution of an acid or a base.
- **titrant**: The solution of unknown concentration used in a titration.
- **equivalence point**: The point at which the moles of acid that were initially present in the flask are equal to the moles of base that were added via the buret.
- **titration curve**: A plot of pH vs. the amount of titrant added.

Check Your Understanding

- What information can we obtain from an acid equilibrium constant?

Introduction

If you have ever been stung by a bee, you've likely experienced the painful burning sensation left by the stinger. This burning or stinging is caused by an acid in the bee's stinger. One way to relieve this discomfort is to apply a paste made of baking soda to the sting. Baking soda contains a weak base called sodium hydrogen carbonate which reacts with the acid and helps relieve the sting. In this lesson you will learn about various acid-base reactions and how they work.

Neutralization of Acids and Bases

The Neutralization Reaction

So far, we have been looking at the interaction between acids and water (in which water acts as a very weak base) or bases and water (in which water acts as a very weak acid). However, acids and bases can react directly with each other as well. A typical acid-base reaction would have the following form:

$$\text{acid} + \text{base} \rightarrow \text{salt} + \text{water}$$

where the term salt can refer to essentially any ionic compound. An example would be the reaction between hydrochloric acid and potassium hydroxide:

$$HCl(aq) + KOH(aq) \rightarrow KCl(aq) + H_2O(l)$$

Recall from the chapter *Chemical Reactions* that there are several different ways to write reactions between ionic substances that take place in water. The equation above is the molecular equation for this reaction. We can also write the ionic equation as follows:

$$H^+(aq) + Cl^-(aq) + K^+(aq) + OH^-(aq) \rightarrow K^+(aq) + Cl^-(aq) + H_2O(l)$$

Removing the spectator ions, which do not change over the course of the reaction, we get the following net ionic equation:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

The reaction between an acid and a base is referred to as a **neutralization** reaction, since the more reactive H^+ and OH^- ions combine to produce neutral water. When equal amounts of a strong acid and a strong base are combined, we are left with a neutral solution (pH = 7).

How Antacids Work

Have you ever experienced heartburn? Heartburn is actually a condition caused by stomach acid, rather something in your heart. The stomach produces HCl, which is a necessary component of digestion. However, excessive amounts of stomach acid can cause a great deal of discomfort. Various factors can cause the overproduction of acid, mostly related to the types (and amounts) of food and beverages that are being consumed. Caffeine and other oils in coffee (even decaf) will increase HCl production in the stomach. Smoking cigarettes and drinking alcohol also increase the formation of stomach acid.

To relieve the discomfort associated with excess stomach acid, many people turn to antacids. Antacids are essentially just bases that react with some of the unwanted HCl via a neutralization reaction. Strong bases like NaOH are far too harsh to ingest, but some less soluble hydroxide bases can be consumed as suspensions. For example, milk of magnesia is a suspension of $Mg(OH)_2$. $Al(OH)_3$ is also available as a safe formulation. Both of these compounds will remain largely undissolved until they reach the stomach, where they will react with the excess acid without subjecting other parts of the body to strongly basic conditions. However, these can lead to other types of issues with continued use, such as constipation, kidney damage, and possibly even bone depletion.

These days, the most common antacids use weak bases, such as carbonate or bicarbonate ions, to neutralize the HCl. The resulting carbonic acid can then decompose into water and carbon dioxide. For example, drinking a solution of sodium bicarbonate (baking soda) will result in the following reactions:

FIGURE 21.5

Many antacid tablets use calcium carbonate as an active ingredient.

$$\begin{aligned} HCl(aq) + NaHCO_3(aq) &\rightarrow NaCl(aq) + H_2CO_3(aq) \\ H_2CO_3(aq) &\rightarrow H_2O(l) + CO_2(g) \end{aligned}$$

It should be noted that a newer class of antacids does not work by directly neutralizing stomach acid. Instead, they act to inhibit the proton pumps that generate the acid in the first place. Proton pump inhibitors decrease the activity of these pumps and lower the amount of acid produced by the stomach, but they do not neutralize the acid already present.

Acid-Base Titrations

A **titration** is a laboratory technique that very accurately measures the concentration of a solution of acid or base. It makes use of a neutralization reaction and the fact that pH changes very rapidly for neutral (and nearly neutral) solutions.

The following is a typical procedure for titration of a strong acid with a strong base: Let's say you have a solution of HCl, but the concentration is not known. First, a known volume of the acid is placed in a flask, and a few drops of an acid-base indicator, such as phenolphthalein, are added. Because this solution is acidic, and phenolphthalein is colorless at low pH values, the solution remains clear.

Next, a solution of a strong base, such as NaOH is placed into a piece of glassware called a buret (**Figure** 21.6). This solution, which has a known concentration, is referred to as the **titrant**. Then, the titrant is added drop by drop to the acid while swirling the flask. Because phenolphthalein turns pink when exposed to base, the drops of the titrant may initially appear pink when they hit the acid, but after swirling, the base is neutralized by the HCl, and the pink color fades. Once the pink color no longer fades after swirling, the solution in the flask is basic (pH >7), which means all of the HCl has been neutralized by the NaOH titrant. The volume of the titrant that was added to the acid can be measured by looking at the initial and final levels of the solution in the buret.

At this point, called the **equivalence point**, the moles of acid that were initially present in the flask are equal to the number of moles of base that were added via the buret. Remember that to calculate the number of moles of solute, we multiply the concentration of the solution (in mol/L) by the volume of the solution (in L). At the equivalence point:

$$\text{moles acid} = \text{moles base}$$

FIGURE 21.6

$$M_{acid} \times V_{acid} = M_{base} \times V_{base}$$

where M and V are the concentration and volume, respectively, of the two solutions. After performing the titration above, we know the volume of the initial acid in the flask, the concentration of the base, and the volume of the titrant that was required to reach the equivalence point. We can therefore solve for the concentration of the HCl solution.

Example 21.6

A 25.0 mL sample of an HCl solution is titrated with 0.050 M NaOH. The equivalence point is reached after the addition of 46.7 mL of the NaOH solution. What is the concentration of the HCl solution?

Answer:

Simply plug these values into the equation above:

$$M_{acid} \times V_{acid} = M_{base} \times V_{base}$$
$$M_{acid} \times 25.0 \text{ mL} = 0.050 \text{ M} \times 46.7 \text{ mL}$$
$$M_{acid} = 0.093 \text{ M}$$

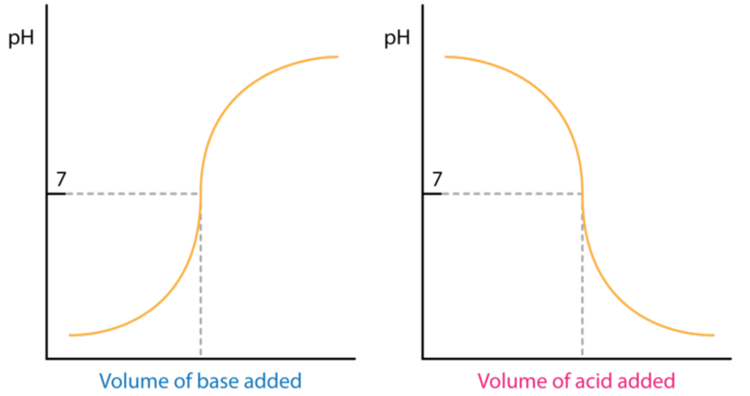
Titration Curves

If the pH of a solution is tracked with a pH meter over the course of the titration, we can get even more useful information about what is occurring in solution. A **titration curve** is a plot of pH vs. the amount of titrant added. The shape and position of the curve can be used not just to determine the equivalence point, but also to determine whether the acid is strong or weak and the K_a value (for weak acids).

Figure 21.7 shows two titration curves. The curve on the left represents the experiment we just described, in which a strong base (NaOH) is added to a strong acid (HCl). The volume of base added is plotted on the x-axis, and the pH obtained is plotted on the y-axis. We see a very sharp rise in pH as the equivalence point is reached. The dotted line shows us the volume of base that must be added to get to this point.

The graph on the right shows a titration of a strong base with a strong acid. Although the pH is decreasing rather than increasing, the principle is the same. At the equivalence point, the moles of added acid are equal to the moles of base that were initially present, so the same equation can be used to determine the unknown concentration.

This approach can also be used to titrate a weak acid. In **Figure** 21.8, we see a comparison between the titration curves obtained for HCl and for acetic acid (a weak acid). There are a couple of noteworthy differences. First, the



Titration curve of a strong acid (HCl) with a strong base (NaOH)

Titration curve of a strong base (NaOH) with a strong acid (HCl)

FIGURE 21.7

curve for the weak acid has a small plateau about halfway to the equivalence point. We will not go into the details, but as it turns out, the pH at the flattest point of this plateau can be used to determine the K_a of the acid according to the following equation:

$$pH = -\log(K_a)$$

Additionally, the pH at the equivalence point is higher than 7 when titrating a weak acid. This is because the anion from the weak acid (acetate) is slightly basic, whereas the anion from the strong acid (chloride) is an extremely poor base.

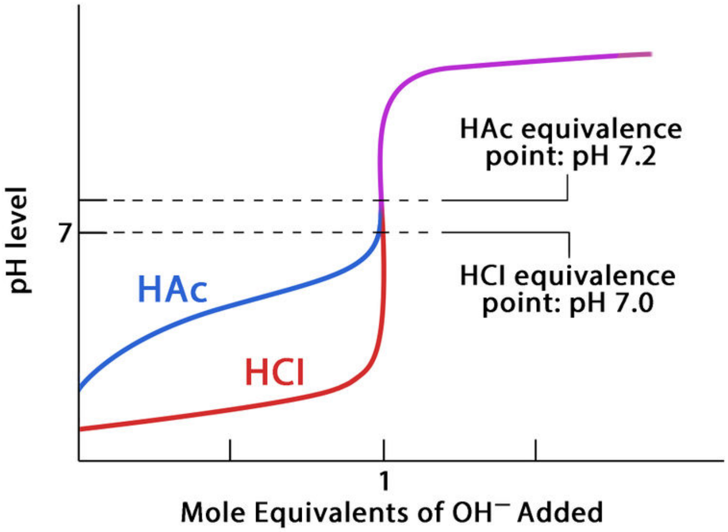


FIGURE 21.8

Polyprotic acids have distinctive titration curves. These acids have multiple dissociation constants, one for each acidic proton. For example, phosphoric acid has three acidic hydrogens:

$$H_3PO_4 \overset{K_{a_1}}{\rightleftarrows} H^+ + H_2PO_4{}^- \overset{K_{a_2}}{\rightleftarrows} H^+ + HPO_4{}^{2-} \overset{K_{a_3}}{\rightleftarrows} H^+ + PO_4{}^{3-}$$

$$K_{a_1} = 7.5x10^{-3} \quad K_{a_2} = 6.2x10^{-8} \quad K_{a_3} = 4.8x10^{-13}$$

On the titration curve for phosphoric acid, we can see three vertical inflection points corresponding to the equivalence points for each acidic proton. (The third one is not very clear, because $HPO_4{}^{2-}$ is not much more acidic than water.) As in the case of a monoprotic weak acid, the plateaus in the curve above can be used to determine the K_a values for each acidic hydrogen in phosphoric acid.

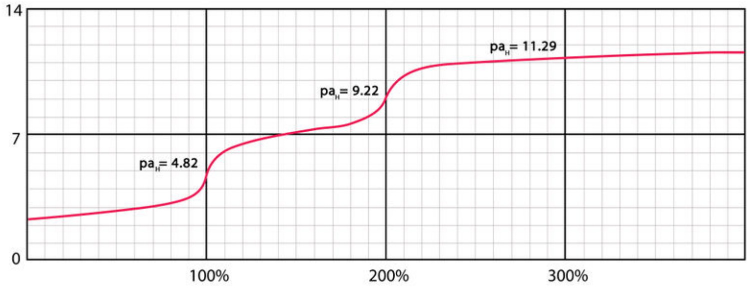


FIGURE 21.9

Lesson Summary

- Combining an acid and a base results in a neutralization reaction. For strong acids and bases, the net ionic equation is simply $H^+ + OH^- \rightarrow H_2O$.
- Weak bases or poorly soluble strong bases can be ingested to neutralize excess stomach acid.
- The concentration of an acid or base can be determined by titration.
- A pH meter allows the construction of a titration curve. The data from a titration curve can be used to determine the equivalence point, the type of acid or base (strong vs. weak), and the K_a or K_b value of the acid or base being titrated.

Lesson Review Questions

1. What are the products of a typical acid-base reaction?
2. Why are acid-base reactions referred to as neutralization reactions?
3. How do antacids relieve heartburn?
4. Read the ingredients on a container of antacids. Write equations for the neutralization of HCl based on those ingredients.
5. What property of near-neutral solutions do titration procedures rely on?
6. Define "titrant" and "indicator" as they pertain to titration procedures.
7. Estimate the pH at the equivalence point for the following acid-base titrations (i.e. =7, >7, <7):
    a. strong acid-strong base
    b. weak acid-strong base
    c. strong acid-weak base
8. 30. mL of an HBr solution is titrated with 0.075 M KOH. If 39.1 mL of KOH is required to reach the equivalence point, what is the concentration of the acid?
9. 45.0 mL of an NaOH solution is titrated with 0.12 M HCl. If 29.6 mL is required for neutralization, what is the concentration of the NaOH solution?
10. You have two weak acids in unlabeled bottles (a very bad practice, by the way). Explain how you could determine which one was acetic acid and which one was phosphoric acid.

Further Reading/Supplementary Links

- Acid and base titrations: http://www.sparknotes.com/chemistry/acidsbases/titrations/section1.html
- Neutralization of acids and bases: http://www.iun.edu/~cpanhd/C101webnotes/chemical%20reactions/acidbase.html
- Titration video: http://www.youtube.com/watch?v=g8jdCWC10vQ

Points to Consider

- Many biochemical processes require strict pH control. How can we take advantage of the properties of weak acids and bases to stabilize a solution at a specific pH?

21.5 Salt Solutions

Lesson Objectives

- Describe salt solutions as acidic, basic, or neutral.
- Calculate the pH of a salt solution when given relevant data.
- Explain how buffers work to maintain pH.

Vocabulary

- **conjugate base**: The deprotonated form (A^-) from a given acid acid (HA).
- **conjugate acid**: The resulting molecule after the base accepts a proton.
- **buffer**: Solutions which resist small changes in pH when an acid or a base is added to the system.
- **pK_a**: The negative logarithm of the K_a; a lower pK_a indicates a more acidic compound.

Check Your Understanding

- How do you calculate the concentrations of various reaction components at equilibrium?

Introduction

Neutralization reactions between an acid and a base yield a salt and water. In some cases, this results in a completely neutral solution. However, some salts are weakly acidic or basic. How can we tell whether a given salt will act as an acid or base? Looking at the relative strengths of the acid and base that were used to form the salt can give us information on the acid-base properties of the resulting solution.

Salts and Their Interactions with Water

Salts Forming Neutral Solutions

The simplest situation is a salt formed by combining a strong acid and a strong base. These salts are neither acidic nor basic, so they do not affect the pH of the solution when dissolved in water. For example, the ionic compound $NaNO_3$ could be prepared by combining the strong acid HNO_3 and the strong base NaOH. If we were to dissolve $NaNO_3$ in water, it would dissociate into Na^+ and ${NO_3}^-$ ions. Neither ion is a strong enough acid or base to cause any noticeable proton transfers, so the pH of the pure water is not altered.

Salts Forming Basic Solutions

A salt formed from a weak acid and a strong base will form a solution that has a pH greater than than 7. For example, sodium acetate could be formed by neutralizing acetic acid with sodium hydroxide. Dissolving sodium acetate in water will produce sodium ions and acetate ions. The Na^+ ion is not a strong enough acid or base to donate or accept any protons, but the acetate ion is a weak base:

$CH_3COO^- + H_2O \rightleftarrows CH_3COOH + OH^-$

Although this equilibrium favors the reactants (acetate is still a weak base), there will still be some additional hydroxide produced, skewing the H^+ / OH^- balance and increasing the pH of the solution. The equilibrium constant for this reaction can be written as follows:

$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} = 5.6 \times 10^{-10}$

Salts Forming Acidic Solutions

A salt formed from a strong acid and a weak base will give an acidic solution when dissolved in water. For example, NH_4Cl, which is formed by neutralizing the weak base ammonia with HCl, would dissociate into the following ions:

$NH_4Cl \overset{H_2O}{\rightarrow} NH_4{}^+ + Cl^-$

The ammonium ion then acts as a weak acid, while the chloride ion is not a strong enough base to affect the pH of the solution.

$NH_4{}^+ \rightleftarrows NH_3 + H^+$

Calculations involving acidic and basic salts are carried out in the same way as other acid-base equilibrium calculations. Depending upon the data available, we can calculate equilibrium constants or the pH of a solution with a known concentration.

Buffer Solutions

Consider the generic equilibrium for the dissociation of an acid:

$HA \rightleftarrows H^+ + A^-$

In the reverse direction, the anion A^- is acting as a base by accepting a proton. For a given acid (HA), its deprotonated form (A^-) is referred to as its **conjugate base**. The conjugate base of a strong acid is an extremely poor base, which is why the reverse reaction essentially does not proceed. For example, HCl dissociates completely in water, and the chloride ion (its conjugate base) is not really thought of as a base. In contrast, the conjugate base of a weak acid is a weak base. For example, the acetate ion, which is the conjugate base of acetic acid, is slightly basic.

A similar terminology is used when dissolving bases in water. After the base accepts a proton, the resulting molecule or ion is referred to as its **conjugate acid**. For example, the ammonium ion ($NH_4{}^+$) is the conjugate acid of ammonia (NH_3).

We can take advantage of the properties of conjugate acids and bases to make **buffer** solutions, which resist small changes in pH when an acid or a base is added to the system. Biological buffers play important roles in maintaining a constant pH in cells and tissues, which is required in order for many biochemical reactions to proceed efficiently.

Buffers can be generated in the laboratory by making a mixture of both a weak acid and its conjugate base. Consider the following equilibrium between acetic acid and the acetate ion:

$CH_3COOH \rightleftarrows H^+ + CH_3COO^-$

If we dissolved both acetic acid and some source of acetate anion (such as sodium acetate) in water, the resulting solution would be set up to absorb small amounts of added acid or base without major changes to the concentration of H^+. For example, if a strong acid was added, most of the resulting H^+ ions would combine with acetate ions to make molecules of acetic acid. The addition of a strong base would cause mostly deprotonation of the acetic acid, and very little increase in the concentration of the hydroxide ion.

If we know the concentration of both the acid and its conjugate base, we can calculate the pH of the buffer based on the ratio between these two components. For example, say we made a solution that contained 0.10 M acetic acid and 0.20 M sodium acetate. The equilibrium expression for this reaction has the following form:

$$\mathrm{K_a} = \frac{[\mathrm{CH_3COO^-}][\mathrm{H^+}]}{[\mathrm{CH_3COOH}]}$$

Plugging in the known concentrations, along with the K_a of acetic acid (1.74×10^{-5}) allows us to solve for the concentration of H^+:

$$1.74 \times 10^{-5} = \frac{[0.20][\mathrm{H^+}]}{[0.10]}$$
$$[\mathrm{H^+}] = \frac{[0.10]}{[0.20]}(1.74 \times 10^{-5})$$
$$[\mathrm{H^+}] = 8.70 \times 10^{-6}\ \mathrm{M}$$

Then, we can calculate the pH as usual:

$$\mathrm{pH} = -\log[\mathrm{H^+}]$$
$$\mathrm{pH} = -\log[8.70 \times 10^{-6}]$$
$$\mathrm{pH} = 5.06$$

This buffer would have a pH of 5.06. We can tailor the buffer to a specific pH by changing the ratio of acid to salt in the mixture.

Note that if we have equal concentrations of the acid and its conjugate base, the equilibrium constant expression can be simplified as follows:

$$\mathrm{K_a} = \frac{[\mathrm{CH_3COO^-}][\mathrm{H^+}]}{[\mathrm{CH_3COOH}]}$$
$$\mathrm{K_a} = \frac{[\mathrm{x}][\mathrm{H^+}]}{[\mathrm{x}]}$$
$$\mathrm{K_a} = [\mathrm{H^+}]$$

This also means that the pH can be determined directly from the K_a:

$$\mathrm{pH} = -\log[\mathrm{H^+}]$$
$$\mathrm{pH} = -\log(\mathrm{K_a})$$

The negative logarithm of the K_a is known as the **pK_a** of an acid. Tables of acid strengths often list pK_a values instead of K_a values so that exponents are not required. As with pH, a lower pK_a indicates a more acidic compound.

Lesson Summary

- A salt formed from a weak acid and a strong base will form a basic solution (pH >7), because the anion acts as a weak base.
- A salt formed from a strong acid and a weak base will form an acidic solution (pH <7), because the cation acts as a weak acid.

- A salt formed from a strong acid and a strong base will form a neutral solution (pH = 7), because neither the cation nor the anion is a sufficiently strong acid or base.
- The deprotonated form of an acid is referred to as its conjugate base. Similarly, the protonated form of a base is referred to as its conjugate acid.
- A mixture of a weak acid and its conjugate base (or a weak base and its conjugate acid) produces a buffer, which is resistant to large changes in pH even when additional acid or base is added.

Lesson Review Questions

1. What types of acids and bases form neutral salt solutions?
2. What types of acids and bases from basic salt solutions?
3. What types of acids and bases form acidic salt solutions?
4. Define conjugate acid and conjugate base in the general acid dissociation equation, $HA \rightleftarrows H^+ + A^-$.
5. Write the formula and charge for the conjugate base of each of the following weak acids:
    a. HNO_2
    b. $HCOOH$
    c. C_6H_5COOH
    d. C_6H_5OH
6. Write the formula and charge for the conjugate acid of each of the following weak bases:
    a. CH_3NH_2
    b. C_5H_5N
    c. $C_6H_5NH_2$
7. When NaF is dissolved in water, the following reaction occurs: $F^- + H_2O \rightleftarrows HF + OH^-$. The K_b for this process is 1.4×10^{-11}. If a 0.1 M solution of NaF is prepared, what is the equilibrium concentration of HF?
8. What initial concentration of KCN is needed to provide an equilibrium HCN concentration of 0.0025 M? The K_b for CN^- is 2.0×10^{-5}.
9. Explain why buffer solutions are able to resist small changes in pH.
10. What ratio of benzoic acid to sodium benzoate should be used to prepare a buffer solution with a pH of 4.3? The K_a for benzoic acid is 6.5×10^{-5}.
11. What is the pH of a solution containing equal concentrations of formic acid and potassium formate? The K_a for formic acid is 1.7×10^{-4}.

Further Reading/Supplementary Links

- Acidic, basic, and neutral salts: http://www.science.uwaterloo.ca/~cchieh/cact/c123/salts.html
- Buffer solutions: http://chemed.chem.wisc.edu/chempaths/GenChem-Textbook/Buffer-Solutions-620.html
- Buffer systems in the blood: http://www.chemistry.wustl.edu/~edudev/LabTutorials/Buffer/Buffer.html

Points to Consider

The pH of a system is very important for sustaining life. Biochemical processes require careful pH control in order to maintain cellular integrity.

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CHAPTER 22

Oxidation Reduction Reactions

Chapter Outline

22.1 NATURE OF OXIDATION AND REDUCTION
22.2 OXIDATION NUMBERS
22.3 BALANCING REDOX EQUATIONS
22.4 REFERENCES

Have you ever seen someone breathe into a device like this? This person is breathing into a breathalyzer, a device used to detect the presence of ethanol (an alcohol) in a person's breath. One version of the breathalyzer works by measuring the color change of a solution of the dichromate ion. In the presence of ethanol, the solution changes from orange to green as the dichromate ion is converted to a chromium(III) ion. The extent of the color change is then related to actual blood-alcohol content. The device is very accurate, because the chemical reaction on which the device is based is very predictable. This is an example of an oxidation-reduction reaction.

Courtesy of Senior Airman Natasha Stannard, US Air Force. commons.wikimedia.org/wiki/File:Breathalyzer_study.jpg. Public Domain.

22.1 Nature of Oxidation and Reduction

Lesson Objectives

- List three ways in which oxidation has been defined.
- List three ways in which reduction has been defined.
- Identify oxidation-reduction (redox) reactions.
- Identify common oxidizing agents and reducing agents.

Lesson Vocabulary

- **oxidation-reduction reaction**: A chemical reaction in which one substance is being oxidized and another is being reduced.
- **oxidation**: Classified by gain of oxygen atoms, loss of hydrogen atoms, or loss of electrons.
- **reduction**: Classified by loss of oxygen atoms, gain of hydrogen atoms, or gain of electrons.
- **oxidizing agent**: The reduced species; causes the other reactant to become oxidized.
- **reducing agent**: The oxidized species; causes the other reactant to become reduced.

Check Your Understanding

What happens when metallic sodium is added to water?

Introduction

What do the rusting of a nail, the tarnishing of silverware, and the burning of propane gas all have in common? As you have seen, there are many types of chemical reactions that occur depending on the combination of reactants and the conditions under which the reactants are placed. The processes we have just mentioned are all classified as oxidation-reduction reactions. In this lesson you will learn some possible ways to classify oxidation-reduction reactions based on certain characteristics.

Identifying Oxidation and Reduction

If an iron nail is exposed to the elements for a long enough period of time, it will eventually rust. This process is due to the following reaction between metallic iron and molecular oxygen:

$$4\ \mathrm{Fe}(s) + 3\ \mathrm{O_2}(g) \rightarrow 2\ \mathrm{Fe_2O_3}(s)$$

FIGURE 22.1

Rust on a car caused by the oxidation of iron.

The rusting process is often accelerated when the metal comes into contact with electrolytes, such as the salts used to melt ice on streets in the winter.

Similarly, silverware will tarnish when exposed to some sulfur-containing compounds. The layer of black tarnish (Ag_2S) can easily be removed by cleaning the silverware with a mixture of aluminum and baking soda:

$$3\ Ag_2S(s) + 2\ Al(s) \rightarrow 6\ Ag(s) + Al_2S_3(s)$$

FIGURE 22.2

Tarnished silver. The object on the left has tarnished. The plate on the right and the object being held have both been polished.

Many homes are heated by burning propane gas, which combusts in the presence of oxygen:

$$CH_3CH_2CH_3 + 5\ O_2 \rightarrow 3\ CO_2 + 4\ H_2O$$

FIGURE 22.3

Some fireplaces use propane gas rather than wood as fuel.

All of these seemingly disparate processes are examples of **oxidation-reduction (redox) reactions**. In a redox reaction, one substance is undergoing an **oxidation** and another is undergoing a **reduction**. The ways in which these terms are defined have varied over the years. The broadest definitions of oxidation and reduction are related to oxidation numbers, which will be discussed in the following lesson. However, many redox reactions can be identified on the basis of earlier definitions. Three general types of oxidation processes are listed below:

1. Gain of oxygen –When one or more oxygen atoms are added to a compound over the course of a reaction, that compound is being oxidized. This is the oldest definition of the word and the origin of the name. For example, when carbon monoxide is used to extract iron from iron ore, the following reaction takes place:

$Fe_2O_3(s) + 3\ CO(g) \rightarrow 2\ Fe(s) + 3\ CO_2(g)$

The carbon monoxide molecule is being oxidized; it gains an oxygen atom to form carbon dioxide.

2. Loss of hydrogen –When one or more hydrogen atoms leave a compound during a chemical reaction, this is often a type of oxidation. For example, when ethanol reacts with potassium dichromate, the ethanol molecule loses two hydrogen atoms:

CH_3CH_2OH (ethanol) → CH_3CHO (acetaldehyde)

In this process, ethanol is being oxidized to form acetaldehyde. The other components of the reaction are not shown, in order to highlight the oxidation.

It should be noted that not all losses of hydrogen are oxidations. For example, in the previous chapter on *Acids and Bases*, we saw many reactions in which a hydrogen ion is transferred from an acid to a base. However, because H^+ is being transferred but all of the electrons remain with their original compounds, this is actually *not* an oxidation process. This distinction will become clearer in the next lesson when we introduce the concept of oxidation numbers.

3. Loss of electrons –If an atom, ion, or molecule loses one or more electrons during a reaction, it is being oxidized. For example, when a neutral metal is converted to a metal cation, the metal is being oxidized. An example would be the reaction of metallic sodium with water:

$$2\ Na(s) + 2\ H_2O(l) \rightarrow 2\ NaOH(aq) + H_2(g)$$

Over the course of this reaction, neutral sodium atoms are being converted to sodium cations (Na^+). This net loss of an electron is a common type of oxidation.

The opposite of each of these criteria generally indicates that a reduction is occurring.

1. Loss of oxygen –When one or more oxygen atoms are removed from a compound, it is generally being reduced. Look again at the reaction between ferric oxide and carbon monoxide:

$$Fe_2O_3(s) + 3\ CO(g) \rightarrow 2\ Fe(s) + 3\ CO_2(g)$$

Oxygen atoms are being removed from the iron oxide, so that component is being reduced. The term reduction originated from this type of process, where a metal oxide is "reduced" to its pure metal form by treating it with the appropriate chemicals.

2. Addition of hydrogen –The oxidation of ethanol (shown above) can be reversed by reacting acetaldehyde with hydrogen gas in the presence of an appropriate catalyst:

$$CH_3CHO(l) + H_2(g) \rightarrow CH_3CH_2OH(l)$$

In this reaction, acetaldehyde is being reduced.

3. Gain of electrons –When metallic sodium is treated with gaseous chlorine, a violent reaction occurs:

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

On the reactant side, we see two neutral chlorine atoms covalently bonded into a chlorine molecule. On the product side, each chlorine atom has gained an electron to become Cl^- ions. Chlorine is being reduced in this reaction.

Two things should be emphasized at this point. First, not all processes that involve the gain or loss of oxygen or hydrogen are redox reactions. Although those definitions often work well with organic (carbon-based) compounds, there are many situations in inorganic chemistry for which they are insufficient. Second, oxidation and reduction must always take place together. In order for one compound to be oxidized, another must be reduced, and vice versa. For example, based on the electron-transfer definition, one compound must lose electrons (be oxidized) in order for another compound to gain electrons (be reduced).

Oxidizing and Reducing Agents

If a species is oxidized, there must be something present to make that process happen. This “something” is known as an **oxidizing agent**. When something is reduced, a **reducing agent** is necessary to for the reaction to occur. In every oxidation-reduction reaction, there is an oxidizing agent and a reducing agent. You cannot have an oxidation-reduction reaction without both being present.

Look again at the following reaction:

$$Fe_2O_3 + 3\ CO \rightarrow 2\ Fe + 3\ CO_2$$

In this process, carbon monoxide is being oxidized (oxygen is added), and iron oxide is being reduced (oxygen is lost). Because the added oxygen is provided by the iron oxide, Fe_2O_3 is the oxidizing agent in this reaction. Similarly, because CO is required to "remove" oxygen from the iron oxide, carbon monoxide is the reducing agent.

We can also identify oxidizing and reducing agents in terms of which species are undergoing each type of transformation. In a redox reaction, the substance that is oxidized causes the other substance to be reduced; it is therefore the reducing agent. The substance that is reduced causes the other substance to be oxidized; it is therefore the oxidizing agent.

Lesson Summary

- Oxidation often involves the loss of hydrogen, the gain of oxygen, or the loss of electrons.
- Reduction often involves the gain of hydrogen, the loss of oxygen, or the gain of electrons.
- An oxidizing agent causes the oxidation of another species in the reaction.
- A reducing agent causes the reduction of another species in the reaction.
- Oxidations and reductions always take place together; you cannot have a complete reaction in which only one of the two processes is occurring.

Lesson Review Questions

1. Explain in your own words the following oxidation processes:
    a. Gain of oxygen
    b. Loss of hydrogen
    c. Loss of electrons
2. Explain in your own words the following reduction processes:
    a. Loss of oxygen
    b. Gain of hydrogen
    c. Gain of electrons
3. What is the purpose of the oxidizing agent?
4. What is the purpose of the reducing agent?
5. In each of the following reactions, indicate which substance is oxidized, which is reduced, which is the oxidizing agent, and which is the reducing agent:
    a. $Mg + 2\ HCl \rightarrow MgCl_2 + H_2$
    b. $2\ Fe + 3\ V_2O_3 \rightarrow Fe_2O_3 + 6\ VO$
    c. $2\ Na + FeCl_2 \rightarrow 2\ NaCl + Fe$
    d. $AgNO_3 + Cu \rightarrow CuNO_3 + Ag$

e. $2\ Na + 2\ H_2O \rightarrow 2\ NaOH + H_2$

Further Reading/Supplementary Links

- Oxidation-reduction basics: http://library.kcc.hawaii.edu/external/chemistry/basic_model.html
- Oxidation-reduction video: http://www.youtube.com/watch?v=a6RR4kPsnlE

Points to Consider

- How can we tell which species are oxidized and which are reduced in a complex reaction?
- What types of reactions are redox reactions?

22.2 Oxidation Numbers

Lesson Objectives

- Be able to assign an oxidation number to each atom in a compound based on the given set of guidelines.
- Determine whether an atom is oxidized or reduced based on changes in oxidation number over the course of a chemical reaction.
- Give examples of typical oxidation-reduction reactions.

Lesson Vocabulary

- **oxidation number**: The charge that an atom would have if all polar covalent and ionic bonds resulted in a complete transfer of electrons from the less electronegative atom to the more electronegative one. Also referred to as oxidation state.

Check Your Understanding

1. If a neutral iron atom were to lose one, two, or three electrons, what would the charge be on each of the resulting ions?
2. If a neutral chlorine atom were to gain an electron during a reaction with another chemical species, what would be the charge of the resulting chloride ion? Is it likely that a chlorine atom would gain more than one electron? Why or why not?
3. How many valence electrons would be assigned to aluminum and oxygen before and after the following reaction takes place?

$4\ \mathrm{Al} + 3\ \mathrm{O_2} \rightarrow 2\ \mathrm{Al_2O_3}$

Introduction

In the previous lesson, we looked at the rusting of iron as an example of an oxidation-reduction (redox) reaction.

The formation of rust is summarized by the following chemical equation:

$4\ \mathrm{Fe}(s) + 3\ \mathrm{O_2}(g) \rightarrow 2\ \mathrm{Fe_2O_3}(s)$

Based on the definition of a redox reaction as an electron-transfer process, we can easily see that rusting is a redox reaction. Metallic iron is losing electrons (being oxidized), and nonmetallic oxygen is gaining electrons (being reduced). The result is an ionic compound composed of metal cations and nonmetal anions. There are many other examples of redox reactions between metals and nonmetals to make ionic compounds. However, not all redox reactions are so obvious. For example, consider the following reaction:

FIGURE 22.4

An ancient cannon covered in rust.

$3\ Cu_2 + 14\ HNO_3 \rightarrow 6\ Cu(NO_3)_2 + 2\ NO + 7\ H_2O$

Is this a redox reaction? If so, what is being oxidized, and what is being reduced? As it turns out, this is a redox reaction. In order to determine whether electron transfers are occurring, chemists have developed a system of assigning electrons to various atoms. By assigning each valence electron in a compound to a particular atom, each atom can be given an oxidation number. In this lesson, we will learn how to determine the oxidation numbers for atoms in various compounds and how to use that information to identify whether a given reaction is a redox process.

Rules for Assigning Oxidation Numbers

Overall, the **oxidation number** (or *oxidation state*) of an atom is the charge that the atom would have if all polar covalent and ionic bonds resulted in a complete transfer of electrons from the less electronegative atom to the more electronegative one. Oxidation numbers can be assigned by looking at the Lewis structure for a given substance, but for many simpler compounds, they can also be assigned using the set of rules outlined below.

First, the oxidation numbers for the atoms in any substance or compound must add up to the overall charge of that species. As a result:

1. The atoms in any neutral elemental substance each have an oxidation state of zero. This includes neutral metals (e.g., Na, Be, K), diatomic molecules of a single element (e.g., H_2, Br_2, O_2), and sometimes more complex structures (e.g., P_4, S_8).
2. Monatomic ions have an oxidation number equal to their charge. Li^+ has an oxidation state of +1, Ba^{2+} has an oxidation state of +2, I^- has an oxidation state of -1, and so on.
3. If we know the oxidation numbers for all but one of the atoms in a substance, we can deduce the oxidation state of the unknown atom by comparing the sum of the other oxidation states with the overall charge of the compound or ion (this will be illustrated with examples later).

Additionally, many elements take on the same oxidation number in most or all of their compounds.

1. Elements with very low electronegativity values tend to lose all of their valence electrons when present in a compound, so the resulting oxidation state is equal to the number of valence electrons in the neutral atom.

   a. Alkali metals have an oxidation state of +1 in their compounds. Although neutral alkali metals still have an oxidation state of zero, as soon as they react with other elements, alkali metals tend to give up their single valence electron, resulting in a charge of +1.
   b. Alkaline earth metals have an oxidation state of +2 in their compounds. The reasoning is the same as for the Group 1 metals.
   c. Aluminum tends to have an oxidation state of +3 in its compounds. However, this is not always the case for some of the more electronegative members of Group 13.
2. Elements with very high electronegativity values often have an oxidation number equal to the charge of the ion that would be formed in order to attain a noble gas configuration.
   a. Fluorine has an oxidation state of -1 in all of its compounds. Because fluorine is the most electronegative element, it is assigned any shared electrons. The only way for fluorine to have a stable octet without an oxidation state of -1 is for it to be bonded to another fluorine atom. (The oxidation state of fluorine in F_2 is zero.)
   b. Oxygen has an oxidation state of -2 in most of its compounds. Oxygen is the second most electronegative element, so it also tends to be assigned all shared electrons. Exceptions include O_2 (oxidation state = 0), peroxides, in which two oxygen atoms are connected by a single bond (oxidation state usually = -1), and any compound in which oxygen is bonded to fluorine (pretty rare and reactive).
   c. Other halides often have an oxidation state of -1, but this trend breaks down when they are bonded to more electronegative atoms, such as nitrogen, oxygen, or fluorine.
3. The oxidation state of hydrogen can also be predicted based on the atoms to which it is bonded.
   a. As with other pure elements, hydrogen has an oxidation state of zero in H_2.
   b. When bonded to other nonmetals, which are nearly all *more* electronegative than hydrogen, hydrogen has an oxidation state of +1.
   c. When bonded to metals, which are nearly all *less* electronegative than hydrogen, hydrogen has an oxidation state of -1.

Other elements also have preferred oxidation numbers when forming compounds, but we must look at the additional elements in the compound to know which of these states is present. Some preferred oxidation states for various transition metals are shown in **Table** 22.1.

TABLE 22.1: Transition metal oxidation states

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
8																●										●				
7					●										●	○									●					
6				●	●	○								●	●	●	○							●	○	●	○			
5			●	○	●	●							●	●	○	○	○						●	●	●	○				
4		●	●		●	○	○					●	●	●	●	●	●	●				●	●	●	●	●	●	●		
3	●	●	●	●	●	●	●	●			●	●	●	●		●	●				●	○	●	●	●	○	●		●	
2		●	●	●	●	●	●	●	●	●		○	●	●		●	●	●	○	●			○	○	●	○	○	●		●
1									●										●										●	●

This table shows some of the possible oxidation states found in compounds of the transition metals. A solid circle represents a common oxidation state, and a ring represents a less common (energetically less favorable) oxidation state.

For many compounds, all of the atoms can be assigned an oxidation state based on the rules above. Sometimes, there will be one atom in a compound whose oxidation state is not as easy to predict as the others. When this is the case, we can make use of the fact that the sum of the oxidation states must equal the overall charge of the compound. Let's take a look at how this might work:

Example 22.1

Assign oxidation numbers to each atom in the compound $KMnO_4$.

Answer:

Potassium is an alkali metal, so we would expect it to have an oxidation state of +1, and we can assume that oxygen has an oxidation state of -2. Overall, this is a neutral compound, so the sum of all the oxidation states must equal zero. Therefore:

$$\begin{aligned} &K + Mn + 4(O) = 0 \\ &\qquad +1 + Mn + 4(-2) = 0 \\ &\qquad Mn - 7 = 0 \\ &\qquad Mn = +7 \end{aligned}$$

In this compound, manganese has an oxidation state of +7. Note that we must include an oxidation state of -2 for *each* of the four oxygen atoms. Let's look at another example.

Example 22.2

What is the oxidation state of iron in Fe_2O_3? Does it have a different oxidation state in $FeCl_4{}^{2-}$?

Answer:

In the first compound, we can assume that oxygen has an oxidation state of -2, since it is bonded to a metal, which would be significantly less electronegative.

$$\begin{aligned} &2(Fe) + 3(O) = 0 \\ &\qquad 2(Fe) + 3(-2) = 0 \\ &\qquad 2(Fe) - 6 = 0 \\ &\qquad 2(Fe) = +6 \\ &\qquad Fe = +3 \end{aligned}$$

In iron(III) oxide, iron has an oxidation state of +3. Note that this is the same as its charge when we dissociate this compound into its ions. Because the polyatomic ion has an overall charge, the oxidation states in $FeCl_4{}^{2-}$ will add up to -2, not zero. We can assume that chlorine has an oxidation state of -1, because it is bonded to a metal and not a very electronegative nonmetal.

$$\begin{aligned} &Fe + 4(Cl) = -2 \\ &\qquad Fe + 4(-1) = -2 \\ &\qquad Fe - 4 = -2 \\ &\qquad Fe = +2 \end{aligned}$$

In this ion, iron has an oxidation state of +2. Both of these are common oxidation states for iron, so we must look at the surrounding atoms to determine which is present in a given compound.

Identifying and Analyzing Redox Reactions

The system of assigning oxidation numbers allows for a more general definition of redox reactions. A redox process is one in which the oxidation numbers of one or more atoms change over the course of the reaction. Any atom whose oxidation number becomes more positive (or less negative) is being oxidized, and an atom whose oxidation number becomes more negative (or less positive) is being reduced. By assigning oxidation numbers to each atom in a reaction, we can determine whether or not it is a redox reaction.

In our previous chapter on *Chemical Reactions*, we talked about various different ways that reactions could be classified. Some of the reaction types we studied included combination (synthesis), decomposition, single and double replacement, and combustion. Any of these general reaction types may also be a redox reaction. In this section, we will look at examples of redox reactions that fall into each of these categories.

Combination Reactions

In combination or synthesis reactions, two chemical species combine to produce a new compound. The general expression for a combination reaction is:

$$A + B \rightarrow C$$

One example of this type of reaction is the rusting of iron, which we have already looked at extensively in this chapter:

$$4\ Fe(s) + 3\ O_2(g) \rightarrow 2\ Fe_2O_3(s)$$

Here is a short video showing the oxidation of iron.

MEDIA

Click image to the left for more content.

We saw in example problem 22.2 that the oxidation states of the atoms in iron (III) oxide are +3 for iron and -2 for oxygen. The atoms in the reactants are all pure elemental substances, so they have oxidation numbers of zero. Over the course of this reaction, iron is being oxidized (from 0 to +3), and oxygen is being reduced (from 0 to -2).

There are many other examples of redox reactions in which two neutral elements combine to make a compound. These often take the form of a metal being oxidized and a nonmetal being reduced, resulting in an ionic compound. Two nonmetallic elements can also undergo a redox reaction of this type, in which the less electronegative element is oxidized and the more electronegative element is reduced.

Decomposition Reactions

A decomposition process is the exact opposite of a combination process; one reactant compound breaks down into two or more products:

$$C \rightarrow A + B$$

For example, hydrogen peroxide will decompose over time to produce water and oxygen gas. The equation is written below, along with the oxidation numbers for each atom:

$$2\overset{+1}{H}_2\overset{-1}{O}_2 \rightarrow 2\overset{+1}{H}_2\overset{-2}{O} + \overset{0}{O}_2$$

In this reaction, some atoms of oxygen are being reduced to water (from -1 to -2), while others are being oxidized to molecular oxygen (from -1 to 0). For a redox decomposition reaction, the single reactant must act as both the oxidizing agent and the reducing agent. This is one type of reaction that is very difficult to recognize as a redox reaction by any of the previous definitions of oxidation and reduction; oxidation numbers must be assigned in order to see that changes in oxidation state are occurring.

Single Replacement Reactions

Single replacement reactions are quite common and often include a pure metal reacting with an aqueous solution of an acid or a salt. They have the following generic form:

A + BC → AC + B

When a reactive enough pure metal is placed in an acidic solution, the following reaction often takes place:

Metal + acid → metal salt + hydrogen gas

For example, if a piece of solid zinc is added to a solution of HCl, hydrogen bubbles will immediately start to form on the surface of the zinc:

FIGURE 22.5

Zinc metal reacting with a solution of hydrochloric acid. Notice the hydrogen bubbles surrounding the zinc metal.

At the same time, some of the zinc atoms are released into the solution as Zn^{2+} cations. The balanced chemical equation for this single displacement reaction is shown below.

$$\overset{0}{Zn} + 2\overset{+1}{H}\overset{-1}{Cl} \rightarrow \overset{+2}{Zn}\overset{-1}{Cl_2} + \overset{0}{H_2}$$

Notice how the oxidation states change for the elements involved in this process. One pure element (with an oxidation state of 0) is being oxidized (in this case, to an oxidation state of +2), and a cationic species (H^+, which has an oxidation state of +1) is being reduced to a neutral element (H_2, which has an oxidation state of 0). In this reaction, the chloride anion is acting as a spectator ion, so its form (and its oxidation state) does not change.

Another example of a single displacement reaction is when a solid metal is placed in a solution containing cations of a less reactive metal. The metal in the solid phase will dissolve into solution as a cation, and the metal cations in solution will precipitate out of solution as a solid metal. For example, if we were to place a piece of zinc in a solution of an iron salt, the following process would take place:

$$\overset{0}{Zn} + \overset{+2}{Fe}\,\overset{+6}{S}\,\overset{-2}{O_4} \rightarrow \overset{0}{Fe} + \overset{+2}{Zn}\,\overset{+6}{S}\,\overset{-2}{O_4}$$

Notice that the oxidation states only change for the two metal species. Zinc is oxidized from 0 to +2 and Fe is reduced from +2 to 0. The oxidation states of the elements in the spectator ion ($SO_4{}^{2-}$) do not change.

Combustion Reactions

In a combustion reaction, a hydrocarbon reacts with molecular oxygen to produce carbon dioxide and water. The molecular oxygen (oxidation state = 0) is reduced (oxidation state = -2 in both CO_2 and H_2O), while the carbon atoms in the hydrocarbon are oxidized (to +4 in carbon dioxide). A familiar combustion reaction involves the burning of fossil fuels to produce heat or electricity, or to power a motor vehicle or other machine. The process of cellular respiration, in which our bodies break down sugar molecules into water and carbon dioxide in order to harness the resulting release of energy, can also be thought of as a form of combustion, albeit a relatively slow and complex one. Cellular respiration in our bodies is governed by a series of enzymatic steps, whereas burning a marshmallow in a hot fire is a fast and uncontrolled reaction. However, the gradual digestion and the fast combustion of sucrose both result in the same net reaction:

$$C_{12}H_{22}O_{11} \text{ (sucrose)} + 12\ O_2 \rightarrow 12\ CO_2 + 11\ H_2O$$

FIGURE 22.6

Combustion reaction of a marshmallow (sucrose) and wood (cellulose).

Lesson Summary

- Oxidation numbers can be defined for each atom in a compound based on a set of rules.
- Oxidation and reduction are currently defined according to changes in oxidation number over the course of a reaction.
- All elements have an oxidation number of zero in their pure form.
- Many elements have only one common oxidation state in chemical compounds. These can serve as guidelines for determining the oxidation states of more variable elements, using the fact that all oxidation states in a chemical species must add up to the overall charge of the atom, molecule, compound, or ion.
- Examples of redox reactions are found in various categories of chemical reactions, including combination, decomposition, single replacement, and combustion.

Review Questions

1. Determine the oxidation number for the indicated element.
    a. calcium metal
    b. F in NaF
    c. S in Na_2SO_4
    d. Cl in $KClO_3$
    e. Ca in CaO
2. State the type of reaction illustrated by each of the following equations.
    a. $ZnS + 2\ O_2 \rightarrow ZnSO_4$
    b. $Fe + CuSO_4 \rightarrow FeSO_4 + Cu$
    c. $2KClO_3 \rightarrow 2KCl + 3O_2$
    d. $2Hg + O_2 \rightarrow 2HgO$
3. For each reaction in problem 2, indicate which atom was oxidized and which was reduced. Show the changes in oxidation number in each case.
4. Running a strong enough electric current through water will cause it to decompose into hydrogen and oxygen gas. Write the balanced chemical equation for this process. What is being oxidized, and what is being reduced?
5. Write the balanced chemical equation for the following reaction, including all oxidation numbers: Magnesium metal is placed in a solution of hydrochloric acid.
6. Write the balanced chemical equation for the following combination reaction: Hydrogen and oxygen gas react explosively to produce water. Which substance is being oxidized, and which is being reduced?
7. Write the chemical equation for the following combustion reaction, including all oxidation numbers: Methanol (CH_3OH) combusts in the presence of oxygen to produce carbon dioxide and water.
8. Assign oxidation numbers to each of the atoms in the following compounds/ions:

Further Reading/Supplementary Links

- Determining oxidation numbers: http://www.occc.edu/kmbailey/chem1115tutorials/oxidation_numbers.htm
- Common types of oxidation-reduction reactions: http://www.wisc-online.com/objects/ViewObject.aspx?ID=GCH7904
- Combustion of magnesium metal: http://www.youtube.com/watch?v=m2i9jLPXprQ

Points to Consider

- Why do you suppose oxidation numbers are used to describe the mechanics of redox processes? Why can't the charge of a given chemical species suffice?

22.3 Balancing Redox Equations

Lesson Objectives

- Be able to write half-reactions for oxidation-reduction processes.
- Be able to distinguish the oxidation half-reaction from the reduction half-reaction.
- Be able to balance redox reactions.

Lesson Vocabulary

- **half-reaction**: Describes half of the redox reaction process.

Check Your Understanding

Study the following diagram, which depicts the mass change that occurs when steel wool burns in air.

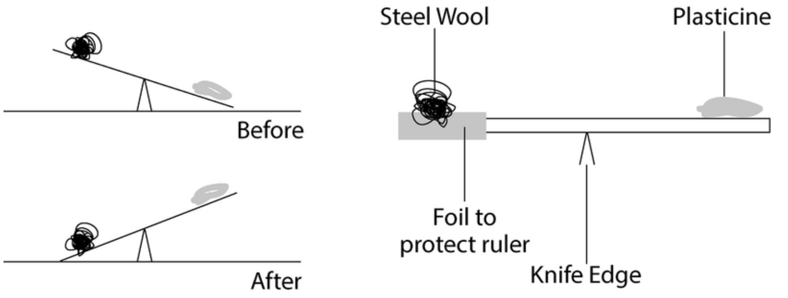

FIGURE 22.7

Mass changes for steel wool burning in air.

What happens to the mass of the steel wool as the reaction proceeds? Given that mass must be conserved in chemical reactions (it cannot come from nowhere), what is your explanation for the change in the mass of the steel wool?

Introduction

You have already learned the basic methods for balancing chemical equations to describe chemical reactions. Sometimes complicated reactions can be identified as redox reactions, in which case a special method of balancing chemical equations can be used to simplify the process and prevent unnecessary guessing and checking. In this lesson you will learn how to use this method.

Oxidation-Reduction Half-Reactions

In some cases, it can be helpful to analyze the oxidation and reduction processes separately for a complete redox reaction. A **half-reaction** contains only half of the entire redox process. One half-reaction illustrates the oxidation component and is the oxidation half-reaction; the other illustrates the reduction component and is the reduction half-reaction. For example, consider the following combination reaction:

$$\mathrm{ZnS(aq)+2O_2(g) \rightarrow ZnSO_4(aq)}$$

First, we need to assign oxidation states to each atom. Some of these compounds have multiple atoms for which the oxidation states are not easily predicted. However, if we convert this to an ionic equation, our task becomes simpler:

$$\mathrm{Zn^{2+}(aq)+S^{2-}(aq)+2O_2(g) \rightarrow Zn^{2+}(aq)+SO_4^{2-}(aq)}$$

On the reactant side, each component is a pure element, so the oxidation states are simply equal to the charge of the ion or molecule. Zinc has an oxidation state of +2, sulfur is -2, and oxygen is 0. Now look at the product side. Zinc is still a monatomic ion with a charge of +2, so nothing has changed. Zinc is a spectator ion. In the sulfate ion, we can assume that oxygen has its usual oxidation state of -2. The oxidation state of sulfur can then be calculated as follows:

S + 4(O) = -2
S + 4(-2) = -2
S - 8 = -2
S = +6

Based on the changes in oxidation number, we can identify the oxidation and reduction processes separately. The oxidized element, sulfur, is losing electrons, and the reduced element, oxygen, is gaining them. The superscript of zero on the reactant oxygen atom simply indicates that it begins with an oxidation state of 0.

$$\mathrm{S^{2-} \rightarrow S^{6+}+8e^-} \text{ Oxidation Half-Reaction}$$
$$\mathrm{O^0+2e^- \rightarrow O^{2-}} \text{ Reduction Half-Reaction}$$

Note that these are purely theoretical processes. Sulfur does not physically become an ion with a charge of +6, because electrons are not fully transferred from the sulfur anion to the oxygen atoms. Additionally, the oxygen atoms don't exist as neutral, isolated species; they are always covalently bonded to at least one other atom. However, being able to break a reaction down into theoretical half-reactions is a useful tool, as we will see in the next section and in the following chapter on *Electrochemistry*.

Using Half-Reactions to Balance Equations

One use for half-reactions is to help balance very complex chemical equations. We will illustrate the overall process with a simple reaction first. Let's say that we were given the *unbalanced* version of the combination reaction from the previous section.

$$\mathrm{ZnS(aq)+O_2(g) \rightarrow ZnSO_4(aq)}$$

Pretend for a moment that this was not a very easy equation to balance by trial and error. We determined that this could be broken down into the following half-reactions:

$$S^{2-} \rightarrow S^{6+} + 8e^-$$
$$O^0 + 2e^- \rightarrow O^{2-}$$

In the complete reaction, both of these processes occur simultaneously. However, free electrons are not actually a reactant or product of this reaction. In order for the electrons to cancel out, we would need the number of electrons lost by oxidation to be equal to the number gained during reduction. This can be accomplished by multiplying the entire second reaction by 4:

$$S^{2-} \rightarrow S^{6+} + 8e^-$$
$$4O^0 + 8e^- \rightarrow 4O^{2-}$$

For the electron flow in this reaction to be balanced, four oxygen atoms are reduced for each sulfur atom that is oxidized. Therefore, for each unit of ZnS (which contains one sulfur atom), we would need two molecules of O_2 (four oxygen atoms total). The ratio of reactants must be the following:

$$\mathrm{ZnS(aq)} + 2\mathrm{O_2(g)} \rightarrow$$

We can then find the coefficient of the product (in this case, 1) by inspection:

$$\mathrm{ZnS(aq)} + 2\mathrm{O_2(g)} \rightarrow \mathrm{ZnSO_4(aq)}$$

Now that we have seen the basic procedure, let's try a more difficult problem.

Example 22.3

Balance the following equation using the half-reaction method:

$$\mathrm{KMnO_4(aq)} + \mathrm{KNO_2(aq)} + \mathrm{H_2SO_4(aq)} \rightarrow \mathrm{MnSO_4(aq)} + \mathrm{H_2O(l)} + \mathrm{KNO_3(aq)} + \mathrm{K_2SO_4(aq)}$$

Answer:

First, determine which atoms are being oxidized and which are being reduced. In order to assign oxidation numbers, we should convert this molecular equation into an ionic one (no coefficients are used, since we are not starting with a balanced equation anyway):

$$\mathrm{K^+(aq)} + \mathrm{MnO_4^-(aq)} + \mathrm{NO_2^-(aq)} + \mathrm{H^+(aq)} + \mathrm{SO_4^{2-}(aq)} \rightarrow \mathrm{Mn^{2+}} + \mathrm{SO_4^{2-}(aq)} + \mathrm{H_2O(l)} + \mathrm{K^+(aq)} + \mathrm{NO_3^-(aq)}$$

There are 6 elements in this reaction. All of the monatomic ions have oxidation numbers equal to their charges. Additionally, we can assign an oxidation state of -2 to each oxygen atom and +1 to each hydrogen atom. Now, we just need to assign the oxidation states of manganese in MnO_4^-, nitrogen in the nitrite and nitrate ions, and sulfur in the sulfate ion. These can be determined by choosing a value for which all of the oxidation states in the ion add up to its overall charge. For example, in the nitrite ion:

N + 2(O) = -1
N + 2(-2) = -1
N - 4 = -1
N = +3

Nitrogen has an oxidation number of +3 in the nitrite ion. Similar reasoning shows us that manganese is +7 in MnO_4^-, nitrogen is +5 in NO_3^-, and sulfur is +6 in SO_4^{2-}. The only two elements that change oxidation numbers over the course of the reaction are Mn (from +7 in MnO_4^- to +2 in Mn^{2+}) and N (from +3 in NO_2^- to +5 in NO_3^-). Thus, we can write the two half-reactions as follows:

$$N^{3+} \rightarrow N^{5+} + 2e^-$$
$$Mn^{7+} + 5e^- \rightarrow Mn^{2+}$$

In order to equalize the number of electrons for these two half-reactions, we need to multiply the oxidation portion by 5 and the reduction portion by 2:

$$5N^{3+} \rightarrow 5N^{5+} + 10e^-$$
$$2Mn^{7+} + 10e^- \rightarrow 2Mn^{2+}$$

For every five nitrogen atoms that are oxidized, two manganese atoms are reduced. Now let's look back at the original equation:

$$KMnO_4(aq) + KNO_2(aq) + H_2SO_4(aq) \rightarrow MnSO_4(aq) + H_2O(l) + KNO_3(aq) + K_2SO_4(aq)$$

Nitrogen and manganese are each in only one compound on each side of the equation. Start by putting the coefficients from the balanced half-reactions on their corresponding compounds:

$$2KMnO_4(aq) + 5KNO_2(aq) + H_2SO_4(aq) \rightarrow 2MnSO_4(aq) + H_2O(l) + 5KNO_3(aq) + K_2SO_4(aq)$$

The coefficients for $KMnO_4$, KNO_2, $MnSO_4$, and KNO_3, are now set, but we can alter the coefficients on H_2SO_4, H_2O, and K_2SO_4 to finish balancing the equation. In order for potassium to be balanced, the coefficient on K_2SO_4 must be 1.

$$2KMnO_4(aq) + 5KNO_2(aq) + H_2SO_4(aq) \rightarrow 2MnSO_4(aq) + H_2O(l) + 5KNO_3(aq) + 1K_2SO_4(aq)$$

Then, H_2SO_4 is the last unbalanced compound that contains sulfur. In order for sulfur to be balanced (3 atoms on each side), H_2SO_4 must have a coefficient of 3.

$$2KMnO_4(aq) + 5KNO_2(aq) + 3H_2SO_4(aq) \rightarrow 2MnSO_4(aq) + H_2O(l) + 5KNO_3(aq) + 1K_2SO_4(aq)$$

Finally, hydrogen and oxygen can be balanced by changing the coefficient on H_2O. There are 6 hydrogen atoms on the left side, so water would need a coefficient of 3.

$$2KMnO_4(aq) + 5KNO_2(aq) + 3H_2SO_4(aq) \rightarrow 2MnSO_4(aq) + 3H_2O(l) + 5KNO_3(aq) + K_2SO_4(aq)$$

Double-checking our oxygen atoms, we see that there are 30 on each side. This is a fully balanced equation. Of course, most of the equations that you will be required to balance are not this difficult. However, it does demonstrate that using the half-reaction method gives you a good starting point for balancing especially complicated redox reactions.

Lesson Summary

- Oxidation-reduction half-reactions single out the changes in oxidation state of certain elements within a chemical equation.
- Balancing the electrons lost and gained in two simultaneously occurring half-reactions can be used to help balance complicated redox equations.

Review Questions

1. Write half-reactions for the following redox processes:
    a. $Fe + V_2O_3 \rightarrow Fe_2O_3 + VO$
    b. $K_2Cr_2O_7 + SnCl_2 + HCl \rightarrow CrCl_3 + SnCl_4 + KCl + H_2O$
    c. $K_2Cr_2O_7 + H_2O + S \rightarrow SO_2 + KOH + Cr_2O_3$
2. Write the balanced chemical equations for the following reactions:
    a. Magnesium carbonate is heated strongly to produce magnesium oxide and carbon dioxide gas.
    b. Hydrogen peroxide decomposes to produce water and oxygen gas.
    c. Solid potassium chlorate is heated in the presence of manganese dioxide as a catalyst to produce potassium chloride and oxygen gas.
    d. Lead sulfide reacts with molecular oxygen to form sulfur dioxide and lead(II) oxide.
3. Write oxidation and reduction half-reactions for the following single-replacement reaction: $Fe(s) + CuSO_4(aq) \rightarrow FeSO_4(aq) + Cu(s)$.
4. Use the half-reaction method to balance the following redox equation: $As_4 + NaOCl + H_2O \rightarrow NaCl + H_3AsO_4$.

Further Reading / Supplemental Links

Explanation and practice for balancing redox equations: http://www.mpcfaculty.net/mark_bishop/redox_balance_oxidation.htm

Points to Consider

- Although oxidation and reduction processes must occur simultaneously, they do not necessarily have to occur in the same space. How can this be used to generate electricity, which is essentially the flow of electrons through a wire?

22.4 References

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CHAPTER 23 Electrochemistry

Chapter Outline

23.1 ELECTROCHEMICAL CELLS
23.2 CELL POTENTIAL
23.3 ELECTROLYSIS
23.4 REFERENCES

There is worldwide concern about the relationship between climate change and the use of fossil fuels. Many scientists believe that increased use of these fuels (in vehicles and other gas-powered equipment) has the potential to irreversibly damage our environment. In addition to the environmental concerns, supplies of fossil fuels are finite, and because they are non-renewable energy sources, we will eventually need alternatives. New developments in batteries and other energy storage devices are being explored to help deal with these issues. Electrochemical processes are at the heart of these new technologies.

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23.1 Electrochemical Cells

Lesson Objectives

- Use the activity series to predict whether a given oxidation-reduction reaction will occur spontaneously.
- Describe the components and function of a galvanic cell.
- Describe how power is produced by lead-acid batteries, dry cell batteries, and fuel cells.

Lesson Vocabulary

- **activity series**: A ranking of various metals on their ability to lose electrons.
- **galvanic cell**: A cell in which two solutions are connected by a wire in order to facilitate the flow of electrons and generate an electric current.
- **battery**: A cell which employs oxidation-reduction reactions to generate a flow of electrons and supply electricity.
- **lead-acid battery**: A battery with two poles, one of lead and one of lead oxide, submerged in sulfuric acid and separated by a barrier permeable to ions and water; typically used in cars.
- **dry cell battery**: Contains a paste (often a mixture of ammonium chloride and manganese dioxide) that acts as the positive electrode.
- **fuel cell**: A cell that is able to produce an electric current directly from a chemical reaction; fuel cells commonly operate on the platinum catalyzed reaction between hydrogen and oxygen gases to be used to power vehicles.

Check Your Understanding

Recalling Prior Knowledge

- Write half reactions for the following redox process:

$2\text{ Na} + \text{Cl}_2 \rightarrow 2\text{ NaCl}$

What is being oxidized, and what is being reduced?

Introduction

Electrochemistry is the study of chemical processes that occur at the interface between an electron conductor, such as a wire, and a solution of electrolytes, which is often simply an ionic substance dissolved in water. Electrochemical processes involve a transfer of electrons between the wire and the solution. These reactions can be used to create electrical power, to purify metals, and to carry out a number of useful chemical transformations.

The Activity Series

In the previous chapter, we looked at a number of oxidation-reduction reactions. We assumed that the reactions occurred as written, but how do we know that a certain redox reaction will take place without actually running the experiment? Which metals will react with water or acid? How do we know if one metal will undergo a single-replacement reaction with a solution of a different metal cation?

Detailed study has made possible the construction of an **activity series**, sometimes referred to as the electromotive series, in which various neutral metals are ranked by their ability to lose electrons (to undergo oxidation). The most reactive metals are listed at the top and will undergo a reaction simply by exposure to moisture. As we go down the list, we find that some other metals will react with water, but only at elevated temperatures. Others will not react with pure water but will undergo redox processes in the presence of acid. Finally, some of the least active metals are inert even when submerged in very acidic solutions.

TABLE 23.1: **Activity Series**

Metal	Symbol	Reactivity
Lithium Potassium Strontium Calcium Sodium	Li K Sr Ca Na	*Reacts with water, steam, and acids to produce H_2 and metal hydroxides*
Magnesium Aluminum Zinc Chromium	Mg Al Zn Cr	*Reacts with steam and acids to produce H_2 and metal hydroxides*
Iron Cadmium Cobalt Nickel Tin Lead Hydrogen gas	Fe Cd Co Ni Sn Pb H_2	*Will not react with water, but reacts with acids to produce H_2 and metal salts*
Antimony Arsenic Bismuth Copper	Sb As Bi Cu	*Will not react with water or acids to form H_2; forms oxides with O_2*
Mercury Silver Palladium Platinum Gold	Hg Ag Pd Pt Au	*Found as a pure element in nature; oxides decompose with heating*

This table summarizes a lot of useful information. For example, cations of a given metal can be reduced back to their elemental form by any more active metal (higher in the activity series), but not by less active metals. For example, we can predict that the following reaction will occur spontaneously:

$$2\ \mathrm{K} + \mathrm{Mg}^{2+} \rightarrow 2\ \mathrm{K}^{+} + \mathrm{Mg}$$

Potassium is more active than magnesium. Potassium has a stronger driving force causing it to give up its valence electrons than magnesium, so we are left with K^+ cations instead of Mg^{2+} cations at the end of the reaction. Similarly, we would predict that the following reaction would *not* occur spontaneously as written:

$$Sn + Fe^{2+} \rightarrow Sn^{2+} + Fe$$

Iron is more active than tin, so neutral iron could be used to reduce tin cations, but not the other way around. The activity series (sometimes referred to as the electromotive series) is a very useful tool as we explore how to generate electric currents.

Galvanic Cells

One of the many useful applications of electrochemistry is in the generation of electric current. We saw earlier how electrons can be transferred from one atom to another in an oxidation-reduction reaction. If we place a strip of metallic zinc in a solution of copper sulfate, we will soon see a single-displacement reaction, in which zinc is oxidized to its corresponding cations, and the copper cations will plate out on the strip as neutral copper. The electron transfer from the zinc to the copper is direct, because the metal surface is in direct contact with the ions in the solution.

Alternatively, we can channel the electron flow from zinc to copper through a wire by using a voltaic cell. Forcing the electrons to travel through a wire in order to get from one species to another allows us to harness that energy and use it to perform mechanical work, something that is not possible for the situation described above in which the oxidizing and reducing agents were in direct contact. The first such cell was developed by Alessandro Volta in 1800. Similar concepts were explored by Luigi Galvani in the late 1700s, so these cells are often referred to as **galvanic cells**. A typical cell is illustrated in **Figure** 23.1.

There are two major components to this cell. A solution of $Zn(NO_3)_2$ (on the left) has a zinc strip immersed in it. On the right, we see a copper strip in a solution of $Cu(NO_3)_2$. A porous barrier separates the two solutions. The solutions are not in direct contact with one another, but ions can flow freely through the barrier. The two metal strips are connected by a wire that allows electrons to move from one strip to the other.

Referring to our activity series, we see that Zn is more active than Cu. As a result, Zn will spontaneously give up its electrons to reduce copper cations, but Cu will not spontaneously reduce zinc cations. In the cell shown above, Zn can undergo a reaction that produces Zn^{2+} and two electrons. The two electrons flow through the wire (powering a meter or device if one is present) towards the copper electrode. Once the electrons reach the copper sulfate solution, they are used to reduce Cu^{2+} ions to metallic copper, which plates out on the copper electrode. When a metal "plates out," it is transferred from an aqueous ion in solution to a neutral metal atom in its solid form.

The porous disk allows for the transfer of anions from the copper side to the zinc side. During the reaction, more Zn^{2+} accumulates on the left side of the cell, and Cu^{2+} is being depleted from the right side of the cell. Without the porous disc, this would cause an unstable buildup of positive charge on the zinc side and negative charge on the copper side. To relieve this imbalance, anions essentially move through the porous disk from right to left, balancing the positive charge of the newly formed Zn^{2+} ions and moving away from the side with a decreasing concentration of positively charged Cu^{2+} ions.

Batteries

Records from ancient Greece mention that Thales of Miletus (a Greek philosopher, mathematician, and astronomer who lived from 620-546 BC) rubbed fur with amber and generated a strange phenomenon, which we now call static electricity. Although the ancient Greeks did not have a good understanding of what was happening, we now have well-developed theories about how to generate and use electric currents.

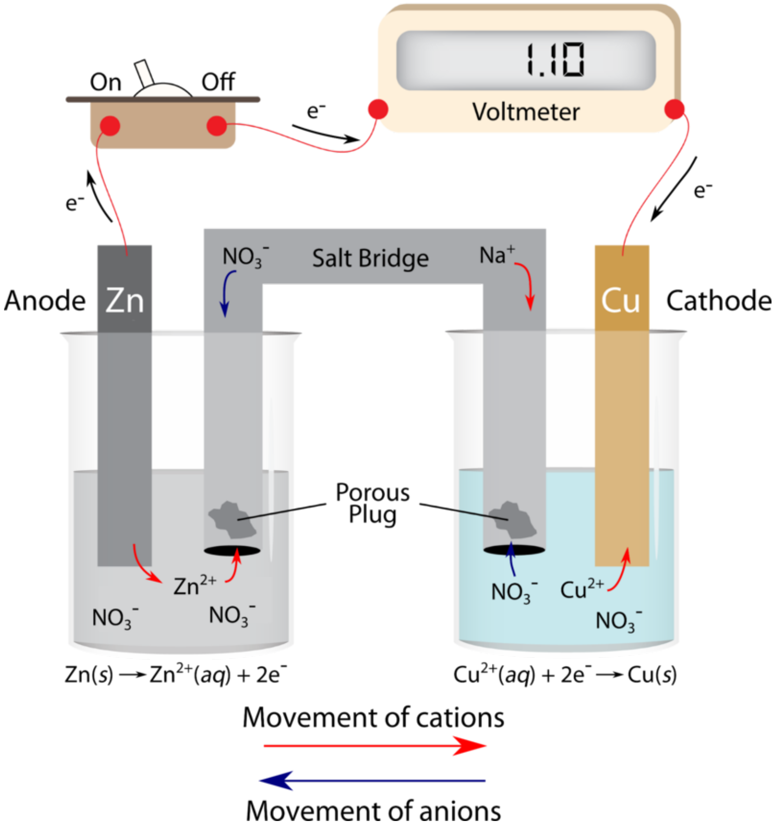

FIGURE 23.1

A galvanic (or voltaic) cell.

There are many situations where an electric current is needed to make a device work, but it is inconvenient (or impossible) to plug the device into a wall circuit. A cell phone or digital watch would not be very useful if we had to plug the device into a power outlet in order for it to function.

Batteries provide us with a portable source of electricity that can be used when a power outlet is not available. The first battery was developed by Alessandro Volta (1745-1827) in 1800. He constructed a "voltaic pile" consisting of alternate discs of silver and zinc that were separated by paper soaked in salt water. According to some sources, Volta tested the battery by measuring the strength of the electric current. His "measurement" involved seeing how intense the shock produced by the battery was on a person (never a good idea).

A modern **battery** employs oxidation-reduction reactions to generate a flow of electrons. The material being oxidized will release electrons that can flow through an electrical circuit and produce work of some sort. The electrons then flow into the material that is being reduced. This process will be illustrated through specific examples as we look at a few common types of batteries that are in use today.

Lead-Acid Batteries

One common type of battery is the type used to start a car. When the circuit is open (the poles are not connected), no electrons are flowing. However, when the circuit is closed by turning the ignition key to "on," the poles are connected and electrons can flow from one pole to the other. This flow of electrons will create a spark in the engine cylinders that ignites the gasoline. The ignition causes the piston to move up and down, powering the car.

A typical car battery involves two poles, one made of lead, and the other made of lead oxide. Each pole is submerged in sulfuric acid, and the two compartments (one containing each pole) are separated by a barrier that is permeable to ions and water. Based on its components, this type of battery is referred to as a **lead-acid battery**. The overall reaction that takes place is the following:

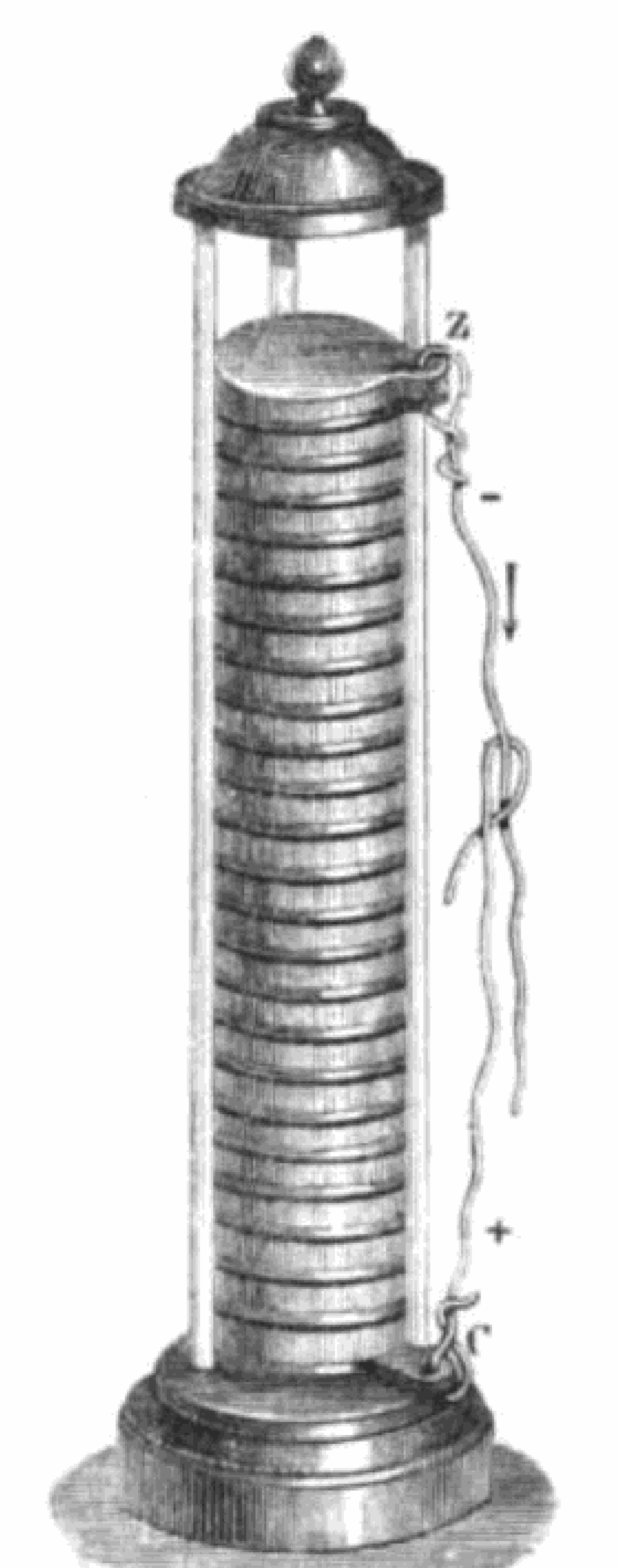

FIGURE 23.2

A drawing of Alessandro Volta's voltaic pile, the first electric battery. It was built of many individual cells, each consisting of a disk of copper or silver and a disk of zinc separated by a cloth soaked in acid or brine. A 23-cell pile like this would have produced around 36 volts.

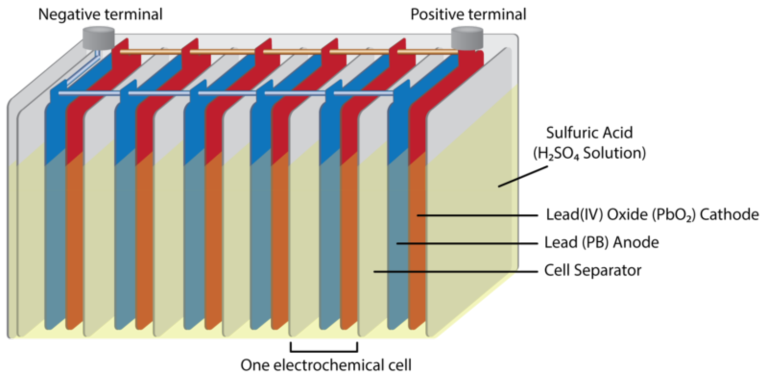

FIGURE 23.3

Car battery

$$\mathrm{Pb} + \mathrm{PbO_2} + 2\mathrm{H_2SO_4} \rightarrow 2\mathrm{PbSO_4} + 2\mathrm{H_2O}$$

If we were to assign oxidation numbers to each atom, we would see that the only element changing state is lead. The pure lead (oxidation state = 0) is oxidized to Pb^{2+}, and the lead (IV) oxide (oxidation state = +4) is reduced to Pb^{2+}. We can therefore write the following two half-reactions:

$$\mathrm{Pb}^0 \rightarrow \mathrm{Pb}^{2+} + 2\mathrm{e}^-$$
$$\mathrm{Pb}^{4+} + 2\mathrm{e}^- \rightarrow \mathrm{Pb}^{2+}$$

By separating the Pb^0 from the Pb^{4+}, we can force the electrons to flow through a wire in order to complete the redox reaction. Eventually, both metal poles are converted to $\mathrm{PbSO_4}$, and the battery can no longer produce a flow of electrons. However, the battery can be recharged by forcing the reaction to run in the opposite direction by using an external source of energy (such as the energy given off by the combustion of gasoline).

The description given above describes the process that occurs in one cell of a lead-acid battery. Because cars require a battery with a higher voltage than can be obtained with a single cell, car batteries generally consist of several cells connected together to produce the desired voltage output. A typical car battery will generate twelve volts of electricity.

Dry Cell Batteries

The car battery is an example of a "wet cell" battery, because there is a liquid electrolyte (sulfuric acid) present in the system. These batteries must operate in an upright position so the liquid material does not spill out. In contrast, **dry cell batteries** contain a paste that serves as the positive electrode. The composition and voltage depends on the specific battery, but typical voltage outputs are in the 1.0-1.5 volt range.

One common material used for the positive electrode is a mixture of ammonium chloride and manganese dioxide. The half-reaction at this pole is the following:

$$2\ \mathrm{NH_4}^+ + 2\ \mathrm{MnO_2} + 2\mathrm{e}^- \rightarrow \mathrm{Mn_2O_3} + 2\ \mathrm{NH_3} + \mathrm{H_2O}$$

Simplifying this to just the atom being oxidized, we get the following:

$$\mathrm{Mn}^{4+} + \mathrm{e}^{\texttt{[U+2500]}} \rightarrow \mathrm{Mn}^{3+}$$

The electrons for this half-reaction are provided by oxidation of metallic zinc:

$$\mathrm{Zn} \rightarrow \mathrm{Zn}^{+2} + 2\mathrm{e}^-$$

Also included in this setup are $ZnCl_2$ (part of the paste) and an inert carbon rod that acts as a conductor. Over time, the zinc container will be partially consumed and weakened by the oxidation half-reaction. These batteries cannot be recharged. Running the reaction in reverse would regenerate solid zinc, but not in a form that would have the same structural properties as the original container.

"Alkaline" batteries use either NaOH or KOH in place of the ammonium chloride. The half-reactions in an alkaline battery are shown below:

$$Zn + 2\ OH^- \rightarrow ZnO + H_2O + 2e^-$$
$$2\ MnO_2 + 2e^- + H_2O \rightarrow Mn_2O_3 + 2\ OH^-$$

This type of battery lasts longer than the ammonium chloride version, because zinc corrodes more slowly in a basic medium than it does in an acidic medium.

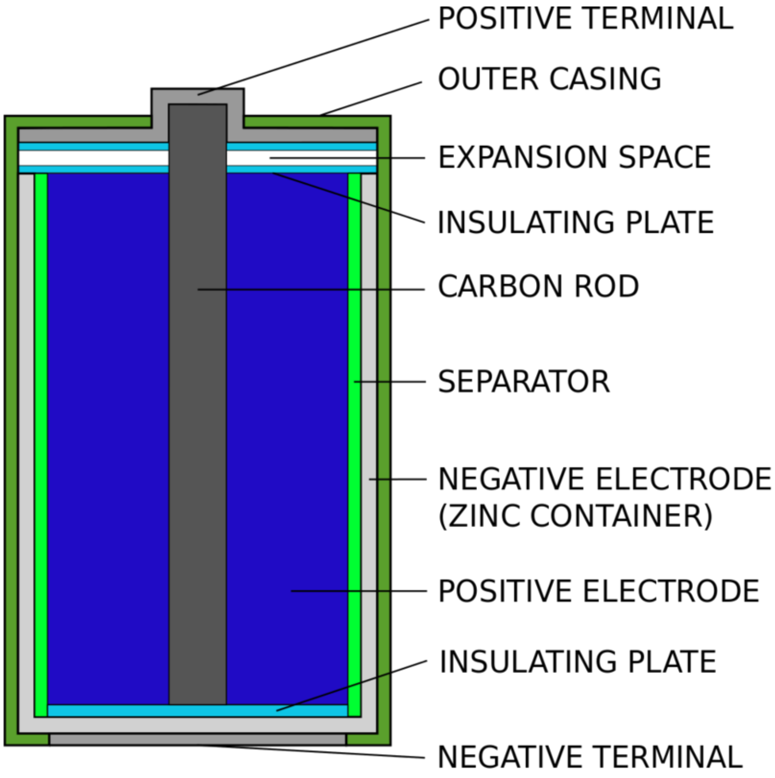

FIGURE 23.4

Alkaline battery.

Figure 23.4 illustrates a typical setup for a dry cell battery. The zinc container provides the source of electrons, and the manganese-containing paste provides a place for those electrons to be used. Because there are insulating layers in between these two components, very little electron flow occurs when the battery is not hooked up to anything. However, a low resistance pathway is provided if the two terminals are connected with a wire. Starting at the zinc container, electrons can flow freely through the negative terminal, the wire, the positive terminal, and the conductive carbon rod, finally reaching the electron-accepting paste, in which manganese is reduced. If the wire runs through a light or mechanical device, the movement of the electrons through the wire will provide the power necessary to operate the device.

Rechargeable dry cell batteries are used in a wide variety of applications, from small devices like digital cameras and cell phones to cars, including both hybrids that run on a combination of gas and electricity and all-electric vehicles that must be recharged after each short trip. These batteries are generally of the nickel-metal hydride (NiMH) type.

In a nickel-metal hydride battery, the negative electrode is composed of nickel (II) hydroxide and some other alkaline electrolyte, such as KOH. The nickel serves as the source of electrons via the following half-reaction:

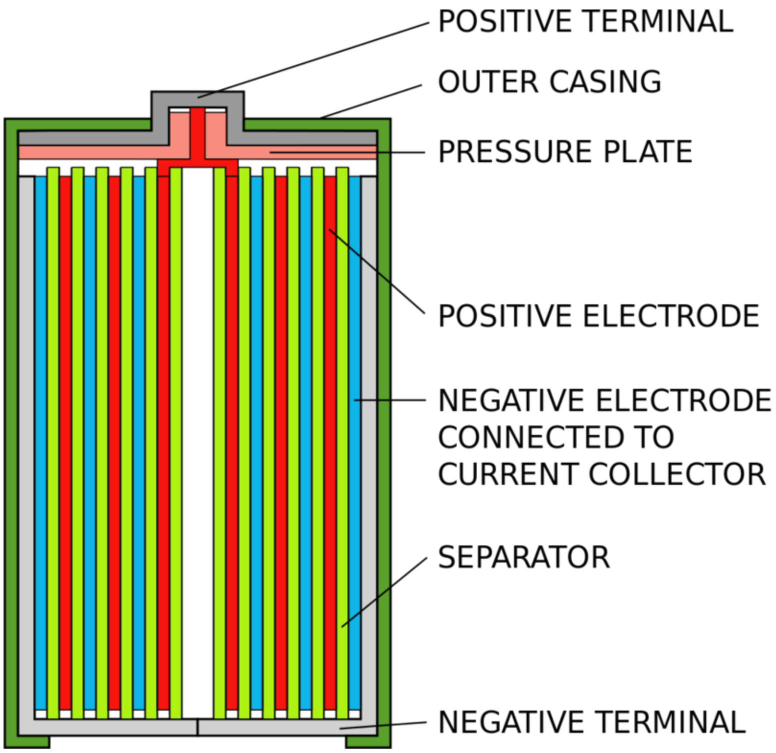

FIGURE 23.5

Rechargeable battery.

$Ni(OH)_2 + OH^- \rightarrow NiO(OH) + H_2O + e^-$

Looking only at the element that changes oxidation state (the nickel), we could also write the following:

$Ni^{2+} \rightarrow Ni^{3+} + e^-$

The positive electrode is a complex mixture of neutral metals, some of which are generally rare earth metals (e.g., lanthanum, cerium, and neodymium) and others that are more plentiful (e.g., nickel, cobalt, manganese, and aluminum). The half-reaction at this electrode has the following general form:

$H_2O + M + e^- \rightarrow OH^- + MH$

where M is a neutral metal (oxidation number = 0), and MH is a metal hydride. Note that in metal hydrides, hydrogen has an oxidation number of -1, so the metal exists as a cation. Both half-reactions are readily reversible, allowing the battery to be recharged.

Fuel Cells

There are a wide variety of different **fuel cells** available. Many are large devices that would be most suitable for stationary generators. The type we will consider in this section is portable and can be used to power a car or similar vehicle. This cell is referred to as a polymer exchange membrane fuel cell (PEMFC).

The basic operation of this type of fuel cell involves an initial reaction of hydrogen gas with the platinum catalyst (purple area), which facilitates the following half-reaction:

$H_2 \rightarrow 2\ H^+ + 2\ e^-$

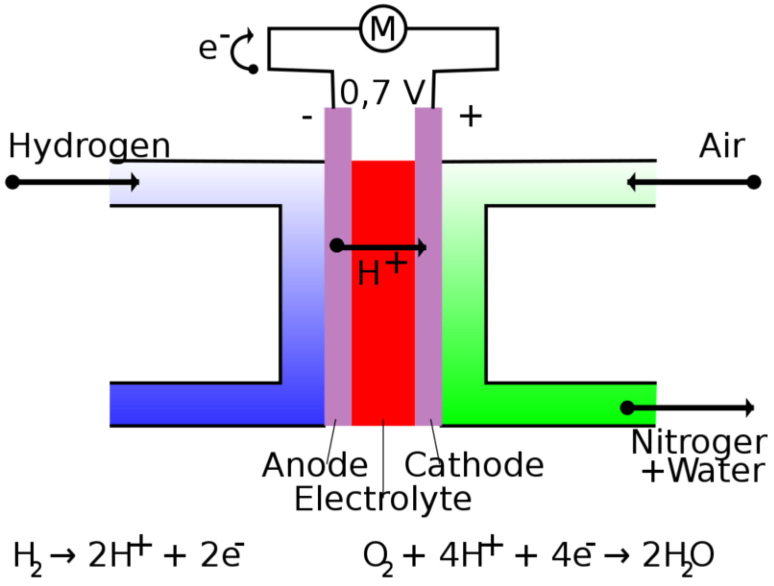

FIGURE 23.6

Typical hydrogen fuel cell.

The electrons are passed through the circuit, providing energy to the system, while the hydrogen ions move across the proton exchange membrane (the red area), which is permeable only to cations. At the other electrode, oxygen from the air reacts with electrons that have gone through the external circuit and the protons that pass through the red membrane area according to the following equation:

$$O_2 + 4\,H^+ + 4\,e^- \rightarrow 2\,H_2O$$

One major advantage of a hydrogen fuel cell is that the only waste product is water (and leftover nitrogen from the air, which is not involved in any chemical reactions). However, a major drawback is the need for pure hydrogen, which is flammable and difficult to store. A variety of techniques are being explored in an attempt to solve this storage problem.

Lesson Summary

- The activity series (or electromotive series) ranks metals in terms of their ability to be oxidized.
- Batteries are based on galvanic (voltaic) cells, which use oxidation-reduction reactions to generate a flow of electrons that can be employed for useful work.
- The lead-acid battery in a car is a "wet cell" battery in which there is a net transfer of electrons from Pb to PbO_2.
- "Dry cell" batteries use a paste instead of a liquid solution. A common type of dry cell battery uses zinc as a reducing agent and a manganese compound as an oxidizing agent.
- One type of rechargeable battery uses water as the electron acceptor, resulting in the formation of metal hydrides. These can easily be converted back to the original metal by running the reaction in the reverse direction using an external energy source.
- A common type of fuel cell uses the platinum catalyzed reaction between hydrogen and oxygen gases to generate power.

Lesson Review Questions

1. What does the metal reactivity series indicate about the ability of cations of a given metal to be reduced back to their elemental form?
2. Sketch a basic galvanic cell, indicating the location of the anode, cathode, salt bridge, and the direction of electron flow.
3. What causes the electrons to flow through a wire in a lead-acid battery?
4. Write half-reactions for a dry cell battery composed of nickel(II) oxide and cadmium.
5. In a dry cell battery that uses oxidation-reduction reactions involving silver and zinc, which metal will be spontaneously oxidized by cations of the other metal?
6. Explain how a car battery works.
7. Write the oxidation and reduction half-reactions for the lithium battery shown in the **Figure** 23.7, and explain how it generates electron flow.

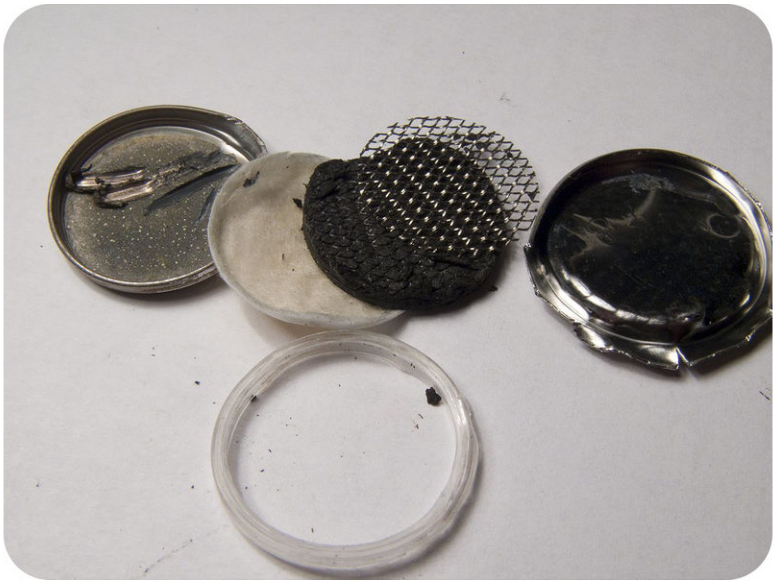

FIGURE 23.7

Disassembled CR2032 lithium battery. From the left (the negative terminal) - Cup from the inner side with a layer of lithium (which oxidizes when exposed to air), separator (porous material), layer of manganese dioxide, metal grid (current collector), metal casing (damaged while opening the cell). On the bottom is plastic sealing ring.

8. What characteristic of rechargeable batteries (such as nickel-metal hydride batteries) allows the batteries to recharge?
9. Write the half-reactions that would occur when each neutral element below is placed in an aqueous solution of the following compound. If no reaction would occur, indicate why.
   (a) $Ca + H_2O$
   (b) $Bi + HCl$
   (c) $Mg + NiO$
   (d) $Pb + Al(NO_3)_3$
   (e) $Cr + CuSO_4$
10. What is an advantage of using hydrogen fuel cells to generate power?

Further Reading/Supplementary Links

- Activity series: http://antoine.frostburg.edu/chem/senese/101/redox/faq/activity-series.shtml
- Car battery tutorial: http://www.batterystuff.com/kb/articles/battery-articles/battery-basics.html
- Fuel cell basics: http://americanhistory.si.edu/fuelcells/basics.htm

Points to Consider

- We have talked about the components necessary to create an electrical current, but we have not talked about the flow of electrons in a quantitative manner. In the next lesson, we will learn how to determine the amount of electricity generated by an electrochemical cell.

23.2 Cell Potential

Lesson Objectives

- Diagram and explain the operation of a standard hydrogen cell.
- Explain how to determine standard reduction potentials.
- Use standard reduction potentials to calculate the total potential of a given electrochemical cell.
- Use the Nernst equation to calculate reduction potentials under non-standard conditions.

Lesson Vocabulary

- **electrical potential**: A measurement of the ability of a voltaic cell to produce an electric current; typically measured in volts (V).
- **standard reduction potential**: A measurement of the tendency of a given half-reaction to occur as a reduction in an electrochemical cell.
- **cell potential**: The difference in standard reduction potentials between the two half-cells in an electrochemical cell.
- **standard cell potential**: The potential of an electrochemical cell when the temperature is 25°C, all aqueous components are present at a concentration of 1 M, and all gases are at the standard pressure of 1 atm.
- **standard hydrogen electrode (SHE)** : A reference half-cell that can be used with another electrode (half-cell) to determine its standard reduction potential.
- **anode**: The cell in which the oxidation takes place.
- **cathode**: The cell in which the reduction takes place.

Check Your Understanding

- How do you use the activity series to determine whether a given redox reaction will occur spontaneously?

Introduction

When designing electrochemical cells such as batteries, scientists and engineers must be able to calculate electrical potentials in order to create powerful and sensible energy sources. By comparing and combining reduction reactions, different cell potentials can be obtained and utilized to conduct an effective electric current. In this lesson you will learn how to predict whether or not a redox reaction will occur spontaneously based on the electrical potentials of various cells.

Reduction Potential

The activity series that was presented in the previous lesson allows us to predict the relative reactivities of different materials when used in oxidation-reduction processes. We also saw that appropriate combinations of half-reactions can be used to generate an electric current. However, we have not yet looked at the energy changes associated with any of these redox reactions. **Electrical potential** is a measurement of the ability of a voltaic cell to produce an electric current. It is typically measured in volts (V). Like energy, electrical potential is a relative term; it can only be measured by comparison with something else. The voltage that is produced by a given voltaic cell is the difference in electrical potential between the two half-cells, but it is not possible to measure the electrical potential of an isolated half-cell. For example, if only a zinc half-cell were constructed, no complete redox reaction can occur, so no electrical potential can be measured. It is only when another half-cell is combined with the zinc half-cell that an electrical potential difference, or voltage, can be measured.

The electrical potential of a cell results from a competition for electrons between two different chemical species. The "winner" of this battle is reduced (gains electrons), while the "loser" is oxidized (loses electrons). A **standard reduction potential** measures the tendency of a given half-reaction to occur as a reduction in an electrochemical cell. In a given voltaic cell, the half-cell that has the greater reduction potential is the one in which reduction will occur. In the half-cell with the lower reduction potential, the reverse process (oxidation) will occur. The **cell potential** (E_{cell}) is the difference in standard reduction potential between the two half-cells in an electrochemical cell.

Standard Cell Potentials

The **standard cell potential** ($E°_{cell}$) is the potential of an electrochemical cell when the temperature is 25°C, all aqueous components are present at a concentration of 1 M, and all gases are at the standard pressure of 1 atm. The standard cell potential can be calculated by finding the difference between the standard reduction potentials of the two half-cells.

$$E^\circ_{\text{cell}} = E^\circ_{\text{red}} - E^\circ_{\text{oxid}}$$

Since the reduction potentials for half-cells cannot be measured independently, it is necessary to establish a standard to serve as a reference. This reference is given a standard reduction potential of 0 volts by definition. Every other half-cell can then be compared to this standard electrode in order to determine the reduction potential for any half-cell. The **standard hydrogen electrode** (SHE) is a reference half-cell that can be used with another electrode (half-cell) to determine its standard reduction potential. A standard hydrogen electrode is shown in **Figure** 23.8.

The electrode itself is made of platinum, which serves as an inert surface upon which the oxidation or reduction reaction takes place. The electrode is then placed in contact with both hydrogen gas (at a pressure of 1 atm) and an acidic solution in which the concentration of H^+ is 1.0 M. Written as a reduction, the following half-reaction takes place in a SHE:

$$2H^+(aq) + 2e^- \rightarrow H_2(g) \qquad E^\circ = 0.00 \text{ V}$$

Depending on the relative electrical potential of other half-cell that the SHE is combined with, the hydrogen ions may be reduced or the hydrogen gas may be oxidized. In general, reversing a reaction will also reverse the sign of the corresponding electrical potential. However, reversing the above reaction has no effect on the standard potential, because the opposite of zero is still zero.

$$H_2(g) \rightarrow 2H^+(aq) + 2e^- \qquad E^\circ = 0.00 \text{ V}$$

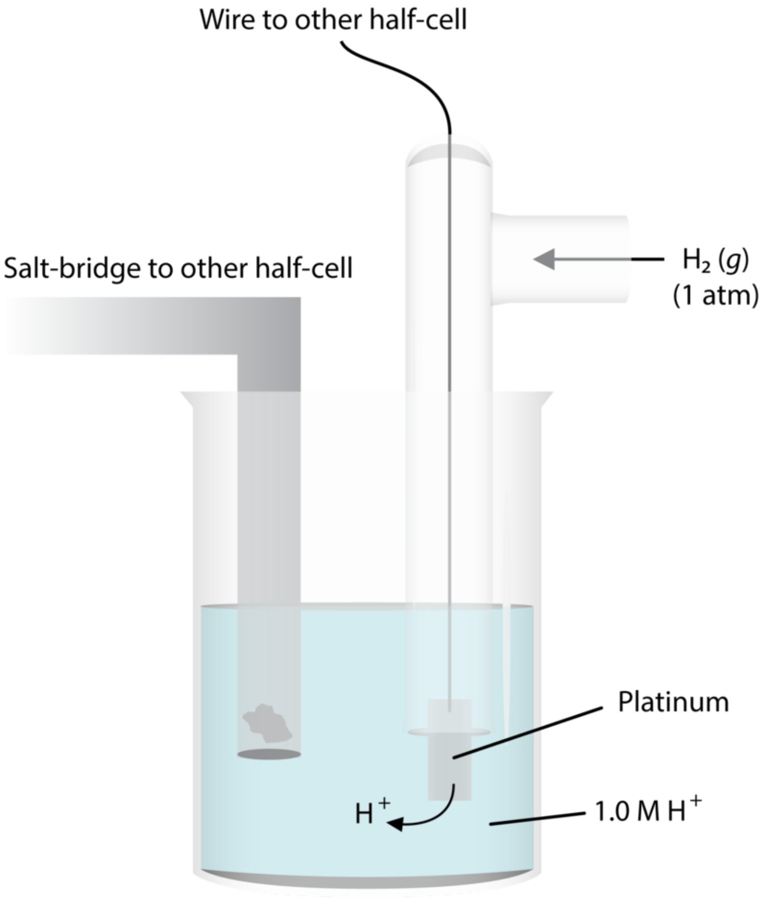

FIGURE 23.8
The standard hydrogen electrode is an arbitrary reference cell that is assigned a standard reduction potential of 0.00 V.

Determining Standard Reduction Potentials

When a standard hydrogen half-cell is connected to a standard copper half-cell and connected to a voltmeter (**Figure** 23.9 (A)), the reading is 0.34 V.

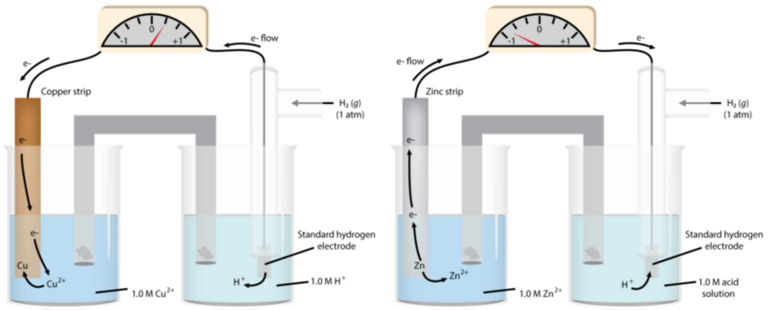

FIGURE 23.9
(A) The standard hydrogen half-cell is paired with a Cu/Cu^{2+} half-cell. H_2 is oxidized, while Cu^{2+} is reduced. (B) The standard hydrogen half-cell is paired with a Zn/Zn^{2+} half-cell. Zn is oxidized, while H^+ is reduced.

Observation of the cell shows that the copper(II) ion is reduced to copper metal, while the hydrogen gas is oxidized to hydrogen ions. This is shown below along with the overall reaction taking place in the cell.

$$\begin{array}{ll}
\text{Oxidation:} & H_2(g) \rightarrow 2H^+(aq) + 2e^- \\
\text{Reduction:} & Cu^{2+} + 2e^- \rightarrow Cu(s) \\
\hline
\text{Overall:} & H_2(g) + Cu^{2+}(aq) \rightarrow 2H^+(aq) + Cu(s)
\end{array}$$

In this particular galvanic cell, the SHE is the **anode** (where oxidation takes place), and the copper half-cell is the **cathode** (where reduction takes place). Electrons flow from the SHE to the copper electrode. The standard cell potential (E°_{cell}) is the measured value of 0.34 V, while the potential of the SHE is defined to be zero. This allows us to determine the reduction potential of the copper half-cell.

$$\begin{aligned}
&E^\circ_{cell} = E^\circ_{red} - E^\circ_{oxid} \\
&0.34\text{ V} = E^\circ_{Cu} - 0.00\text{ V} \\
&E^\circ_{Cu} = 0.34\text{ V} - 0.00\text{ V} = +0.34\text{ V}
\end{aligned}$$

The standard reduction potential for the $Cu^{2+}|Cu$ half-cell is thus equal to +0.34 V. In a similar way, the reduction potential for any half-cell can be determined by connecting it to a SHE and measuring the voltage. Notice the line notation used for the copper half-cell, $Cu^{2+}|Cu$, which indicates the phase boundary between the aqueous copper cations and the neutral copper metal atoms. This line notation is used as a standard to distinguish between the components of the electric cell.

When a standard hydrogen half-cell is connected to a standard zinc half-cell (**Figure** 23.9 (B)), the measured voltage is 0.76 V. However, it is observed that the zinc electrode is oxidized to zinc ions while the hydrogen ion is reduced to hydrogen gas.

$$\begin{array}{ll}
\text{Oxidation:} & Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \\
\text{Reduction:} & 2H^+(aq) + 2e^- \rightarrow H_2(g) \\
\hline
\text{Overall:} & Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)
\end{array}$$

The SHE is now the cathode, while the zinc electrode is the anode. Now it is the E° for the oxidation half-cell that is the unknown in the standard cell potential equation.

$$\begin{aligned}
&E^\circ_{cell} = E^\circ_{red} - E^\circ_{oxid} \\
&0.76\text{ V} = 0.00\text{ V} - E^\circ_{Zn} \\
&E^\circ_{Zn} = 0.00\text{ V} - 0.76\text{ V} = -0.76\text{ V}
\end{aligned}$$

The standard reduction potential for the Zn^{2+}/Zn half-cell is equal to -0.76 V. A negative standard reduction potential for a particular species means that is easier to reduce H^+ than to reduce that species. A positive standard reduction potential for a species means that it reduces more easily than H^+. The **Table** 23.2 lists many reduction potentials under standard conditions. From top to bottom, they are listed in decreasing order of their tendency to occur in the forward direction, as a reduction. Fluorine gas is the most easily reduced, while lithium ions are the most difficult to reduce. Note that this table is the exact opposite of the activity series. Lithium ions are very difficult to reduce, which means that lithium metal is very easy to oxidize.

TABLE 23.2: **Standard Reduction Potentials at 25°C**

Half Reaction	E° (V)
$F_2 + 2e^- \rightarrow 2F^-$	+2.87
$PbO_2 + 4H^+ + SO_4{}^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	+1.70
$MnO_4{}^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	+1.51
$Au^{3+} + 3e^- \rightarrow Au$	+1.50
$Cl_2 + 2e^- \rightarrow 2Cl^-$	+1.36
$Cr_2O_7{}^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	+1.33
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	+1.23
$Br_2 + 2e^- \rightarrow 2Br^-$	+1.07
$NO_3{}^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	+0.96
$2Hg^{2+} + 2e^- \rightarrow Hg_2{}^{2+}$	+0.92
$Hg^{2+} + 2e^- \rightarrow Hg$	+0.85
$Ag^+ + e^- \rightarrow Ag$	+0.80
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.77
$I_2 + 2e^- \rightarrow 2I^-$	+0.53
$Cu^+ + e^- \rightarrow Cu$	+0.52
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	+0.40
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	+0.13
$2H^+ + 2e^- \rightarrow H_2$	0.00
$Pb^{2+} + 2e^- \rightarrow Pb$	−0.13
$Sn^{2+} + 2e^- \rightarrow Sn$	−0.14
$Ni^{2+} + 2e^- \rightarrow Ni$	−0.25
$Co^{2+} + 2e^- \rightarrow Co$	−0.28
$PbSO_4 + 2e^- \rightarrow Pb + SO_4{}^{2-}$	−0.31
$Cd^{2+} + 2e^- \rightarrow Cd$	−0.40
$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44
$Cr^{3+} + 3e^- \rightarrow Cr$	−0.74
$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	−0.83
$Mn^{2+} + 2e^- \rightarrow Mn$	−1.18
$Zr^{4+} + 4e^- \rightarrow Zr$	−1.45
$Al^{3+} + 3e^- \rightarrow Al$	−1.66
$Be^{2+} + 2e^- \rightarrow Be$	−1.70
$Mg^{2+} + 2e^- \rightarrow Mg$	−2.37
$Na^+ + e^- \rightarrow Na$	−2.71
$Ca^{2+} + 2e^- \rightarrow Ca$	−2.87
$Sr^{2+} + 2e^- \rightarrow Sr$	−2.89
$Ba^{2+} + 2e^- \rightarrow Ba$	−2.90
$Rb^+ + e^- \rightarrow Rb$	−2.92
$K^+ + e^- \rightarrow K$	−2.92
$Cs^+ + e^- \rightarrow Cs$	−2.92
$Li^+ + e^- \rightarrow Li$	−3.05

When using these values, keep the following points in mind:

1. $E°$ values apply to the reaction as written in the left-to-right direction. If the reaction is reversed, the sign changes, but the value stays the same.

2. The more positive $E°$ is, the greater the tendency for the material to be to reduced.
3. Under standard-state conditions, any species on the left side of a half-cell reaction will spontaneously react with any species on the right side of a half-cell reaction that is ranked below it.
4. Multiplying an entire half-reaction by a constant does *not* change the associated reduction potential. This is different than the rules for manipulating ΔH_{rxn} values.

Calculating Standard Cell Potentials

In order to function, any electrochemical cell must consist of two half-cells. **Table** 23.2 can be used to determine the reactions that will occur and the standard cell potential for any combination of two half-cells without actually constructing the cell. The half-cell with the higher reduction potential according to the table will undergo reduction, while the half-cell with the lower reduction potential will undergo oxidation. If those specifications are followed, the overall cell potential will be a positive value. The cell potential must be positive in order for the redox reaction in the cell to be spontaneous. If a negative cell potential were calculated, the reaction would not be spontaneous. However, that reaction would be spontaneous in the reverse direction.

Example 23.1

Calculate the standard cell potential of a voltaic cell that uses the Ag|Ag$^+$ and Sn|Sn^{2+} half-cell reactions. Write the balanced equation for the overall cell reaction that occurs. Identify the anode and the cathode.

Answer:

The silver half-cell has a reduction potential of +0.80 V, whereas the tin half-cell has a reduction potential of -0.14 V. Reduction will happen in the silver half-cell, because its standard reduction potential is more positive. The tin half-cell will undergo oxidation.

$$\begin{array}{ll} \text{Oxidation (anode):} & \mathrm{Sn}(s) \rightarrow \mathrm{Sn}^{2+}(aq) + 2\mathrm{e}^- \\ \text{Reduction (cathode):} & \mathrm{Ag}^+(aq) + \mathrm{e}^- \rightarrow \mathrm{Ag}(s) \end{array}$$

Before adding the two reactions together, the number of electrons lost in the oxidation must equal the number of electrons gained in the reduction. The silver half-cell reaction must be multiplied by two. Then, adding in the tin half-reaction, we get the full redox process:

$$\mathrm{Sn(s)} + 2\mathrm{Ag^+(aq)} \rightarrow \mathrm{Sn^{2+}(aq)} + 2\mathrm{Ag(s)}$$

The overall cell potential can be calculated as follows:

$$\mathrm{E^\circ_{cell}} = \mathrm{E^\circ_{red}} - \mathrm{E^\circ_{oxid}}$$
$$\mathrm{E^\circ_{cell}} = +0.80\ \mathrm{V} - (-0.14\ \mathrm{V}) = +0.94\ \mathrm{V}$$

The standard cell potential is positive, so the reaction is spontaneous as written. Tin is oxidized at the anode, while Ag$^+$ is reduced at the cathode. Note that the voltage for the silver ion reduction is not doubled even though the reduction half-reaction had to be doubled to balance the overall redox equation.

The Nernst Equation

Up to this point, our discussion of cell potentials has focused on the standard states. However, in real life we will rarely be using standard state conditions, so we need a way to work with more practical situations. For conditions that are not standard-state, we use the Nernst equation, named after the German chemist Walther Nernst (winner of the 1920 Nobel Prize in Chemistry).

FIGURE 23.10

Walther Nernst.

The Nernst equation has the following form:

$$E = E^{\circ} - \frac{RT}{nF} \ln Q$$

where E is the reaction potential under the actual conditions, E° is the reaction potential under standard conditions, R is the universal gas constant (8.314 J/K•mol), T is the temperature (in Kelvin), n is the number of moles of electrons transferred in the redox reaction, F is a value known as the Faraday constant (96,485 C/mol), and Q is the reaction quotient. Recall that the reaction quotient takes the same form as the equilibrium constant expression, except that it is true even when the reaction is not at equilibrium. For example, the reaction quotient for the following generic reaction is given below:

$$aA + bB \rightarrow cC + dD$$

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

If the reaction is run at the standard temperature of 25°C, and it is just the concentrations that are non-standard, the Nernst equation simplifies as follows:

$$E = E^\circ - \frac{0.02569\ \text{volts}}{n} \ln Q$$

Or, if you prefer base-10 logarithms:

$$E = E^\circ - \frac{0.05619\ \text{volts}}{n} \log Q$$

Let's look at an example problem to see how this equation is used.

Example Problem 23.2

Calculate the cell potential at 25°C for the following reaction:

$$Cu(s) + 2Fe^{3+}(aq) \rightarrow Cu^{2+}(aq) + 2Fe^{2+}(aq)$$

The ions are present in the following concentrations: 1.0 x 10^{-4} M Fe^{3+}, 0.25 M Cu^{2+}, and 0.20 M Fe^{2+}.

Answer:

The Nernst equation has the following form at 25°C:

$$E = E^\circ - \frac{0.05619\ \text{volts}}{n} \log Q$$

In order to find the cell potential (E), we need to find values for E°, n, and Q. Let's start by splitting this reaction into half-reactions. Because there are only two different metals, we can easily see that the unbalanced half-reactions will have the following forms:

$$Cu(s) \rightarrow Cu^{2+}(aq)$$
$$2Fe^{3+}(aq) \rightarrow 2Fe^{2+}(aq)$$

Then, balance each of these half-reactions by adding electrons to the appropriate side (enough to balance the charge on each side of the equation):

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$$
$$2Fe^{3+}(aq) + 2e^- \rightarrow 2Fe^{2+}(aq)$$

This gives us two pieces of information. First, we know that the value of n in the Nernst equation is equal to 2 (the coefficient of the electrons in the balanced half-reactions above). Second, we know that copper is being oxidized and iron is being reduced. Now, look at the table of standard reduction potentials to find the appropriate values. What we will find are values for the following two half-reactions:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$
$$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$$

The reduction of $Cu^{2+}(aq)$ to Cu(s) has a standard potential of +0.34 V, and the reduction of $Fe^{3+}(aq)$ to $Fe^{2+}(aq)$ has a standard potential of +0.77 V. To find E° for this complete cell, we subtract the reduction potential of the species being oxidized from the reduction potential of the ion actually being reduced:

$$E^\circ_{cell} = E^\circ_{red} - E^\circ_{oxid}$$
$$E^\circ_{cell} = +0.77 - +0.34$$
$$E^\circ_{cell} = +0.43$$

Note: We can also think of this as reversing the sign of the oxidation half-reaction (from +0.34 to -0.34) and then adding the two values together ((+0.77) + (-0.34) = +0.43). However, do not get mixed up and reverse the sign twice!

Next, we can determine Q, which has the following form for this reaction:

$$Q = \frac{[Cu^{2+}][Fe^{2+}]^2}{[Fe^{3+}]^2}$$
$$Q = \frac{[0.25][0.20]^2}{[1.0\times10^{-4}]^2}$$
$$Q = 1.0 \times 10^6$$

Finally, plug all of these values into the Nernst equation:

$$E = E^\circ - \frac{0.05619 \text{ volts}}{n} \log Q$$
$$E = 0.43 \text{ V} - \frac{0.05619 \text{ V}}{2} \log(1.0 \times 10^6)$$
$$E = 0.43 \text{ V} - 0.17 \text{ V}$$
$$E = 0.26 \text{ V}$$

Under the given conditions, this electrochemical cell has a potential of +0.26 V.

Practice Problem 23.1

Calculate the cell potential at 25°C for the following reaction:

$$Fe(s) + Co^{2+}(aq) \rightarrow Fe^{2+}(aq) + Co(s)$$

The ions are present in the following concentrations: 0.050 M Fe^{2+} and 0.020 M Co^{2+}.

Lesson Summary

- The ability of a particular electrochemical cell to generate an electric current is called its electrical potential. Reduction potentials measure the tendency of a substance to be reduced in a redox reaction.
- The standard hydrogen electrode is arbitrarily assigned a standard reduction potential of 0.00 V, and it serves as a reference by which all other half-cell potentials are measured.
- The standard cell potential for any electrochemical cell can be determined by finding the difference in reduction potentials between the two half-cells. The cell potential must be positive for the overall reaction to be spontaneous.
- Reduction potentials can be used to make predictions about whether reactions will occur and whether a particular oxidizing or reducing agent is strong enough for a given purpose.
- The Nernst equation allows for the calculation of cell potentials under non-standard conditions.

Lesson Review Questions

1. What does standard reduction potential measure?
2. Under what conditions is a particular standard cell potential (E<deg>;$_{cell}$) determined?
3. Explain the operation and usefulness of the standard hydrogen electrode.
4. Distinguish the anode adn the cathode in a galvanic cell.
5. Which species in the following pairs is more likely to be reduced? Explain your answer.
    (a) Br_2 or Cl_2
    (b) Na^+ or K^+
    (c) PbO_2 or $PbSO_4$
6. Using the given table of standard reduction potentials, calculate E° for the following reactions. Under standard conditions, will these reactions spontaneously occur in the forward direction?
    (a) $Al + 3Ag^+ \rightarrow 3Ag + Al^{3+}$

   (b) $Zr + 2I_2 \rightarrow Zr^{4+} + 4I^-$
   (c) $Li^+ + Ag \rightarrow Ag^+ + Li$

7. Define each quantity that appears in the Nernst equation, and make note of the respective units.
8. Use the Nernst equation and the given concentrations to calculate E for the following reaction at 25°C: $NO_3^-(aq) + As(s) \rightarrow NO(aq) + AsO_2^-(aq)$, where $[NO_3^-] = 1.0$ M, $[NO] = 0.20$ M, and $[AsO_2^-] = 0.010$ M. E° for this reaction is equal to +2.91 V.
9. Use the Nernst equation and the given concentrations to calculate E for the following reaction at 25°C: $2H_2O(l) + 3Cl_2(g) + 2Sb(s) \rightarrow 6Cl^-(aq) + 2SbO^+(aq) + 4H^+(aq)$, where $[Cl_2] = 0.80$ M, $[Cl^-] = 1.0$ M, $[SbO^+] = 0.20$ M, and $[H^+] = 0.20$ M. E° for this reaction is equal to +2.34 V.

Further Reading/Supplementary Links

- Table of standard reduction potentials: http://www.jesuitnola.org/upload/clark/refs/red_pot.htm
- Derivation of the Nernst equation: http://www.science.uwaterloo.ca/~cchieh/cact/c123/nernsteq.html
- Using the Nernst equation: http://www.asdlib.org/onlineArticles/ecourseware/Gross_Potentiometry/The%20Nernst%20Equation.pdf

Points to Consider

- How would comparing elements in the activity series by their standard reduction potentials allow us to make predictions about the direction of oxidation-reduction reactions?

23.3 Electrolysis

Lesson Objectives

- Define electrolysis.
- Describe the use of electrolysis in the purification of sodium.
- Understand the basics of the process of refining aluminum.

Vocabulary

- **electrolysis**: The process in which electrical energy is used to cause a nonspontaneous chemical reaction to occur.
- **electrolytic cell**: The apparatus used for carrying out an electrolysis reaction; consists of an electrolyte to carry charge and two electrodes.
- **electrometallurgy**: A technique of extracting and purifying metals from their ores through use of electrolysis.

Check Your Understanding

Recalling Prior Knowledge

- Review the activity series and the standard reduction potential information to predict how metals will interact with one another.

Electrolysis

A galvanic cell uses a spontaneous redox reaction to generate an electric current. It is also possible to do the opposite. When an external source of direct current is applied to an electrochemical cell, a reaction that is normally nonspontaneous can be forced to proceed. **Electrolysis** is the process in which electrical energy is used to cause a nonspontaneous chemical reaction to occur. Electrolysis is responsible for the metal coatings that appear on many everyday objects, such as gold-plated or silver-plated jewelry and chrome-plated car bumpers.

An **electrolytic cell** is the apparatus used for carrying out an electrolysis reaction. **Figure** 23.11 shows an electrolytic cell composed of $Zn|Zn^{2+}$ and $Cu|Cu^{2+}$ half-cells.

Recall that in the last section, this same pair of half-cells was used as an example of a voltaic cell. In the spontaneous direction, Zn metal is oxidized to Zn^{2+} ions while Cu^{2+} ions are reduced to Cu metal. In a voltaic cell, the zinc electrode would be the anode and the copper electrode would be the cathode. However, when the same half-cells are connected to a battery via an external wire, the reaction is forced to run in the opposite direction. The zinc electrode is now the cathode and the copper electrode is the anode.

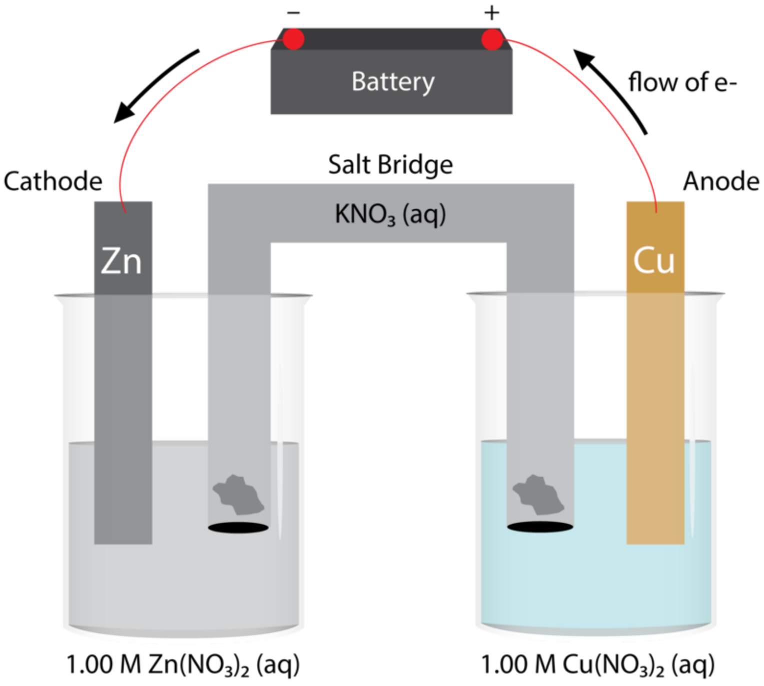

FIGURE 23.11

An electrolytic cell uses an external power source (a battery) to drive a nonspontaneous reaction. The copper half-cell undergoes oxidation, while the zinc half-cell undergoes reduction.

Oxidation (anode):	$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$	$E^0 = -0.34$ V
Reduction (cathode):	$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	$E^0 = -0.76$ V
Overall reaction:	$Cu(s) + Zn^{2+}(aq) \rightarrow Cu^{2+}(aq) + Zn(s)$	$E^0_{cell} = -1.10$ V

The standard cell potential is negative, indicating a nonspontaneous reaction. The battery must be capable of delivering at least 1.10 V of direct current in order for the reaction to occur.

Commercial Electrolysis Reactions

Electrolysis of Molten Sodium Chloride

Several electrolysis reactions are commonly performed on a large scale for the commercial production of certain substances. For example, molten (liquid) sodium chloride can be electrolyzed to produce sodium metal and chlorine gas. The electrolytic cell used in this process is called a Down's cell (**Figure** 23.12).

In a Down's cell, the liquid sodium ions are reduced at the cathode to liquid sodium metal. At the anode, liquid chloride ions are oxidized to chlorine gas. The reactions and cell potentials are shown below.

Oxidation (anode):	$2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$	$E^0 = -1.36$ V
Reduction (cathode):	$Na^+(l) + e^- \rightarrow Na(l)$	$E^0 = -2.71$ V
Overall reaction:	$2Na^+(l) + 2Cl^-(l) \rightarrow 2Na(l) + Cl_2(g)$	$E^0_{cell} = -4.07$ V

The battery must supply over 4 volts to carry out this electrolysis. This reaction is a major industrial source of

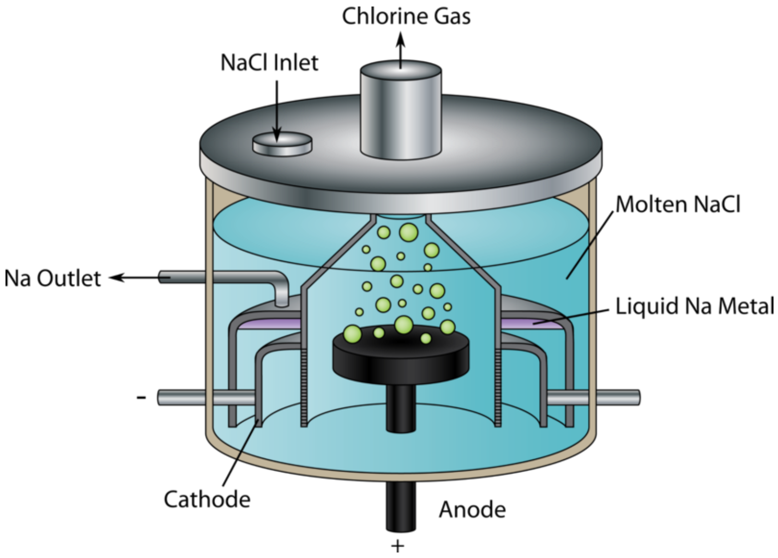

FIGURE 23.12

A Down's cell is used for the electrolysis of molten sodium chloride. Liquid sodium metal is produced at the cathode, while chlorine gas is produced at the anode.

chlorine gas, and it is the primary way to obtain pure sodium metal. Chlorine gas is widely used as a disinfectant, such as in swimming pools.

Electrolysis of Water

The electrolysis of water produces hydrogen and oxygen gases. The electrolytic cell consists of a pair of platinum electrodes immersed in water containing a small amount of an electrolyte, such as H_2SO_4. The electrolyte is necessary because pure water does not contain enough ions to effectively conduct a current. At the anode, water is oxidized to oxygen gas and hydrogen ions. At the cathode, water is reduced to hydrogen gas and hydroxide ions.

Oxidation (anode):	$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$	$E^0 = -1.23$ V
Reduction (cathode):	$4H_2O(l) + 4e^- \rightarrow 2H_2(g) + 4OH^-(aq)$	$E^0 = -0.83$ V
Overall reaction:	$2H_2O(l) \rightarrow O_2(g) + 2H_2(g)$	$E^0_{\text{cell}} = -2.06$ V

The hydrogen ion and hydroxide ions produced in each reaction combine to form water, resulting in the net reaction shown above. The added electrolyte is not consumed in the reaction. In this process, the hydrogen in the water is reduced (from +1 to 0) and the oxygen is oxidized (from -2 to 0). This process was discovered in 1800 by William Nicholson and Johann Ritter. One modern-day application is the generation of oxygen for use in sealed vehicles, such as spacecrafts and submarines.

Electrolysis of Aqueous Sodium Chloride

Earlier we examined the electrolysis of molten sodium chloride. It may be logical to assume that the electrolysis of aqueous sodium chloride, called brine, would yield the same result by the same reactions. However, the reduction reaction that occurs at the cathode does not produce sodium metal, because the water is reduced instead. This is because the reduction potential for water is only -0.83 V compared to -2.71 V for the reduction of sodium ions. This makes the reduction of water preferable, because its reduction potential is less negative. Chlorine gas is still produced at the anode, just as in the electrolysis of molten NaCl.

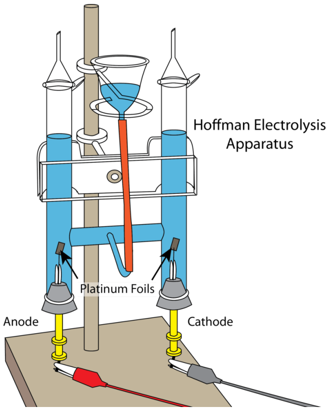

FIGURE 23.13

Apparatus for the production of hydrogen and oxygen gases by the electrolysis of water.

$$\begin{array}{lll} \text{Oxidation (anode):} & 2Cl^{-}(aq) \rightarrow Cl_2(g) + 2e^{-} & E^0 = -1.36 \text{ V} \\ \text{Reduction (cathode):} & 2H_2O(l) + 2e^{-} \rightarrow H_2(g) + 2OH^{-}(aq) & E^0 = -0.83 \text{ V} \\ \hline \text{Overall reaction:} & 2Cl^{-}(aq) \rightarrow O_2(g) + 2H_2(g) & E^0_{\text{cell}} = -2.06 \text{ V} \end{array}$$

Since the hydroxide ion is also a product of the net reaction, the important chemical sodium hydroxide (NaOH) is obtained by evaporating the water after the hydrolysis is complete.

Electrometallurgy

The extraction of metals from ores and the purification of metals is often accomplished using **electrometallurgy**. Most metals are found in nature in an oxidized form (usually an oxide or a sulfide) called an ore. If the ore is either dissolved in an aqueous solution or melted, passing an electric current through the material causes the pure metal to be deposited on one of the electrodes. This process was used by the English chemist Humphrey Davy to isolate metallic sodium from a solution of sodium hydroxide, and several other elements were discovered in the next several years using this same technique.

We saw earlier that sodium is most commonly produced by electrolysis of molten sodium chloride. Many other metals are also isolated and purified using electrometallurgy techniques, including gold, silver, copper, aluminum, lead, and many alkali and rare earth metals. For some metals, this is the only financially viable method of extraction and purification. In addition to the production of a desired metal, these techniques are also being studied for use in the processing of nuclear wastes and the cleanup of environmental contamination by toxic metals.

Aluminum is one example of a substance that was very rare in its pure form before electrometallurgy techniques were developed but is now extremely common. Aluminum ore (bauxite) is predominantly aluminum oxide (Al_2O_3). Refinement of the metal by simple heating, as is done with iron ore, is ineffective, because the melting point of the aluminum ore is so high (>2000°C). Instead, the bauxite is first mixed with sodium hydroxide at high temperatures to remove the other contaminants from the aluminum oxide. This material is then recrystallized and separated from other ore residues. Then, the purified aluminum oxide is dissolved in a molten mixture of calcium fluoride and cryolite (an aluminum fluoride-sodium fluoride salt that melts at 1012°C). The lower melting point of the cryolite allows the aluminum ore to dissolve at a temperature that is much lower than its own melting point. The resulting solution is then electrolyzed using carbon electrodes at a temperature of 950-980Udeg;C. The aluminum cations are reduced to neutral aluminum at the cathode ($Al^{3+} \rightarrow Al^0$), and the oxygen anions are oxidized back to molecular oxygen at the anode ($2\ O^{2-} \rightarrow O_2$).

One problem with current methods of aluminum production is the generation of environmental contaminants. Hydrogen fluoride gas is an extremely corrosive and toxic byproduct that must be trapped and neutralized. Other fluorides and metals contaminants can also pollute water, soil, and air if not carefully managed.

A major expense in the refinement of aluminum is the cost of electrical power. Refining plants are usually located in areas where electricity is abundant and less expensive. Producing aluminum from recycled materials uses only about 5% of the electricity needed to produce the aluminum from bauxite, which makes aluminum recycling profitable as well as environmentally beneficial.

Corrosion

Corrosion involves the formation of an oxidized form of a metal by an electrochemical process. A common example is the rusting of iron when exposed to water and oxygen. The tarnishing of silver and the red or green deposits formed on copper are other examples. Corrosion in all its forms costs the U.S. millions of dollars each year in expenses for metal replacement.

FIGURE 23.14

Rust formation involves a complex series of reactions that are still not well-understood. The first part of the overall process appears to be the following reaction:

$$2\ \mathrm{Fe} + \mathrm{O_2} + 4\ \mathrm{H^+} \rightarrow 2\ \mathrm{Fe^{2+}} + 2\ \mathrm{H_2O}$$

The iron then undergoes further oxidation in the presence of O_2 to form ferric oxide (Fe_2O_3). The complete process is somewhat more complex.

The corrosion of copper involves a reaction with carbonic acid, which is formed when atmospheric carbon dioxide dissolves in water. This acid is weak and unstable, but it can produce significant damage over time. The reaction between copper and carbonic acid generates copper carbonate, which is responsible for the familiar blue-green layer seen on structures such as the Statue of Liberty.

Silver will tarnish through a similar type of reaction with hydrogen sulfide, which is found in low concentrations in the atmosphere and is often generated by foods with a high sulfur content, such as eggs. The tarnish in this case is silver sulfide (Ag_2S).

One common approach to minimize the corrosion of metals is to attach a strip of a more active metal, sometimes called a sacrificial metal, to the structure. For example, putting aluminum rings on iron or steel structures helps prevent rusting. Since aluminum is higher than iron in the activity series, it can be used to reduce iron cations back to neutral Fe. Eventually, the aluminum will all be converted to Al^{3+} cations and must be replaced.

Lesson Summary

- Electrolysis uses an external source of electricity to drive nonspontaneous redox reactions.
- Several metals (including sodium and aluminum) are manufactured using electrolytic processes.
- Corrosion involves the deterioration of a neutral metal into an oxidized form, which exists as an ionic complex with oxide, sulfide, carbonate, or other anions.
- Attaching strips of neutral metals that are higher in the activity series can protect a structure from corrosion.

Lesson Review Questions

1. How does an electrolytic cell differ from a galvanic cell?
2. Explain how to produce sodium from sodium chloride.
3. Define electrometallurgy and explain some of its primary uses.
4. Why is cryolite used to dissolve aluminum oxide in the refining of aluminum?
5. Why is fluoride contamination a problem in the refining of aluminum?
6. Write the molecular equation and the half-reactions for each of the following processes:
    a. copper + carbonic acid
    b. silver + hydrogen sulfide
7. You want to build a boat with a tin bottom. You can use screws made out of either iron or copper. Which metal would be best for fastening the tin to the bottom of the boat?
8. In order to prevent iron storage tanks from rusting, they have magnesium attached to them. Explain why this process minimizes rusting of the iron.

Further Reading/Supplementary Links

- Electrolysis of molten salts: http://www.youtube.com/watch?v=l0V4MBKQXjs
- Mining and refining aluminum: http://science.howstuffworks.com/aluminum2.htm
- Chemistry of corrosion: http://www.ce.sc.edu/deptinfo/members/faculty/ray/web1/Ugrad/ECIV%20303/Corrosion/Set2%20Chemistry%20of%20corrosion.pdf

Points to Consider

- Oxidation-reduction calculations play important roles in other areas of chemistry.
- Cell potentials in biology are another useful application of electrochemistry.

23.4 References

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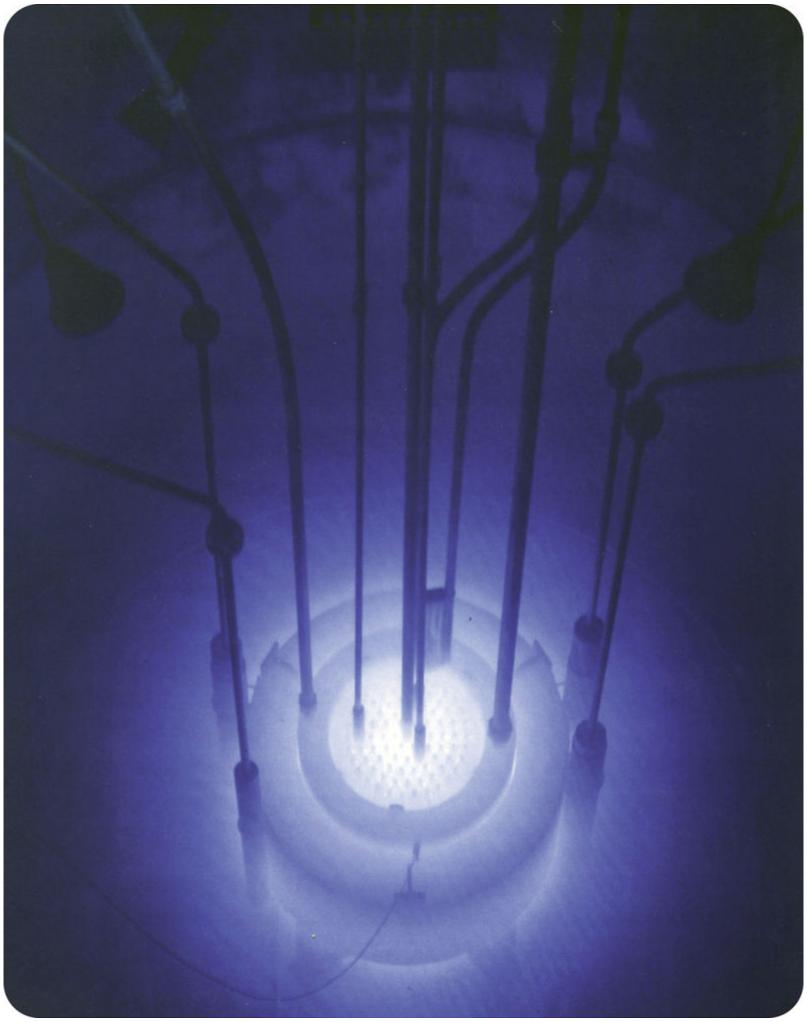
CHAPTER 24 Nuclear Chemistry

Chapter Outline

24.1 NUCLEAR RADIATION
24.2 HALF-LIVES
24.3 FISSION AND FUSION
24.4 APPLICATIONS OF RADIOACTIVITY
24.5 REFERENCES



Cherenkov radiation is produced when charged particles move through water faster than the speed at which light travels through water. Water molecules are excited by this process, and when the excited molecules return to their ground state, they release photons that produce the blue light seen in the figure above. One of the places where this type of situation commonly occurs is inside nuclear reactors. Water is used to cool the rods containing radioactive material in nuclear reactors, which use emissions from radioisotopes to produce heat that can drive a turbine and generate electricity.

Nuclear power plants are used in many countries around the world. As of 2013, there are 434 operational nuclear plants around the world, over 100 of which are found in the U.S. In 2012, nuclear power accounted for 19% of the total U.S. production of electricity. Radioactivity is poorly understood by the general public. Images of nuclear bombs and runaway power plant incidents are of great concern to many. However, there are many useful applications, including medical imaging and treatment using radioisotopes. In this chapter, we will explore basic ideas about radioactivity and see how we can use this phenomenon for constructive purposes.

United States Nuclear Regulatory Commission. commons.wikimedia.org/wiki/File:Cerenkov_Effect.jpg. Public Domain.

24.1 Nuclear Radiation

Lesson Objectives

- Describe the characteristics of radioactive emissions.
- Complete equations involving radioactive decay when given pertinent information.
- Describe how to measure radioactivity.

Lesson Vocabulary

- **radioactivity**: The spontaneous emission of matter and/or energy from the unstable nucleus of an atom.
- **alpha particle**: The nucleus of a helium-4 atom
- **beta particle**: An electron.
- **gamma radiation**: Very high energy electromagnetic radiation.
- **Geiger counter**: A device that measures the frequency of radioactive events; composed of a tube filled with an inert gas that is able to conduct electricity when exposed to charged radiation.

Check Your Understanding

Recalling Prior Knowledge

- How are mass number and atomic number related to the amounts of different subatomic particles in a particular atom?
- What is different about multiple isotopes of a single element?

A Review of Isotopes

John Dalton first proposed his atomic theory in an 1804 lecture to the Royal Institution, a prestigious British scientific society. In this talk, he put forth the idea that all atoms of an element were identical and that atoms were indestructible. In a little over 100 years, both of these ideas were shown to be incorrect. Studies on atomic weights led Frederick Soddy (1877-1956) to the conclusion in 1913 that atoms of a single element can have more than one possible atomic weight. He won the Nobel Prize in Chemistry for this work in 1921.

At least by our current understanding, a given atom can be defined by its atomic number and its mass number. The atomic number is the number of protons in the nucleus. All atoms with a given atomic number are the same element, because the chemical properties of an atom are primarily determined by the number of positive charges in its nucleus (and therefore the number of negatively charged electrons needed to make it neutral). The mass number of an atom is equal to the number of protons plus the number of neutrons. Since these particles both have a mass of approximately

1 amu and electrons are much smaller, the mass number is approximately equal to the mass of the atom in units of amu.

Isotopes are atoms that have the same atomic number but different atomic weights. The difference in weight is due to variations in the number of neutrons within the nucleus. Because they are uncharged, a slight difference in the number of neutrons has very little effect on the chemical properties of a given atom. We can designate the mass number of an isotope (and sometimes the atomic number as well) using numbers to the left of the chemical symbol. The top number is the mass number, and the bottom number (if any) is the atomic number. For example, one isotope of krypton is the following:

$$^{84}_{36}\mathrm{Kr}$$

Because an atomic number of 36 is implied by the fact that this is an atom of krypton, we can also write this as just ^{84}Kr. Other ways to designate this isotope are krypton-84 or Kr-84. The number of neutrons in the nucleus of this isotope can be determined by subtracting the atomic number (36) from the mass number (84), giving a value of 48 neutrons.

Remember that the atomic weights listed on the modern periodic table are weighted averages of all naturally occurring isotopes. For example, the atomic weight of Cl is listed as 35.453, even though none of the isotopes of chlorine actually have that atomic weight. Chlorine has many possible isotopes ranging from ^{28}Cl to ^{51}Cl, but essentially all naturally occurring chlorine atoms are either ^{35}Cl or ^{37}Cl. Based on the ~3:1 ratio in which these isotopes occur, the average atomic weight of chlorine is 35.453 amu. Even though no individual chlorine atom has a mass of 35.453 amu, a mole of naturally occurring chlorine atoms will have a mass of 35.453 grams.

Discovery of Radioactivity

In 1896, a researcher named Henri Becquerel was studying the phosphorescent properties of uranium salts. He believed these properties were related to X-rays, which had just been discovered the previous year by Wilhelm Röntgen. However, he soon found that certain properties of the radiation emitted from uranium did not match those of X-rays. For example, uranium could expose a photographic plate without any external input of energy.

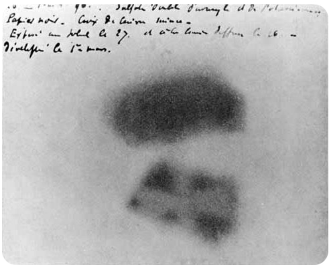


FIGURE 24.1

By placing a metal cross between the plate and the radioactive uranium salt, a shadow is left on the plate due to the effects of exposure to radioactivity.

Pierre and Marie Curie further studied the properties of uranium salts in order to understand the details of this newly discovered **radioactivity**. The major contributions to their work came from Marie, who showed that the amount of radioactivity present was due to the amount of a specific element in the sample and was not the result of a chemical reaction. She discovered the element polonium and named it after her native Poland. Madame Curie shared the 1903 Nobel Prize in Physics with her husband Pierre along with Henri Becquerel. She won the Nobel Prize again in 1911 for her work in Chemistry.

Later on, Ernest Rutherford (whose name you may remember from the Gold Foil Experiment) showed that there are three distinct types of radioactive emissions that differ in their mass, their charge, and their ability to penetrate through various materials. He did not yet know what these emissions were, and designated them as alpha (α), beta (β), and gamma (γ) radiation.

We now know that radioactivity involves the spontaneous emission of matter and/or energy from the nucleus of an atom. The most common radioactive atoms have high atomic numbers and contain a large excess of neutrons. All isotopes of elements with an atomic number of 84 (polonium) or higher are radioactive, including familiar radioactive materials such as radon (atomic number 86), uranium (atomic number 92), and plutonium (atomic number 94). Additionally, two lighter elements (technetium, atomic number 43, and promethium, atomic number 61) have no stable isotopes. Most elements have both stable and radioactive isotopes. For example, hydrogen-1 and carbon-12 are stable, but hydrogen-3 (tritium) and carbon-14 are both radioactive. These isotopes make up an extremely small percentage of any naturally occurring sample of their respective elements.

Types of Radioactive Decay

Alpha Emission

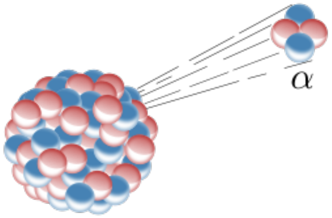


FIGURE 24.2

Alpha (α) radiation was eventually found to be made up of particles that consisted of two protons bound to two neutrons. In other words, an **alpha particle** was simply the nucleus of a helium-4 atom. Because it does not have any electrons, the alpha particle carries a charge of +2. In nuclear equations, alpha particles can be represented by any of the following symbols:

$\alpha \quad {}^{4}_{2}\alpha \quad {}^{4}_{2}\mathrm{He}$

A typical alpha decay reaction is the conversion of uranium-238 to thorium-234:

$${}^{238}_{92}\mathrm{U} \rightarrow {}^{234}_{90}\mathrm{Th} + {}^{4}_{2}\alpha$$

Many of the largest elements in the periodic table are alpha-emitters. Notice that in this nuclear equation, the total mass number and the total atomic number are both conserved. The sum of the mass numbers and atomic numbers of the products are equal to the mass number and atomic number of the parent nucleus. This is a general feature of nuclear reactions. As a result, knowing that a specific nucleus decays by emitting alpha particles allows us to predict the product nucleus; we simply need to decrease the mass number by 4 and the atomic number by 2. The change in atomic number indicates a change in the element's identity. The new element can be found by looking at the periodic table.

Beta Emission

Beta (β) emission is a slightly more complicated process. Unlike α-emission, which simply expels some of the existing subatomic particles from the nucleus, β-emission also involves the transformation of a neutron into a proton and an electron. The proton remains bound to the nucleus, while the electron is ejected.

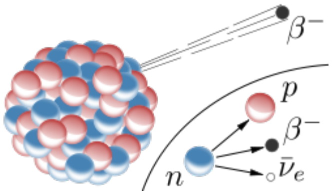


FIGURE 24.3

As it turns out, the beta radiation observed by early nuclear chemists was simply the result of ejected electrons. For historical reasons, the electron is sometimes referred to as a **beta particle** in this context. In nuclear equations, beta particles can be represented by any of the following symbols:

$$\beta \qquad \beta^- \qquad {}^{0}_{-1}\beta \qquad {}^{0}_{-1}e \qquad e^-$$

Although an electron technically has a very small mass, considering an electron as though its mass is zero makes it easier to balance nuclear equations. During beta decay, the parent nucleus increases its atomic number by 1, but the mass number stays the same. This follows the idea that charge is also conserved in radioactive decay. A typical beta decay process involves carbon-14, which is used in radioactive dating techniques:

$${}^{14}_{6}\mathrm{C} \rightarrow {}^{14}_{7}\mathrm{N} + {}^{0}_{-1}e$$

Positron Emission

A **positron** is the antimatter version of an electron. It has the same mass as an electron but the opposite charge. A positron can be designated by the following symbols:

$$\beta^+ \qquad {}^{0}_{+1}\beta \qquad {}^{0}_{+1}e \qquad e^+$$

During a nuclear decay process that occurs by positron emission, a proton is converted into a neutron and a positron. The neutron remains in the nucleus, and the positron is expelled. Overall, the atomic number of the parent nucleus increases by one, and the mass number is unchanged. For example, carbon-11 emits a positron to become boron-11:

$${}^{11}_{6}\mathrm{C} \rightarrow {}^{11}_{5}\mathrm{B} + {}^{0}_{+1}\beta$$

Positrons represent a special case, because they are a form of antimatter. When a positron encounters an electron, the two particles annihilate one another, and all of their mass is converted to pure energy. This energy is released in the form of two gamma photons traveling in exactly opposite directions. Because of the abundance of electrons in any sample of matter, positrons will be consumed almost immediately in essentially all cases.

Gamma Emission

Gamma (γ) radiation was eventually found to be very high energy electromagnetic radiation, even more energetic than X-rays. Many nuclear processes are accompanied by a large release of energy. This energy is sometimes given off as a photon of gamma radiation. For example, both alpha and beta decay are often accompanied by the emission of gamma rays. Because photons have no mass or charge, they do not affect the mass number or atomic number balance in a nuclear equation. When included in the equations, the release of gamma radiation is generally given the symbol ${}^{0}_{0}\gamma$. You will not be required to predict whether a given nuclear reaction includes the release of gamma rays.

Penetrating Ability of Emissions

The various types of emissions discussed above differ considerably in their ability to penetrate through matter. The α particle has the lowest penetrating power, primarily because it is the largest commonly expelled particle. Related to their larger mass, ejected α particles also move much slower than other types of nuclear decay products. A stream of α particles can be blocked by a sheet of paper or a human hand.

Beta particles (electrons) have a higher penetrating power than alpha particles, but they can still be stopped by a thin sheet of aluminum. However, the materials being bombarded with a high-energy stream of electrons can also become excited, potentially leading to additional reactivity.

Of the three basic types of emissions, gamma radiation has the highest penetrating power. Thick, high density materials (such as lead) are required to stop gamma emissions. The thickness of the shielding will determine the effectiveness of the protection offered by the lead.

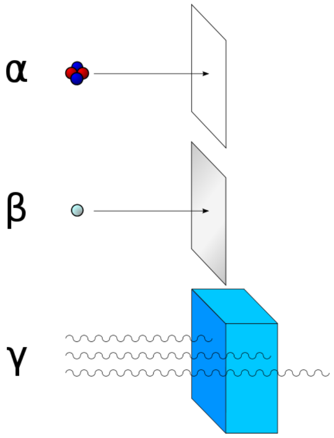


FIGURE 24.4

Detection of Radioactivity

Units of Measurement

Radioactivity is quantified by measuring the number of decay processes per unit time. For example, we can measure radioactivity in terms of counts per minute (cpm), where each "count" is a single decay process, such as the emission of an α-particle. A sample of one particular isotope may have an activity of 5,000 cpm, while an equal amount of another isotope might result in a radiation level of only 250 cpm. For a given nucleus, the amount of radioactivity gives a rough indication of the amount of the radioisotope present –the higher the activity, the more of the radioactive isotope in the sample.

The curie (Ci), named after Marie and Pierre Curie, is another unit that is commonly used to measure the rate of decay. One curie is equivalent to 3.7×10^{10} decay processes per second. Since this is a fairly large value, radiation is often expressed in millicuries or microcuries. Another common unit is the becquerel (Bq), named after Henri Becquerel, which is simply defined as one count per second.

Exposure to Radiation

The units discussed above give us information about the rate of decay for a radioactive sample, but they do not tell us anything about the level of exposure experienced by nearby targets, such as people. The amount of exposure and the resulting medical consequences depend on various factors, including the type of radiation, its intensity, and the length of time that the person is exposed to the radioactive material. A large amount of radiation received over a short period of time is referred to as acute exposure, whereas low levels of exposure over a long period of time are referred to as chronic exposure.

Measurement of exposure to radioactivity is important for anyone who deals with radioactive materials on a regular basis. Perhaps the simplest device is a personal dosimeter, which is a film badge that will fog up when exposed to radiation. The amount of fogging is proportional to the amount of radiation present.

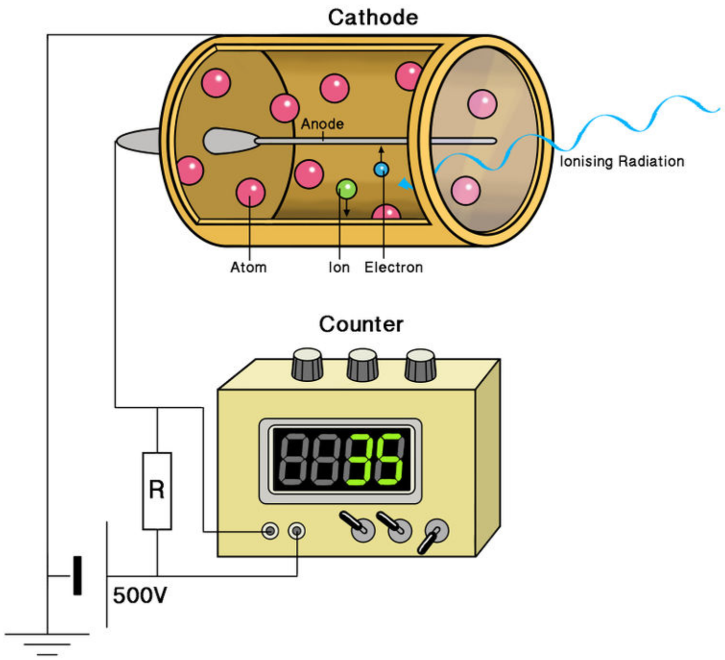


FIGURE 24.5

These devices are not very sensitive to low levels of radiation, but more sensitive devices are also available that reliably measure the frequency of radioactive events. One such device is the Geiger counter. A **Geiger counter** is a tube filled with an inert gas that will conduct electricity when exposed to charged radiation, such as alpha or beta particles. When a charged particle enters the tube, it changes the electrical potential between the anode and the cathode, and this change in potential is registered by an electrical circuit as a single radioactive event. Geiger counters are fairly inexpensive and reliable, so they are useful in a wide range of applications. More complicated types of counters are also available, but are generally used only in sophisticated experiments.

Lesson Summary

- Radioactivity involves the release of particles and/or energy from the nucleus of an atom.
- Alpha emissions consist of the ejection of an alpha particle (a helium-4 nucleus) from a radioactive nucleus.
- Beta emission involves the conversion of a neutron into a proton (which remains in the nucleus) and an electron (beta particle) that is ejected from the nucleus.
- Positron emission involves the conversion of a proton into a neutron (which remains in the nucleus) and a positron, which is ejected from the nucleus.
- Gamma emission is the release of energy in the form of high energy electromagnetic waves.
- Radiation dosage can be measured in several ways, including personal dosimeters and Geiger counters.

Lesson Review Questions

Reviewing Concepts

1. Define radioactivity.
2. Define the terms below, noting their penetration abilities:
    a. alpha particle
    b. beta particle
    c. positron emission
    d. gamma emission
3. Explain how a Geiger counter detects radioactivity.

Problems

1. Americium-241 is a radioactive isotope found in many smoke detectors. If this nucleus decays by alpha emission, what is the decay product?
2. Write the nuclear decay products after the emission of a beta particle by phosphorus-32.
3. Write the nuclear decay products for the emission of a positron by potassium-40.
4. For each reaction below, indicate the product isotope:
    (a) ${}^{180}_{79}\text{Au} \rightarrow \alpha + ?$
    (b) ${}^{189}_{70}\text{Yb} \rightarrow \beta^- + ?$
    (c) ${}^{94}_{43}\text{Tc} \rightarrow \beta^+ + ?$
5. For each reaction below, indicate the initial isotope:
    (a) $? \rightarrow \beta^- + {}^{98}_{41}\text{Nb}$
    (b) $? \rightarrow \alpha + {}^{146}_{64}\text{Gd}$
6. For each reaction below, determine the missing particle:
    (a) ${}^{49}_{24}\text{Cr} \rightarrow ? + {}^{49}_{23}\text{V}$
    (b) ${}^{50}_{19}\text{K} \rightarrow ? + {}^{50}_{20}\text{Ca}$

Further Reading / Supplementary Links

- Radioactive decay processes: http://www.chem.duke.edu/~jds/cruise_chem/nuclear/stability.html
- Table of isotopes and decay modes: http://ie.lbl.gov/decay/parent.pdf
- Radiation dosage: http://www.ccohs.ca/oshanswers/phys_agents/ionizing.html

Points to Consider

- How long does a sample of radioactive material remain hazardous?

24.2 Half-Lives

Lesson Objectives

- Define half-life, and be able to perform calculations relating the half-life of an isotope to the radioactivity of that isotope over time.

Lesson Vocabulary

- **half-life**: The amount of time needed for one-half of a sample to spontaneously decay.

Check Your Understanding

- What tools can be used to determine the rate at which a radioactive substance is undergoing decay?

Half-Life

As radioactive substances gradually decay, there is less and less of the original material present, The **half-life** of an isotope is defined as the period of time needed for one-half of a sample to spontaneously decay. Some isotopes have long half-lives, such as uranium-234, which has a half-life of 245,000 years. Other isotopes have shorter half-lives. Iodine-131, which is used in thyroid scans, has a half-life of 8.02 days, and oxygen-15 has a half-life of only 2 minutes. Information on the half-life of an isotope can be used to calculate how much of that isotope will be present after a certain period of time. The **Table** 24.1 includes the half-lives of a few other radioactive isotopes.

TABLE 24.1:

Isotope	Decay Mode	Half-Life
Cobalt-60	beta	5.3 years
Neptunium-237	alpha	2.1 million years
Polonium-214	alpha	0.00016 seconds
Radium-224	alpha	3.7 days
Tritium (H-3)	beta	12 years

Figure 24.6 illustrates a typical decay curve for a radioactive substance. The amount decreases by one-half after each successive half-life.

One way to measure the amount of radioactive material present is by looking at the frequency of radioactive emissions with a Geiger counter or other device. In this section, we will assume that we are dealing with a nuclear decay process in which the parent nucleus is radioactive but the resulting nucleus is a stable isotope. When this is the

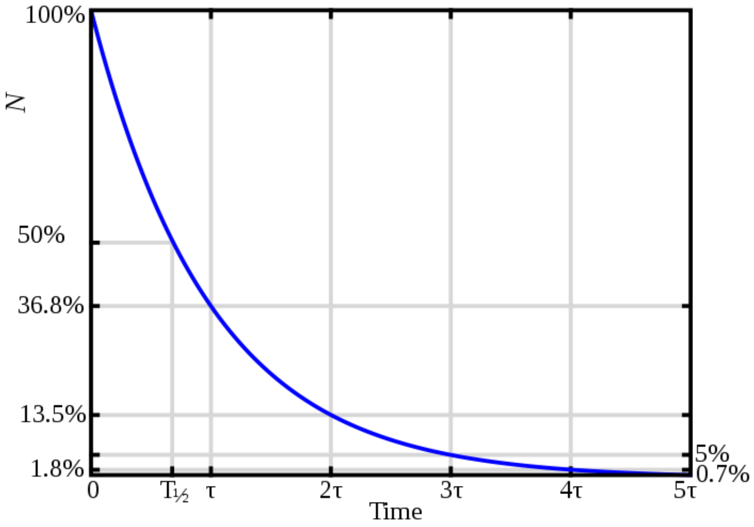


FIGURE 24.6

This graph shows a decay curve in terms of half-lives and mole percent of the substance remaining. This is an example of exponential decay.

case, the measured activity will decrease to one-half of its original value after one half-life has passed. For example, if one hour is required for the radioactivity of a certain sample to decrease from 30,000 cpm to 15,000 cpm, that isotope has a half-life of one hour.

Example 24.1

The isotope iodine-125, which is used in certain medical procedures, has a half-life of 59.4 days. How many half-lives have passed after 178.2 days? If the initial activity of a sample of iodine-125 is 32,000 cpm, what will be its activity after 178.2 days?

Answer:

Since we know that one half-life is equal to 59.4 days, we can determine the number of half-lives as follows:

$$178.2 \text{ days} \times \frac{1 \text{ half-life}}{59.4 \text{ days}} = 3 \text{ half} - \text{lives}$$

Because this value is a whole number, we can simply divide the original activity in half once for each half-life:

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

If the amount of time that has passed is not a simple multiple of the known half-life, we can use the following equation:

$$N_t = N_0 \times (0.5)^{\frac{t}{t_{1/2}}}$$

where N_t is the amount of activity at time t, N_0 is the initial activity (at time = 0), t is the amount of time that has passed, and $t_{1/2}$ is the half-life of the isotope.

Example 24.2

Rubidium-78 has a half-life of 17.67 minutes. If a given sample of Rb-78 has a measured activity of 1.8×10^4 cpm, what will be its activity after one hour has passed?

Answer:

Simply plug the given values into the equation above. Note that the units of the half-life and the total amount of time must match.

$$N_t = N_0 \times (0.5)^{\frac{t}{t_{1/2}}}$$
$$N_t = (1.8 \times 10^4 \ cpm) \times (0.5)^{\frac{60 \ min}{17.67 \ min}}$$
$$N_t = (1.8 \times 10^4 \ cpm) \times (0.5)^{3.396}$$
$$N_t = 1.7 \times 10^3 \ cpm$$

In this section, we have been looking at isotopes that decay directly to a stable nucleus. However, many isotopes, particularly very heavy ones, require many successive decays before reaching a stable nucleus. For example, the decay of uranium-238 results in the production of thorium-234, which is also radioactive. That decays into protactinium-234, which is radioactive as well. The complete decay chain for uranium-238 is illustrated in the **Figure** 24.7.

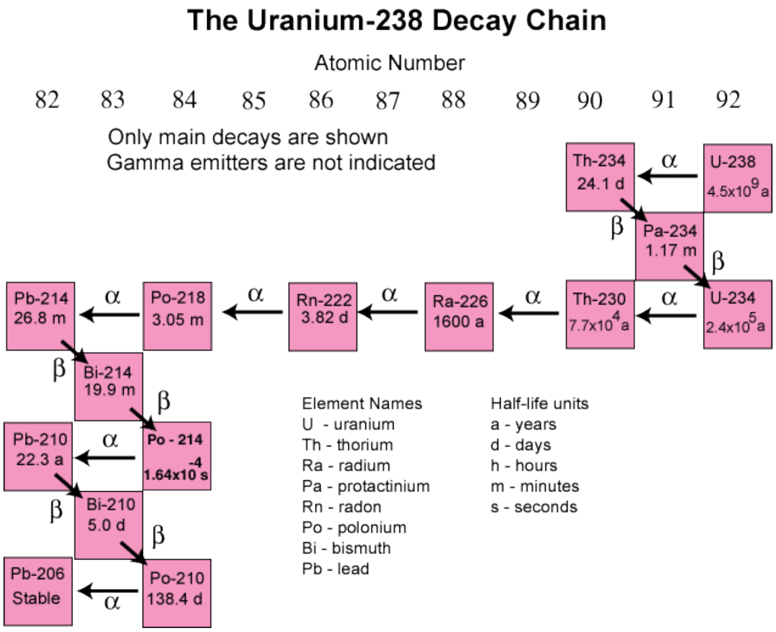


FIGURE 24.7

Decay of uranium-238 to a stable end product.

Lesson Summary

- The half-life of an isotope is the amount of time necessary for one half of a given sample to undergo radioactive decay.
- Half-lives can vary from fractions of a second to millions of years.

Lesson Review Questions

Reviewing Concepts

1. Define half-life.
2. From the chart of half-lives referenced below, list the half-lives of:
    a. californium-251
    b. iodine-131
    c. uranium-238

Problems

1. An isotope has a half-life of 2.4 days. How many half-lives have passed if you measure the activity after 9.6 days?
2. A radioactive sample has an initial activity of 36,000 cpm and a half-life of 14.6 minutes. What will be the activity after three half-lives?
3. A radioactive sample has an activity of 450 cpm three half-lives after the initial activity was determined. What was the original activity?
4. A sample of a certain isotope has an initial activity of 40,000 cpm. After 24.8 days, the activity is 2500 cpm. What is the half-life of this isotope?

Further Reading/Supplementary Links

- Half-life calculator: http://www.1728.org/halflife.htm
- Chart of half-lives for all radioactive isotopes: http://www.evs.anl.gov/pub/doc/tbl2-rad-prop.pdf

Points to Consider

- We have learned of various spontaneous decay processes that cause new isotopes to be produced. Are there other ways to cause nuclear reactions?

24.3 Fission and Fusion

Lesson Objectives

- Define nuclear fission and nuclear fusion.
- Write fission reactions and identify the components of these reactions.
- Describe the fission reactions employed in nuclear power plants.
- Write examples of nuclear fusion reactions.
- List the difficulties associated with using fusion reactions to generate power.

Lesson Vocabulary

- **nuclear fission**: The process of bombarding heavy nuclei with neutrons, causing them to split into two smaller nuclei.
- **nuclear reactor**: A technology used in nuclear power plants to facilitate fission chain reactions in order to vaporize steam, which then powers turbines and generates electricity.
- **nuclear fusion**: The process of combining small nuclei into larger nuclei, creating large amounts of energy.

Check Your Understanding

- What are the various types of spontaneous nuclear decay?

Nuclear Fission

Radioactive decay, such as the emission of alpha or beta particles, is not the only way that nuclei can be transformed into other isotopes. As it turns out, bombarding certain heavy nuclei with neutrons will cause them to split into two smaller nuclei, in a process known as **nuclear fission**. Nuclear fission was first discovered by the German scientists Fritz Strassman and Otto Hahn in the 1930s. They began their work by bombarding atoms of uranium with neutrons, hoping to create other large elements. Instead, they were surprised to find barium-141, a much smaller element. Later on in collaboration with Austrian physicist Lise Meitner, they demonstrated the release of neutrons and a large amount of energy along with the smaller nuclei.

Figure 24.8 illustrates the basic nuclear fission process. A neutron (generally produced by some controlled process, not usually a natural event) collides with an atom of uranium-235. Then, a very unstable U-236 atom forms, which proceeds to split into two smaller nuclei (Kr-92 and Ba-141). This process also results in the release of three new neutrons and a large amount of energy.

In **Figure** 24.9, we see the possible fates of the newly generated neutrons. Some will be lost to the surroundings, and others will collide with non-fissionable nuclei, such as uranium-238. However, some will collide with other U-235

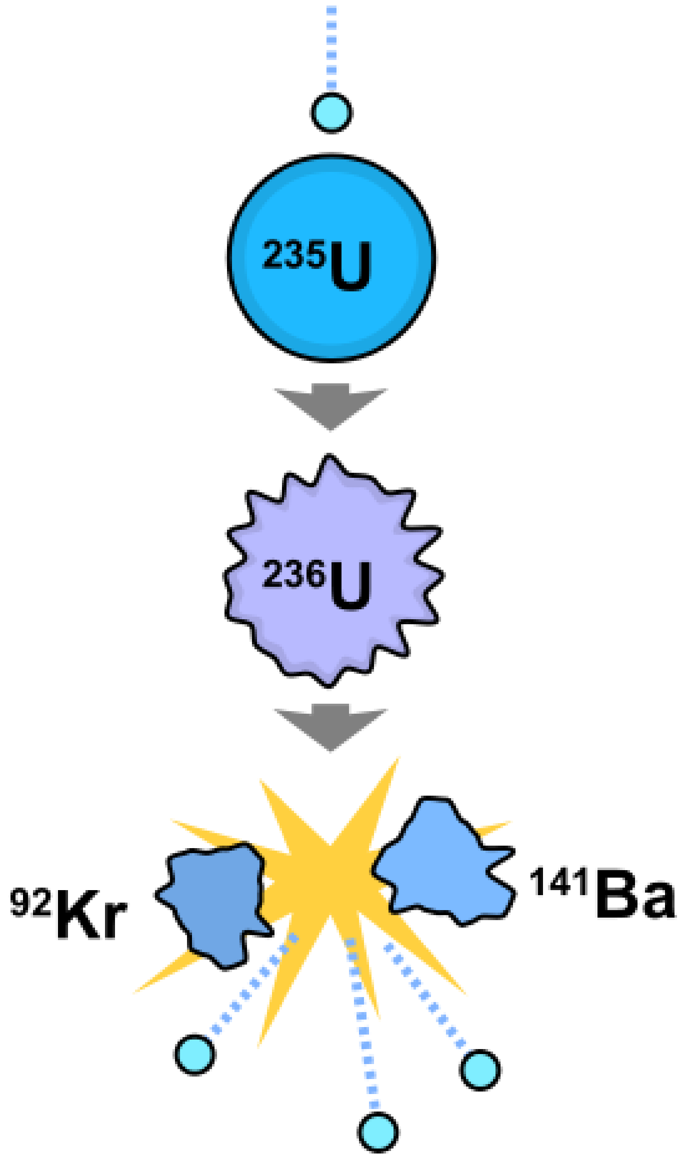


FIGURE 24.8

The products of a nuclear fission reaction include smaller nuclei, neutrons, and energy.

atoms, thus propagating the fission process and releasing even more neutrons. We will see later how this propagation of neutrons can be employed in a nuclear reactor to generate electricity.

As with the equations for nuclear decay, fission reactions are balanced in terms of both mass number and atomic number. For example, the fission process illustrated above is represented by the following equation:

$^{235}_{92}\text{U} + ^{1}_{0}n \rightarrow ^{92}_{36}\text{Kr} + ^{141}_{56}\text{Ba} + 3^{1}_{0}n + \text{energy}$

On each side of the equation, the mass numbers add up to 236 and the atomic numbers add up to 92. Another set of possible fission products from U-235 is formed by the following nuclear reaction:

$^{235}_{92}\text{U} + ^{1}_{0}n \rightarrow ^{87}_{35}\text{Br} + ^{146}_{57}\text{La} + 3^{1}_{0}n + \text{energy}$

Again both the mass numbers and the atomic numbers are balanced on each side of the equation.

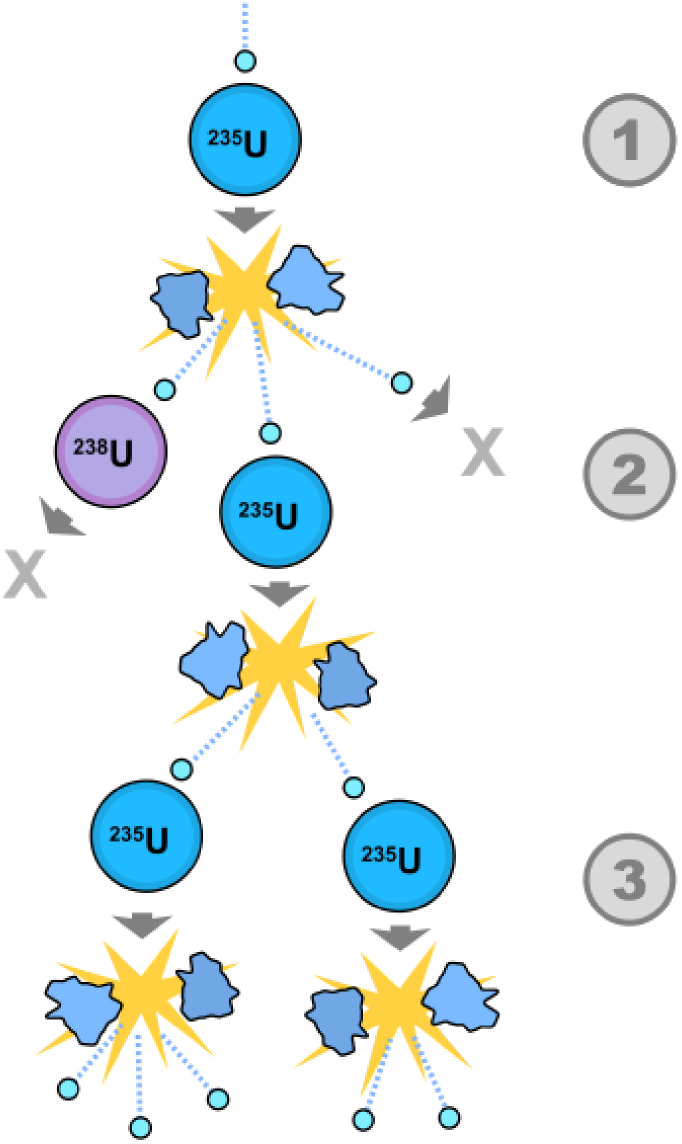


FIGURE 24.9
Nuclear fission can be thought of as a chain reaction.

Nuclear Power Generation

The generation of electricity is critical for the operation of nearly all aspects of modern society. The following diagram illustrates the types of fuels used to generate electrical power in the Unites States. In 2009, almost 45% of the power generated in the U.S. was derived from coal, with natural gas making up another 23% of the total. The third primary source of electrical energy is nuclear power, which accounts for approximately 20% of the total amount generated. All of these fuels give off energy in the form of heat. This heat is used to convert water into steam, which is then used to turn a turbine, thus generating electrical power.

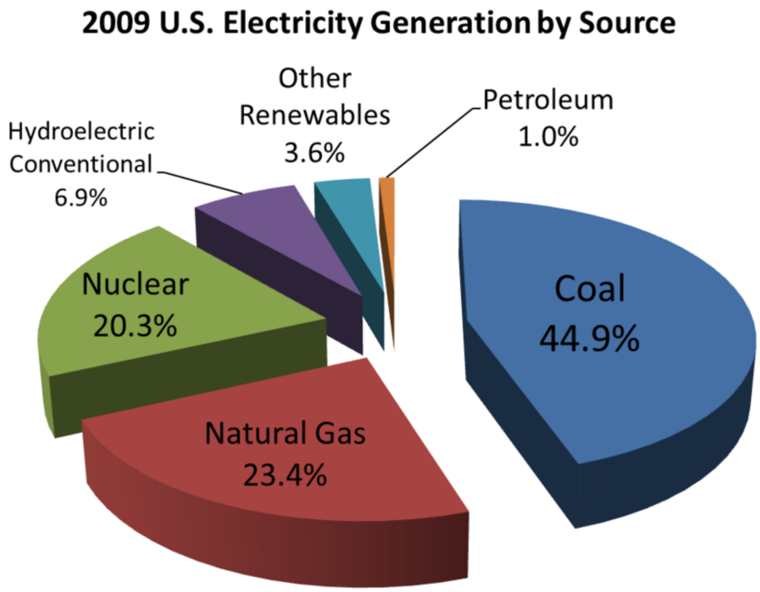


FIGURE 24.10

Electricity is one of the main sources of energy used to generate power and is derived from many processes.

Figure 24.11 shows the layout of a typical nuclear power plant which employs **nuclear reactors** to generate energy. The radioactive rods are in the red container, where the energy released during the fission process is used to vaporize water into steam. The steam passes through the turbine and causes the turbine to spin, generating electricity. As the steam condenses, it is run through a cooling tower to lower its temperature. The water then recirculates through the reactor core to be used again.

The control rods, generally made of boron or various metal alloys, play an important role in the modulation of the nuclear chain reaction. Each fission event produces more neutrons than were present initially. If each neutron caused the fission of another atom of U-235, this chain reaction would accelerate, resulting in more and more energy and neutrons being released. The purpose of the control rods is to absorb excess neutrons, which regulates the rate of the chain reaction and prevents overheating. If enough energy were released all at once, a nuclear meltdown might occur, in which the radioactive material starts to melt and leak out of the reactor core along with the water. Control rods help to prevent this type of situation.

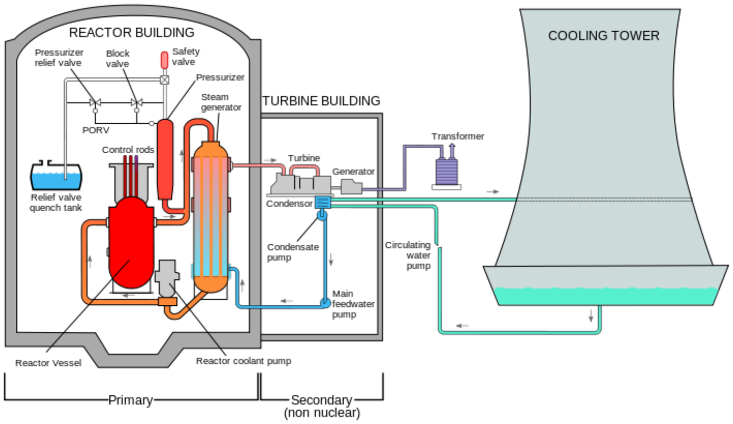


FIGURE 24.11

Nuclear Fusion

In contrast to nuclear fission, in which smaller nuclei are created from a larger nucleus, **nuclear fusion** combines smaller nuclei into larger ones. If the starting nuclei are very small, this process releases an extremely large amount of energy. The fusion of hydrogen atoms into helium is responsible for the energy released by the Sun and other small stars. A typical fusion reaction is shown in the following figure:

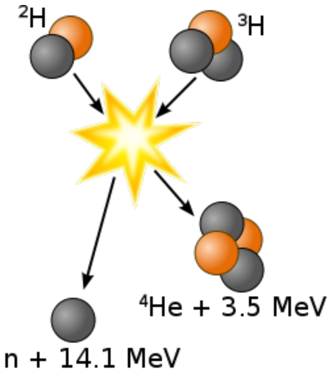


FIGURE 24.12

Collisions between hydrogen atoms demonstrate one form of nuclear fusion.

In this reaction, two different isotopes of hydrogen collide to form a helium-4 nucleus, which is much more stable. A neutron is also ejected, along with the release of large amounts of energy often in the form of gamma rays. Hydrogen-2 (deuterium) and hydrogen-3 (tritium) can be formed by other fusion reactions between isolated protons and neutrons. All of these particles are plentiful in the extremely high temperatures present inside a star.

Larger stars are also fueled by fusion reactions involving heavier nuclei, such as carbon, nitrogen, and oxygen. However, the principle is the same; smaller nuclei collide and fuse into a larger nucleus, resulting in the release of energy.

Because so much energy is released during nuclear fusion, being able to reproduce this process in a controlled fashion would provide almost limitless amounts of energy. Additionally, the waste products from fusion reactions are generally not radioactive, so this would be a much less hazardous source of nuclear energy than fission reactors.

Unfortunately, nuclear fusion reactions generally require temperatures in the millions of degrees, which is very difficult to achieve in the laboratory. The development of other methods to force atoms close enough together to cause a reaction have been limited, and harnessing the energy released by nuclear fusion reactions is not yet a feasible option.

Lesson Summary

- Nuclear fission reactions are initiated when certain heavy nuclei, such as uranium-235, collide with free neutrons. The products of a fission reaction are two smaller isotopes, more neutrons, and a great deal of energy.
- Nuclear reactors use fission reactions to vaporize water. The resulting steam is used to drive a turbine, which generates electricity.
- Nuclear fusion involves the collision of smaller atoms to form larger ones. Extremely large amounts of energy are released in this process.
- Nuclear fusion reactions occur in stars but are difficult to reproduce in a controlled laboratory setting, due to the extreme temperatures required.

Lesson Review Questions

1. Define nuclear fission.
2. What happens to newly generated neutrons in nuclear fission reactions?
3. Write two different fission reactions involving U-235.
4. Explain how radioactive isotopes can be used to generate electricity.
5. Define nuclear fusion.
6. Describe the problems associated with the development of nuclear fusion as a feasible power source.

Further Reading/Supplementary Links

- Animation of nuclear fission process: http://upload.wikimedia.org/wikipedia/commons/8/86/UFission.gif
- Fusion reactions in the sun: http://zebu.uoregon.edu/~soper/Sun/fusionsteps.html
- Nuclear reactions in the sun: http://www.cartage.org.lb/en/themes/sciences/chemistry/nuclearchemistry/NuclearReactions/NuclearFusion/NuclearFusion.htm
- Comparison between fission and fusion reactions: http://www.diffen.com/difference/Nuclear_Fission_vs_Nuclear_Fusion

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Points to Consider

- Do radioisotopes have any constructive uses other than energy production?

24.4 Applications of Radioactivity

Lesson Objectives

- Describe sources of radiation in our environment.
- Describe the effects of nuclear radiation on living systems.
- Describe the use of radioisotopes in the diagnosis and treatment of various diseases.

Lesson Vocabulary

- **cancer cell**: A cell in which the control processes that regulate cell growth and division are not working properly.
- **PET scan**: A medical technique known as positron emission tomography which is used to study processes in the brain.

Check Your Understanding

- What is the relative penetrating power for each type of radioactive decay?
- What happens to a positron when it collides with an electron?

Introduction

Previously, you learned about certain devices such as a Geiger counter which are used to measure exposure to radiation. In this lesson you will learn about the negative effects of different radiation sources in our lives, as well as some positive ways in which radiation can be used in the medical field.

Environmental Sources of Radiation

We are all exposed to a small amount of radiation in our daily lives. Much of this exposure is due to naturally occurring radioactive substances and cosmic radiation (literally high energy particles flying in from space). For example, radon is a colorless, odorless gas formed from the decay of various uranium and thorium isotopes, which are found in the soil throughout much of the U.S. As a noble gas, radon is chemically inert, but it is also radioactive and can easily be inhaled into the lungs. Radon exposure is highest in homes that lack good air circulation, which would allow the gas to be cycled out of the residence. Fortunately, there are a number of inexpensive approaches to decreasing your exposure to radon.

Effects of Radiation

Radiation can seriously harm living organisms, including humans. In order to better understand how nuclear radiation causes damage on the cellular level, we should first understand the basics of how the cell works. DNA in the nucleus is responsible for protein synthesis and for the regulation of many cellular functions. In the process of protein synthesis, DNA partially unfolds to produce messenger RNA (mRNA). The mRNA leaves the nucleus and interacts with ribosomes, transfer RNA, amino acids, and other cellular constituents in the cytoplasm. Through a complex series of reactions, proteins are produced to carry out a number of specialized processes within the organism. Anything that disturbs this flow of reactions can damage to the cell.

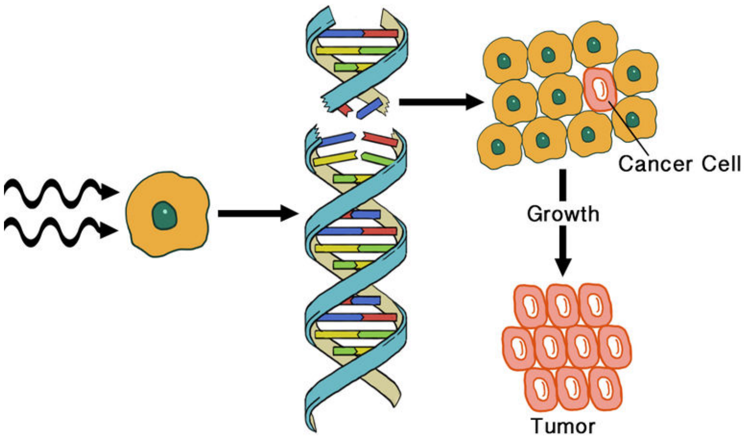

FIGURE 24.13

The most harmful situation is when nuclear radiation does something to alter the structure of the DNA. If this prevents the production of a crucial protein, the cell will malfunction or die. In an even worse scenario, some changes to DNA will cause the cell to become cancerous. In a **cancer cell**, the control processes that regulate cell growth and division are not working properly. As a result, they grow and divide rapidly, often interfering with the functioning of nearby healthy cells. For example, over time internal radon exposure can lead to the development of lung cancer. This is especially problematic for smokers, who already have exposed their lungs to significant amounts of carcinogens. Tissue damage is also common in people with severe exposure to radiation.

Radioisotopes in Medical Diagnosis and Treatment

Radioisotopes are widely used to diagnose, and sometimes treat, various diseases. For diagnosis, the isotope is administered to the patient and then located in the body using a scanner of some sort. The source of the decay product (often gamma emission) can be located by the scanner, and a map of where the isotope was transported in the body can be generated. This information is often very valuable for diagnosing certain medical problems.

For example, a radioactive isotope of iodine (I-131) is used in both the diagnosis and treatment of thyroid cancer. The thyroid will normally absorb some iodine to produce iodine-containing thyroid hormones. An overactive thyroid gland will absorb a larger amount of the radioactive material. If this is the case, more and more radioactive iodine can be administered, where it will cluster in the diseased portion of the thyroid tissue and kill some of the nearby cells. Cancer treatments often cause patients to feel very sick, because while the radiation treatment kills the unwanted cancer cells, it causes damage to some healthy cells in the process.

Technetium-99m is perhaps the most widely used radioisotope in diagnosis and treatment (the "m" stands for metastable indicating a very short half-life). This isotope decays to Tc-99 by gamma emission. If a very low dose of the isotope is administered, the radiation will be of a very low intensity, so cellular damage will be minimal. Additionally, gamma radiation has a very high penetrating power, so most of it will reach the detector in the scanner. The half-life of Tc-99m is about six hours, so it will remain in the body for some time.

Tc-99m is often used to look at cardiac damage. If there is less blood flow in the heart, there will be less of the isotope concentrated in the heart muscle. Similar information can be obtained for blood flow in the brain.

There are presently over 25 different isotopes in use for diagnosis and medical treatment. A very partial list can be seen in **Table** 24.2:

TABLE 24.2: **Isotopes Used for Diagnosis and Medical Treatment**

Isotope	Half-Life	Application
Cr-51	28 days	labeling red blood cells
Fe-59	446 days	study iron metabolism in spleen
Xe-133	5 days	study lung function
Ho-166	26 hours	cancer treatment

PET Scans

One of the more interesting and useful medical applications of radioisotopes is positron emission tomography (PET), often referred to as a **PET scan**. This technique is especially useful for studying processes in the brain. Many compounds do not enter the brain because of the blood-brain barrier, which is a particularly selective filter that prevents many substances in the blood from being transported into brain tissue.

In order to get a good picture of what is happening in the brain, radiolabels (radioactive trackers) are attached to different compounds that are known to enter the brain. Since the brain accounts for about 25% of the body's glucose consumption, this molecule is often labeled with a positron emitter, such as F-18 (half-life of 109.8 minutes), to study brain function in general. Other radiolabels are attached to specific compounds that will localize in certain areas of the brain to look at specific structures.

The PET scanner detects gamma emissions from the collision of a positron with an electron. A positron has the same mass but opposite charge of an electron. As the positron is released from the nucleus of the atom, it will collide with an electron. This meeting of matter (electron) with antimatter (positron) results in annihilation of both particles and the release of two gamma photons that travel in exactly opposite directions. The scanning apparatus detects these gamma rays and stores the data in a computer. From this information, a detailed picture of the brain can be developed.

FIGURE 24.14

One useful application of PET scanning is in the diagnosis of Alzheimer's disease. This debilitating condition associated with memory loss primarily occurs in elderly individuals. A protein known as beta-amyloid gradually forms deposits, or plaques, in the brain. Severe memory loss and impaired movement appear to be direct results of the plaque growth.

The compound known as "Pittsburgh compound B" is often used to identify areas of plaque in the brain. The C-11 atom bound to the nitrogen has a half-life of just 20.38 minutes, so administration and detection must be accomplished very quickly.

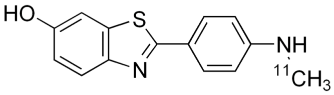

FIGURE 24.15

The label attaches to plaques in the brain and can be observed using a PET scanner.

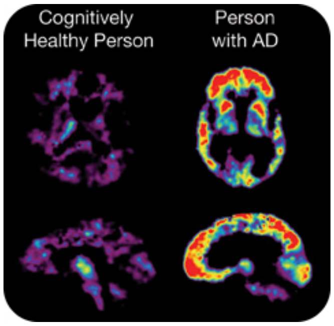

FIGURE 24.16

The computer translates the intensity of the decay from the radioactive isotope into a color scale, with red indicating a high level of radioactivity and yellow indicating somewhat less activity. We can see from the scans that the cognitively healthy individual shows the presence of very little plaque in the brain, whereas the individual with Alzheimer's has high concentrations of beta-amyloid in numerous areas of the brain.

Other studies have used PET scans to look at certain regions of the brain in drug addicts. One of the theories about drug addiction involves activity related to the molecule dopamine, a chemical that helps carry certain nerve impulses from one brain cell to the next. Studies on dopamine activity in the brain have been helpful in understanding the biochemical processes behind addiction.

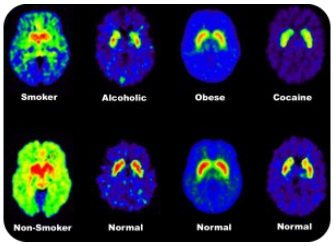

FIGURE 24.17

Figure 24.17 shows the accumulation of radioactive compounds that bind to dopamine receptors. The non-addicted individuals have large numbers of receptors for dopamine. The addicted persons show less binding to these receptors, indicating that fewer receptors are present.

Lesson Summary

- Everyone is exposed to low amounts of background radiation from medical procedures and naturally occurring radioactive substances.
- Radioactive emissions can alter the structure of DNA, which can sometimes lead to cell death or even cancer.
- Radioisotopes are widely used in medical diagnosis. These isotopes need to have short half-lives so that they can be administered in very low doses, thus minimizing damage to cells.
- Radioactive isotopes are also used in the treatment of certain diseases, such as cancer. These isotopes are administered to only the diseased tissue, with the goal of destroying the unhealthy cells.
- PET scans are very useful in looking at brain structure and chemistry.

Lesson Review Questions

1. How are radioactive materials harmful to cells?
2. Why are cancer cells so detrimental in the body?
3. Why should radioisotopes given to patients have short half-lives?
4. Explain how the radioactive isotope of iodine is used to diagnose and treat thyroid cancer.
5. How is Tc-99m used to diagnose bone cancer?
6. Why is PET scanning so useful in studying the brain?

Further Reading/Supplementary Links

- Radioisotopes in medicine: http://www.world-nuclear.org/info/inf55.html
- Use of radioisotopes in diagnosis and treatment: http://www.rsc.org/images/essay5_tcm18-17767.pdf
- Positron emission tomography: http://www.radiologyinfo.org/en/info.cfm?pg=pet

Points to Consider

- Can you think of any historical events in which people may have been exposed to dangerous amounts of radioactivity?

24.5 References

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CHAPTER 25 Organic Chemistry

Chapter Outline

25.1 HYDROCARBONS – THE BACKBONE OF ORGANIC CHEMISTRY

25.2 FUNCTIONAL GROUPS

25.3 ORGANIC REACTIONS

25.4 REFERENCES

From the simple and pleasurable creation of a craft item, like the necklace above, to the heavy-duty pipes that carry water and other materials, polymers are an essential part of today's society. Polymers are very large molecules based on small structural units that are repeated hundreds or even thousands of times. Most of these materials are based on carbon chains, which puts them in the domain of organic chemistry. However, polymers are but one application of modern organic chemistry. The chemistry of carbon-containing compounds encompasses over twenty million compounds and thousands of different reactions, many named after the chemists who developed them. This chapter will give a small sampling of the complex field of organic chemistry.

Jana Lehmann. commons.wikimedia.org/wiki/File:Buttons_necklace.jpg. CC BY 2.0.

25.1 Hydrocarbons – The Backbone of Organic Chemistry

Lesson Objectives

- Describe the bonding characteristics of carbon.
- Differentiate between saturated and unsaturated hydrocarbons.
- Draw and name structures for simple hydrocarbons.

Lesson Vocabulary

- **organic chemistry**: A field of chemistry which studies the structure and reactivity and nearly all carbon-containing compounds.
- **hydrocarbon**: Molecules that contain only carbon and hydrogen atoms.
- **alkane**: Hydrocarbons in which all carbons are connected by single bonds.
- **alkene**: A compound in which a C=C double bond is present.
- **alkyne**: A compound in which a C≡C triple bond is present.
- **saturated**: Hydrocarbons which contain no multiple bonds.
- **unsaturated**: Hydrocarbons which contain at least one double or triple bond.

Check Your Understanding

Recalling Prior Knowledge

- How many covalent bonds does each carbon atom in a molecule usually make?
- How can the hybridization of a given carbon atom be determined?

Introduction

Before the 19th century, scientists had believed that the chemical processes occurring in living systems were fundamentally different from those that could be observed in a test tube. They classified chemistry into two categories: organic and inorganic. Organic processes were thought to take place only in living systems, while inorganic processes occurred in material that was not living. A "vital force" was believed to be necessary for organic reactions to occur. This way of thinking was challenged in 1828 by the German chemist Friedrich Wöhler when he synthesized an organic compound (urea, found in urine) from an inorganic precursor (ammonium cyanate):

Since then, the distinction between organic and inorganic compounds and reactions has blurred. Currently, the field of **organic chemistry** studies the structure and reactivity of nearly all carbon-containing compounds. Over twenty million organic compounds are known, ranging from very simple molecules to complex proteins.

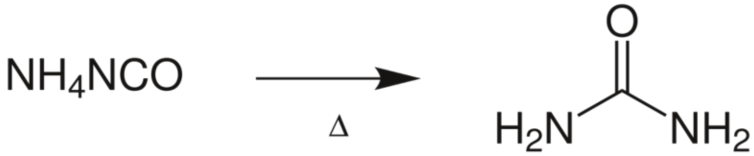


FIGURE 25.1

Reaction of ammonium cyanate to form urea.

Bonding and Hybridization in Carbon

Let's briefly review the basics of covalent bonding as they pertain to carbon. Carbon has four valence electrons, which have a $2s^22p^2$ configuration in isolated carbon atoms. These four electrons allow carbon to form four covalent bonds, which can mean four single bonds or some combination of single, double, and triple bonds.

A carbon atom that has formed single bonds to four different atoms has an sp^3 hybridization. The angles between these bonds are equal to 109.5°.

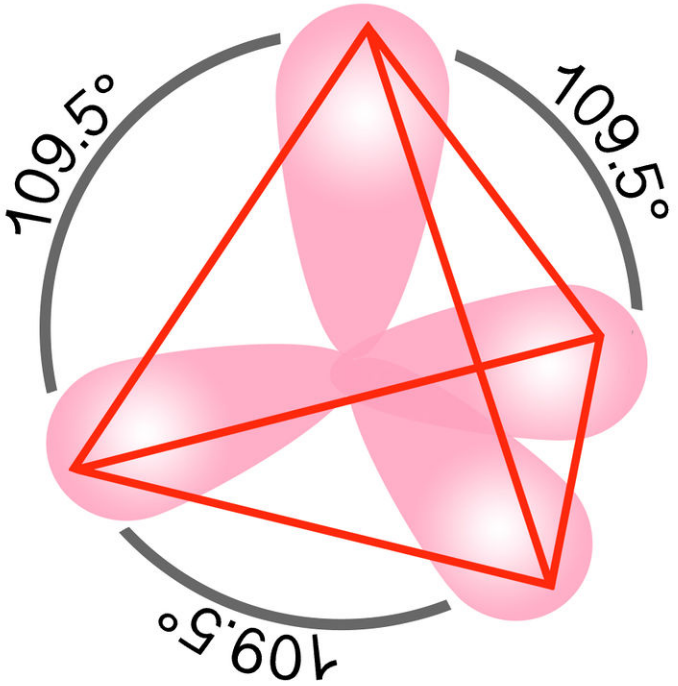
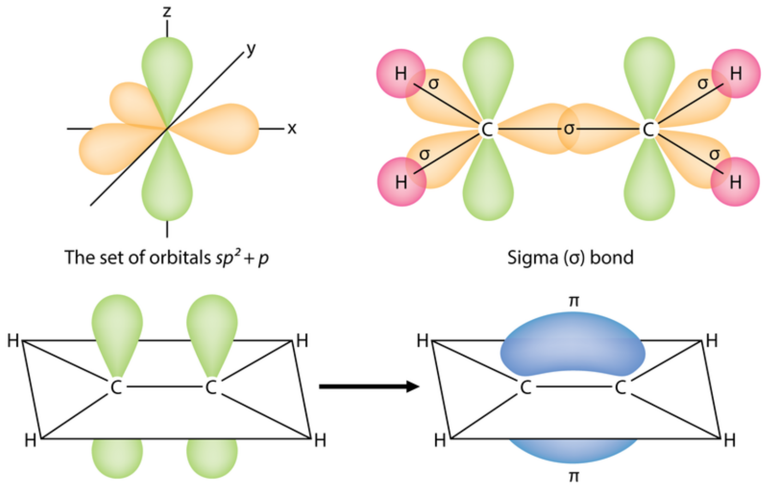


FIGURE 25.2

Hybridization of the valence orbitals in a carbon atom to make a set of four sp^3 orbitals.

Recall that a double bond consists of one sigma bond and one pi bond. In order for a double bond to be formed, each participating carbon atom must have at least one unhybridized p orbital. In a carbon-carbon double bond where both carbons are bonded to two additional atoms, each carbon is sp^2 hybridized. The double bond includes a sigma bond between a hybrid orbital from each carbon and a pi bond between the leftover p orbital from each carbon. The angles between any two bonds for an sp^2 hybridized carbon are approximately 120°.

A triple bond (-C≡C-) requires each of the carbon atoms to be sp hybridized. One hybrid orbital and two p orbitals from each atom are involved in forming the one sigma and two pi bonds that make up a triple bond. Each carbon



The set of orbitals $sp^2 + p$

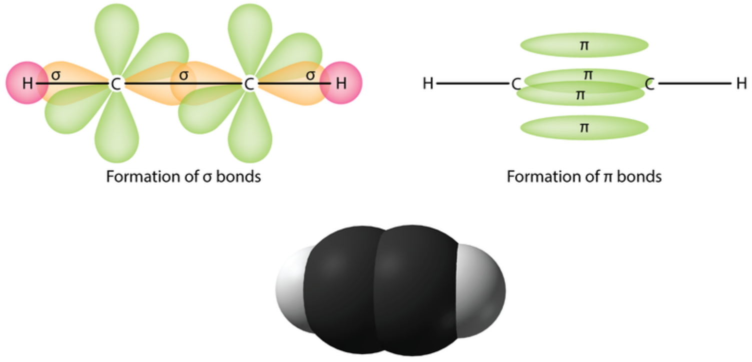
Sigma (σ) bond

Overlap of *p* orbitals leading to pi (π) bond

FIGURE 25.3

Hybridization of the valence orbitals in a carbon atom to make a set of three sp^2 orbitals, with one p orbital left over.

atom is also bonded to one other atom via the other hybrid orbital. The angle between these two bonds for an sp hybridized carbon is 180°.



Formation of σ bonds

Formation of π bonds

Space filling model

FIGURE 25.4

Hybridization of the valence orbitals in a carbon atom to make a set of two sp orbitals, with two p orbitals left over.

Hydrocarbon Structure and Naming

Hydrocarbons are molecules that contain only carbon and hydrogen atoms. Because each carbon atom can form covalent bonds with up to four other atoms, very large and complex molecules can be formed just from these two elements. Hydrocarbons in which all carbons are connected by single bonds are known as **alkanes**. If a C=C double bond is present, the compound is now an **alkene**. A triple bond between two carbons (C≡C) makes the compound an **alkyne**. Hydrocarbons can also be broadly classified as either **saturated**, which means they contain no multiple bonds, or **unsaturated**, which means they contain at least one double or triple bond.

The simplest alkanes are linear chains of carbon atoms, in which no carbon is bonded to more than two other carbon atoms. Branched alkanes are also possible, greatly increasing the complexity of possible structures that can be formed from a given set of carbon and hydrogen atoms. The first six linear alkanes are listed in the **Table** 25.1:

TABLE 25.1: **alkane**

Structure	Name
CH_4	methane
CH_3CH_3	ethane
$CH_3CH_2CH_3$	propane
$CH_3CH_2CH_2CH_3$	butane
$CH_3CH_2CH_2CH_2CH_3$	pentane
$CH_3CH_2CH_2CH_2CH_2CH_3$	hexane

Starting with pentane, linear alkanes are named by adding "-ane" to the Latin prefix corresponding to the number of carbon atoms in the chain.

Since organic chemistry is essentially carbon chemistry, it is important to understand the structure of the hydrocarbon chain. Although alkanes are relatively unreactive, they provide the backbone for more reactive structures known as functional groups, which we will discuss in the following lesson. Most organic reactions will alter only specific functional groups, while the hydrocarbon backbone is generally left intact.

Drawing Organic Structures

We can indicate hydrocarbon structures in several ways. The entire structure of hexane is shown below using the usual rules for drawing Lewis structures. Each atom is indicated with the symbol of its element, and each single covalent bond is represented with a line.

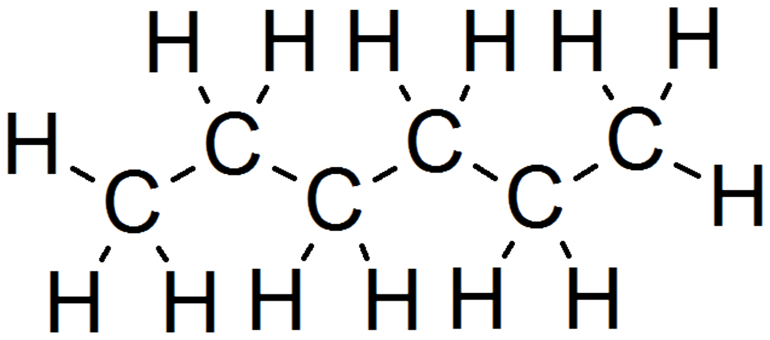


FIGURE 25.5
Hexane structure, with all atoms shown.

However, this type of structure is time consuming to draw and can become very cluttered. Because carbons and hydrogen atoms are so prevalent in organic molecules, a chemical shorthand was developed so that not all atoms need to be explicitly drawn. Below is another way to draw the hexane molecule:

FIGURE 25.6
Skeleton structure for hexane.

In the above structure, the two ends of the chain and each of the intervening corners represents a carbon atom. The six carbon atoms are connected in a linear chain by single bonds. Unless indicated otherwise, we also assume that each carbon makes four total bonds, and any bonds that are not explicitly drawn are connected to hydrogen atoms. The internal carbon atoms above each make single bonds to two other carbons, leaving two bonds not shown. Thus, each of these carbon atoms is connected to two hydrogens. The carbons on the ends of the chain only have one covalent bond drawn in, so they must each be bonded to three hydrogen atoms. Compare these two representations of hexane, keeping in mind that both are conveying the same information.

Locating Functional Groups

Most organic compounds are not simple hydrocarbons; they have functional groups that provide additional reactivity pathways. To indicate the location of a functional group within the name of an organic molecule, the hydrocarbon backbone is generally numbered. For example, the hexane molecule (see above) could serve as a parent chain. It has six carbons in it, which can be numbered C-1, C-2, and so on. As long as there is nothing else attached to the chain, it does not matter where we start counting. There is no way to designate which carbon is C-1 and which carbon is C-6. However, once a substituent is added to the chain, we can then indicate a start and an end to the molecule.

Now, let's introduce a functional group by replacing one of the hydrogen atoms in hexane with a chlorine atom:

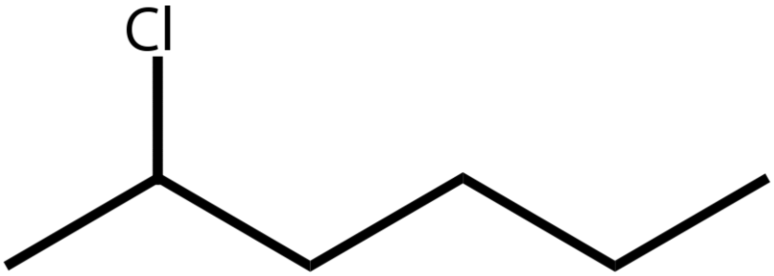


FIGURE 25.7

2-Chlorohexane

To indicate that this molecule has a chlorine atom attached to the hydrocarbon backbone, we could name this compound *chloro*hexane. However, that name would not be enough information to uniquely identify this molecule, since the chlorine could be attached to any of the carbon atoms. To indicate the location of this substituent, we number the chain, starting with the end that will place the functional group on the carbon atom with the lowest number. Depending on which end is C-1, the above compound could be called either 2-chlorohexane or 5-chlorohexane. According to our rule about giving functional groups the lowest possible numbers, this molecule would be called 2-chlorohexane.

Other alkanes with a single halogen atom can be named using a similar strategy, except chloro would be replaced by fluoro, bromo, or iodo, depending on the identity of the halogen.

The location of double and triple bonds must also be indicated with numbers. For example, consider the following two molecules: $CH_3CH_2CH{=}CHCH_3$ and $CH_2{=}CHCH_2CH_2CH_3$. Both of these have one double bond. A simple 5-carbon alkane (no double bonds) would be called pentane, so adding in one double bond changes the name of the structure to pent*ene*, since it is an alk*ene*. However, the location of the double bond affects the physical and chemical properties of the compound.

In order to distinguish between the two molecules above, we again number the carbon chain, starting from the end that will give the functional group (the alkene) the lowest number. For $CH_3CH_2CH{=}CHCH_3$, we would start counting on the right end. The double bond is between carbon atoms 2 and 3, so this molecule would be named pent-2-ene, where the lower of the two numbers is used. For $CH_2{=}CHCH_2CH_2CH_3$, we would start counting on the left end. The double bond is between carbon atoms 1 and 2, so this molecule would be named pent-1-ene.

Triple bonds can be identified in a similar way, except that the suffix *-yne* is used instead of *-ene* (to indicate that we are dealing with an alk*yne* instead of an alk*ene*).

Cyclic Hydrocarbons

Many organic compounds are cyclic in structure. The compound cyclohexane involves a ring of six carbon atoms, each of which is also bonded to two hydrogen atoms. **Figure** 25.8 shows a few different representations of the cyclohexane molecule.

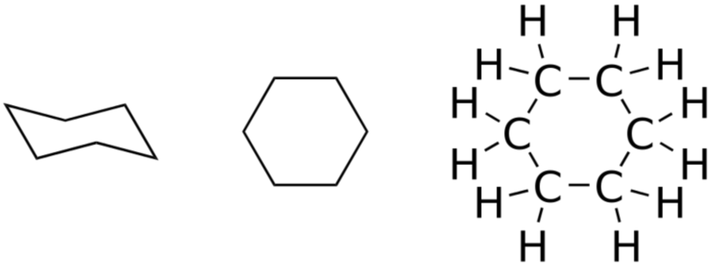


FIGURE 25.8

Ways of representing the structure of cyclohexane.

The structure on the right gives the complete picture, where all atoms are explicitly drawn. The middle structure shows a flat representation of the molecule based on the standard shorthand rules for drawing organic structures. The folded structure on the left highlights an important point about organic chemistry –the three-dimensional structure of a molecule is not always portrayed accurately by flat drawings. The true structure of the cyclohexane molecule has a puckered shape that looks more like the structure on the left than the flat hexagon in the center. The preferred three-dimensional conformations of organic molecules often play an important role in how the molecule reacts. The following structures illustrate some of the interesting and complex shapes organic molecules can take on:

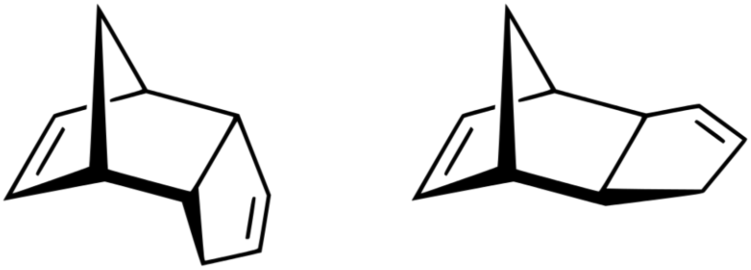


FIGURE 25.9

Complex organic structures.

Aromatic hydrocarbons are a special subset of cyclic hydrocarbons. Although many "aromatic" compounds have distinctive odors, this word is used very differently in organic chemistry than in everyday life. The benzene ring is the foundational structure for most aromatic compounds:

The illustrations above give different perspectives on the actual structure of the molecule. The left-hand illustration shows the six hydrogen atoms attached to the six carbons and indicates that there are three double bonds in the ring, while the next structure shows this symbolically. A more realistic picture is given by the next two models. The circle shows the reality of the bonding. The three pi bonds in the ring overlap one another and form a cloud of electrons above and below the plane of the ring. Benzene and its derivatives do not undergo the same reactions as most carbon-carbon double bonds, due to the special stability that is inherent in this type of interactive pi bonding.

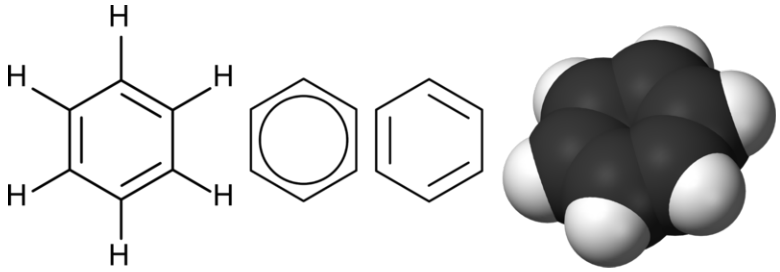


FIGURE 25.10

Ways to represent benzene ring.

Lesson Summary

- Hydrocarbons contain only carbon and hydrogen.
- Alkanes contain only carbon-carbon single bonds.
- Alkenes contain one or more carbon-carbon double bonds.
- Alkynes contain one or more carbon-carbon triple bonds.
- Chemists use a shorthand for drawing organic structures that focuses on functional groups and simplifies the drawing of the hydrocarbon backbone.
- Many hydrocarbons are cyclic and adopt specific three-dimensional structures that influence their physical and chemical properties.
- Aromatic compounds are cyclic and have a cloud of pi electrons above and below the plane of the ring.

Lesson Review Questions

1. What is a hydrocarbon?
2. Classify the following hydrocarbons as saturated or unsaturated, and identify each as an alkane, alkene, or alkyne:
   a. $CH_3CH_2CH_2CH_3$
   b. $CH_3CH{=}CHCH_2CH_3$
   c. $CH_3C{\equiv}CH$
3. Name each of the compounds in the previous problem.

Further Reading/Supplementary Links

- Overview of organic chemistry: http://www.acs.org/content/acs/en/careers/whatchemistsdo/careers/organic-chemistry.html
- Organic chemistry nomenclature: http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/nomen1.htm
- Hydrocarbons: http://chemed.chem.purdue.edu/genchem/topicreview/bp/1organic/hydro.html

Points to Consider

- Is there a systematic way to classify organic compounds?

25.2 Functional Groups

Lesson Objectives

- Describe the importance of functional groups in organic reactions.
- Identify and name functional groups in compounds.
- Draw structures of functional groups.

Lesson Vocabulary

- **functional group**: An atom or group of atoms within a molecule that has similar chemical properties whenever it appears in various compounds.
- **alcohol**: A functional group that involves an oxygen atom that is bonded to one hydrogen atom and one carbon atom.
- **ether**: A functional group that consists of an oxygen atom that forms single bonds with two carbon atoms.
- **amine**: A nitrogen atom bonded to some combination of carbons and hydrogens.
- **carbonyl**: A carbon atom and an oxygen atom connected by a double bond.
- **aldehyde**: A carbonyl in which the carbon atom is most commonly bonded to one carbon atom and one hydrogen atom.
- **ketone**: A carbonyl in which the carbon atom makes single bonds with two other carbon atoms.
- **carboxylic acid**: A functional group in which the carbon atom is bonded to an OH group on one side and either a carbon or hydrogen atom on the other.
- **ester**: A functional group in which the carbon is bonded to one additional oxygen atom and one carbon or hydrogen atom, with the second oxygen atom bonded to another carbon atom.
- **amide**: A carbonyl which is attached to one nitrogen atom and one carbon or hydrogen atom.

Check Your Understanding

- What is organic chemistry?
- What serves as the framework for all organic compounds?

Introduction

With over twenty million known organic compounds in existence, it would be very challenging to memorize chemical reactions for each one. Fortunately, molecules with similar functional groups tend to undergo similar reactions. A **functional group** is defined as an atom or group of atoms within a molecule that has similar chemical properties whenever it appears in various compounds. Even if other parts of the molecule are quite different, certain functional groups tend to react in certain ways.

In the previous lesson, we already looked at two common functional groups: alkenes and alkynes. Although C-C and C-H single bonds are relatively unreactive, the pi bonds in alkenes and alkynes undergo a variety of characteristic reactions. We will look at some of these reactions in the next lesson. The majority of functional groups involve atoms other than carbon and hydrogen. Some of the most common functional groups are presented in the following sections.

Alcohols

The **alcohol** functional group involves an oxygen atom that is bonded to one hydrogen atom and one carbon atom. The carbon atom will be part of a larger organic structure. One way to indicate a generic alcohol would be with the formula R-OH. R represents any organic fragment in which a carbon atom is directly bonded to the explicitly indicated functional group (in this case, OH).

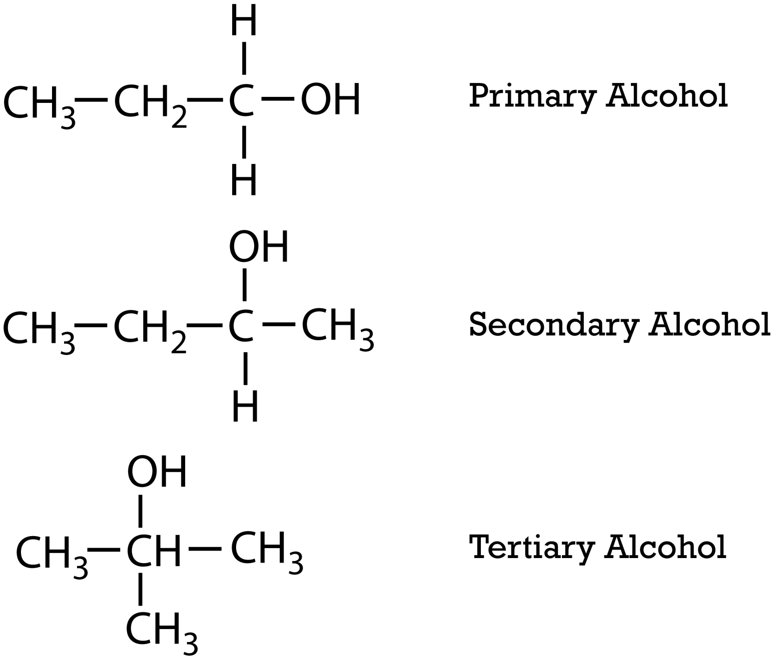


FIGURE 25.11

Alcohols can be classified as primary, secondary, or tertiary based on the characteristics of the carbon to which it is attached. In a primary alcohol, the carbon bonded directly to the oxygen atom is also bonded to exactly one carbon atom, with the other bonds generally going to hydrogen atoms. In a secondary alcohol, the carbon is attached to two other carbon atoms, and in a tertiary alcohol, the carbon is bonded to three other carbon atoms. The type of alcohol being used will determine the product of certain reactions. Note the naming of alcohols as illustrated above. The location of the –OH group is indicated with the number of the carbon to which it is attached.

We are already familiar with several common alcohols. For example, ethanol (CH_3CH_2OH) is the alcohol present in alcoholic beverages. It is also widely used in the industrial manufacture of other chemicals. Methanol (CH_3OH) is used as a gasoline additive or alternative. Additionally, methanol can be used to manufacture formaldehyde, which is employed in the production of plastics, paints, and other useful substances. Isopropanol is commonly known as rubbing alcohol. In addition to its industrial uses, isopropanol is used to clean various surfaces, including computer monitors, whiteboards, and even skin (e.g., before getting blood drawn).

Ethers

The **ether** functional group consists of an oxygen atom that forms single bonds with two carbon atoms.

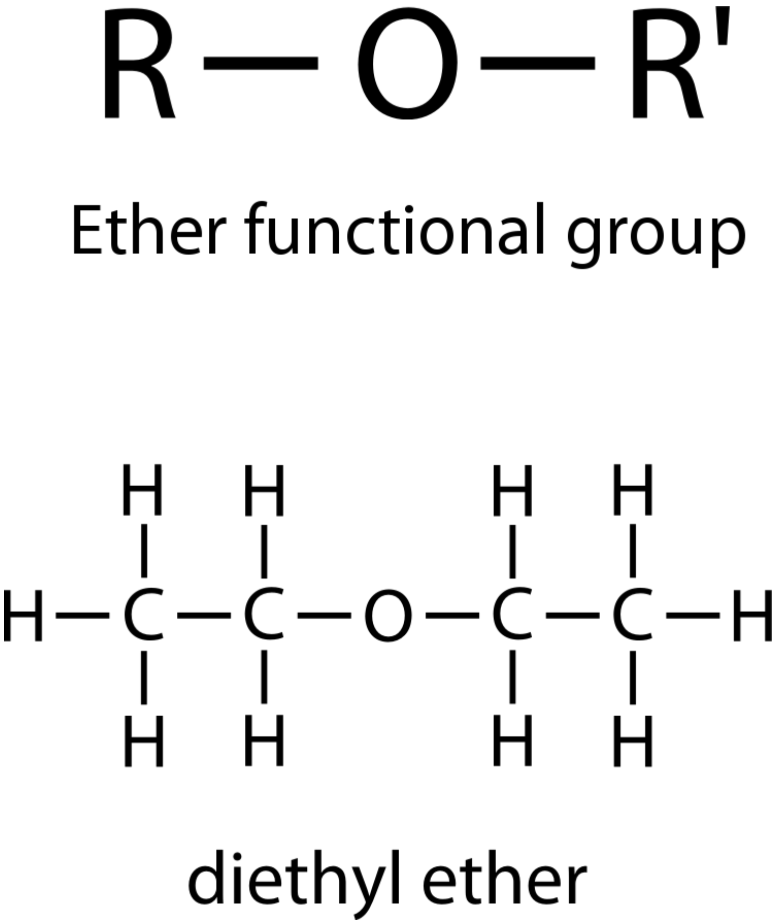


FIGURE 25.12

Ethers are good solvents for other organic compounds because of their low reactivity. They readily dissolve nonpolar molecules. Diethyl ether is perhaps the best known ether. It is widely used as a solvent and has been used as an inhalable anesthetic.

Although ethers themselves are relatively unreactive, they can be converted to peroxides after prolonged exposure to oxygen. Peroxides are very reactive and are often explosive at elevated temperatures. Many commercially available ethers come with a small amount of a peroxide scavenger dissolved in them to help prevent this type of safety hazard.

Amine

An **amine** consists of a nitrogen atom bonded to some combination of carbons and hydrogens.

Like alcohols, amines can be classified as primary, secondary, or tertiary. However, the rules for assigning these categories are slightly different. In an alcohol, the oxygen atom is always bonded to exactly one carbon atom, so we look at the branching on the adjacent carbon, not the oxygen atom itself. In a neutral amine, the nitrogen can be bonded to one, two, or three carbon atoms, and this is how we decide whether it is called a primary, secondary, or

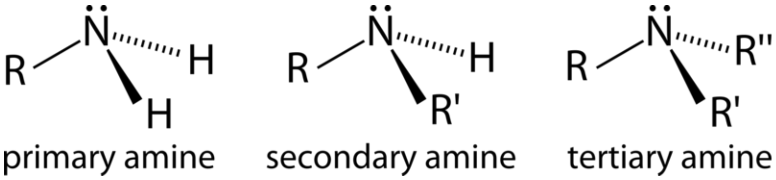


FIGURE 25.13

tertiary amine.

Neutral amines are weak bases, because the lone pair on nitrogen can act as a proton acceptor. Many smaller amines have very strong and offensive odors. For example, the aptly-named compounds cadaverine and putrescine are foul-smelling amines, formed as a part of the decay process after death.

Amines serve a wide variety of uses. Diphenylamine acts as a stabilizer for certain types of explosives. Amines are found as components in some lubricating materials, in developers, and are a part of waterproofing textiles. Some amines, such as novocaine, are used as anesthetics. Many pharmaceutical compounds contain amines, including 8 of the 10 most prescribed medications in 2012.

Aldehydes

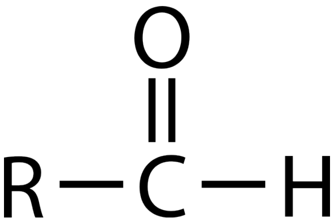


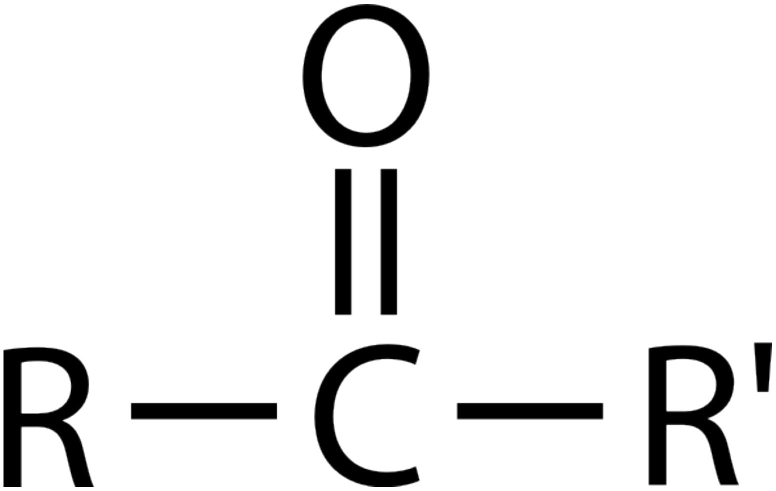
FIGURE 25.14

A very common structural component of organic structures is the **carbonyl**, which is simply a carbon atom and an oxygen atom connected by a double bond. The reactivity of carbonyls is primarily dictated by the polarization of the C=O bond, but the surrounding atoms also play a role in its specific reaction pathways. All of the remaining functional groups that we will be discussing contain a carbonyl, but they have different properties based on the other atoms that are also connected to the central carbon.

An **aldehyde** is a carbonyl in which the carbon atom is bonded to one carbon atom and one hydrogen atom (or two hydrogen atoms, see below). Because the hydrogen atom is so small, the partial positive charge on the carbonyl carbon is very easy for other molecules to approach, making aldehydes a particularly reactive type of carbonyl. Aldehydes are versatile reactants for a wide variety of organic syntheses. Many aldehydes also have distinctive flavors and aromas. For example, the flavor of cinnamon is primarily due to the molecule cinnamaldehyde, and vanillin is the aldehyde most responsible for the smell and taste of vanilla extract.

A special aldehyde is the molecule in which the carbonyl carbon is bonded to two hydrogen atoms. This molecule, called formaldehyde, has a wide variety of uses. By itself, it can be used as a tissue preservative or as a very harsh disinfectant. It is also used as a precursor to various materials, including plastics, resins, and other polymers.

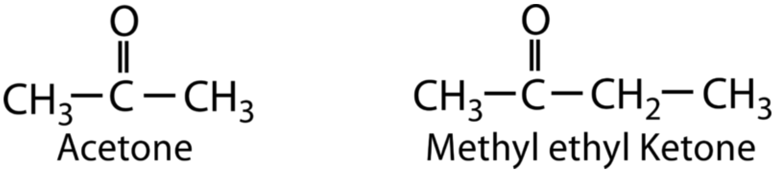
Ketones



$$R-\overset{O}{\overset{\|}{C}}-R'$$

FIGURE 25.15

A **ketone** involves a carbonyl in which the carbon atom makes single bonds with two other carbon atoms. Ketones undergo most of the same reactions as aldehydes, but they tend to be slightly less reactive. The simplest ketone is acetone, in which the carbonyl carbon is bonded to two CH_3 groups. This ketone is commonly used to remove fingernail polish and serves as an industrial solvent. Methyl ethyl ketone is used as a paint stripper and a solvent. Ketones are also used in the production of various polymers, either as a building block or as a solvent.



$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$$

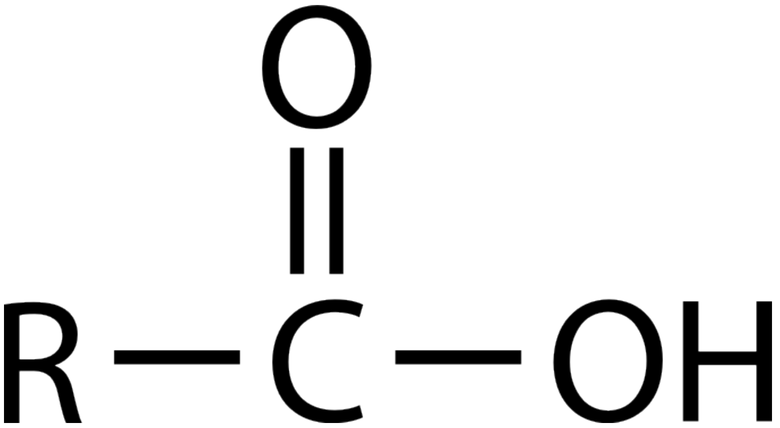
FIGURE 25.16

Carboxylic Acids

Carboxylic acids are another carbonyl-containing functional group, in which the carbon atom is bonded to an OH group on one side and either a carbon or hydrogen atom on the other.

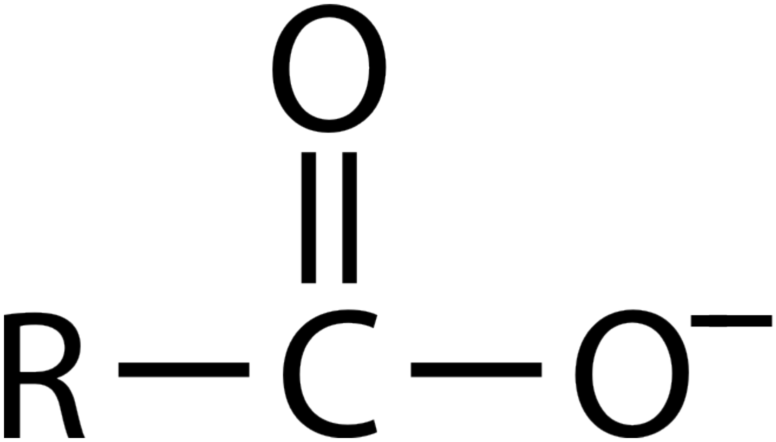
The OH group in an alcohol is not a very good acid; simple alcohols are similar in acidity to water. However, as the name implies, carboxylic acids are weak acids. An OH group that is directly connected to a carbonyl will ionize to a small extent when dissolved in water. The reason for this is the relative stability of the resulting anion. A carboxylate ion (**Figure** 25.18), in which the negative charge is spread over two different oxygen atoms through resonance structures, is more stable than an isolated oxygen-centered anion.

Carboxylic acids are used in a variety of environments. Formic acid acts as a protective chemical for many stinging insects and plants. Acetic acid gives vinegar its characteristic smell and flavor and is a fundamental biological and industrial building block. Carboxylic acids with longer carbon chains (fatty acids) are used by animals as a way of storing energy and are widely used in the manufacture of soaps. Some compounds contain multiple carboxylic acids



$$\mathrm{R-\overset{\overset{\displaystyle O}{\|}}{C}-OH}$$

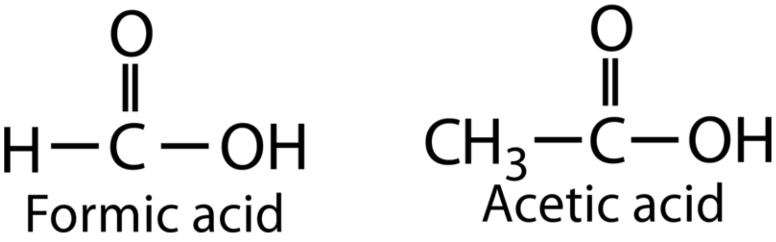
FIGURE 25.17



$$\mathrm{R-\overset{\overset{\displaystyle O}{\|}}{C}-O^{-}}$$

FIGURE 25.18

within a single molecule. For example, citric acid (three carboxyl groups) is especially abundant in citrus fruits and is used as a flavoring and preservative in many foods and beverages.



$$\mathrm{H-\overset{\overset{\displaystyle O}{\|}}{C}-OH} \qquad \mathrm{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH}$$

FIGURE 25.19

Ester

An **ester** is similar to a carboxylic acid, in that it contains a carbonyl where the carbon is bonded to one additional oxygen atom and one carbon or hydrogen atom. However, the second oxygen atom is bonded to another carbon instead of to an acidic hydrogen atom. Structurally, carboxylic acids and esters are related to one another in the same way as alcohols and ethers.

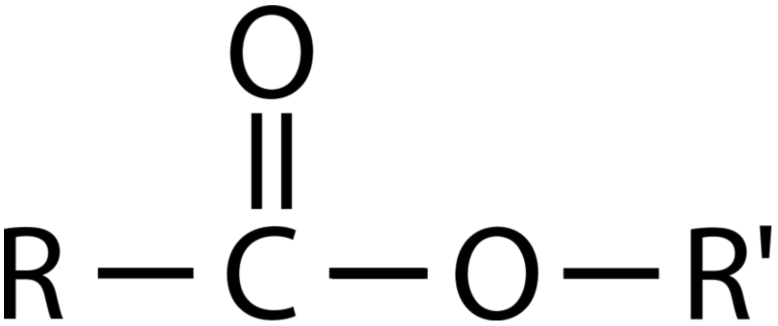


FIGURE 25.20

Esters can be formed by heating carboxylic acids and alcohols in the presence of an acid catalyst. This process is reversible, and the starting materials can be regenerated by reacting an ester with water in the presence of a weak base.

Some esters have very pleasant odors, so they are used in the manufacture of many perfumes. Propyl acetate contributes to the odor of pears, while isoamyl acetate gives bananas their smell. This ester also serves as an alarm signal for honeybees. Esters are employed in the manufacture of fabrics (polyesters) and Plexiglass®. Anesthetics such as procaine and benzocaine also contain esters.

Amide

An **amide** is a carbonyl in which the carbonyl is attached to one nitrogen atom and one carbon or hydrogen atom. Alternatively, we could define an amide as an amine in which one of the carbon atoms attached to the nitrogen is part of a carbonyl.

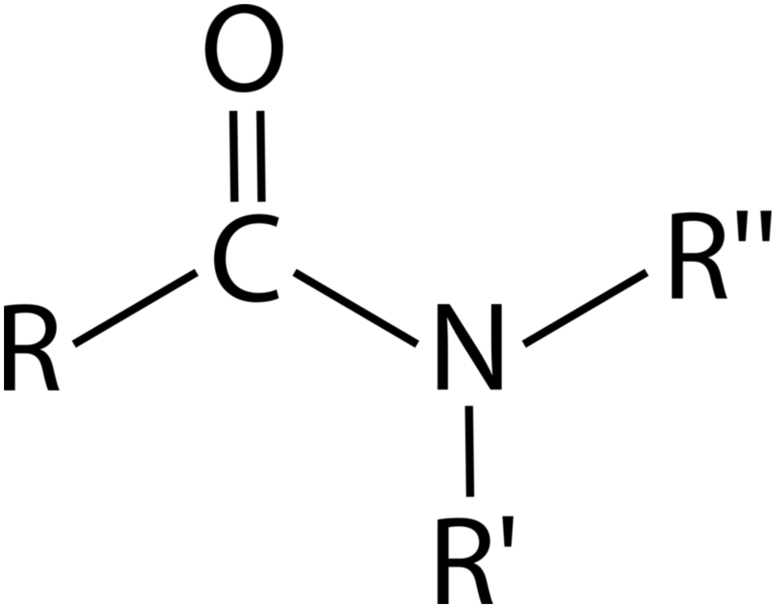


FIGURE 25.21

An amide can be formed by combining a carboxylic acid and an amine. Only primary and secondary amines can be used to form amides, since they have a hydrogen that can be replaced with the carbonyl carbon; tertiary amines will not form amides. The amide shown above was formed from a carboxylic acid and a primary amine.

Amides are used as coloring agents in crayons, pencils, and ink. They are employed in the paper, plastic, and rubber industries. Polyacrylamide is a very widely used amide; it is involved in the treatment of drinking water and sewage, and in plastics manufacture. The amide Kevlar® is widely employed for the production of body armor, and nylon is another type of amide-based polymer.

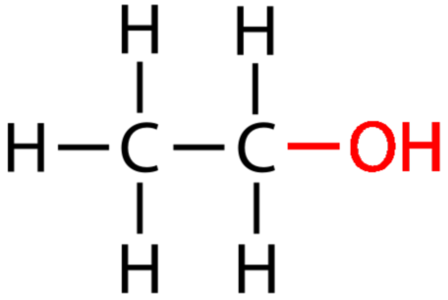
Lesson Summary

- Functional groups retain similar chemical properties in a variety of compounds. Functional groups help to distinguish organic molecules from one another.
- Alcohols consist of an -OH group and commonly appear in the form of ethanol (in alcoholic beverages) and methanol (used in plastic and paint ingredients).
- Ethers are composed of an oxygen atom that forms single bonds with two carbon atoms. Ethers are relatively unreactive making them good solvents for other organic compounds, such as in the formation of anesthetics.
- Amines are composed of a nitrogen atom bonded to some combination of carbons and hydrogens. Amines are weak bases commonly used in pharmaceuticals.
- Carbonyl is composed of a carbon atom double bonded with an oxygen atom, and is a common structural component of many other organic molecules. The reactivity of carbonyl derivatives is largely due to the polarity of the carbon-oxygen double bond.
- Aldehydes are commonly composed of a carbon bonded to one carbon atom and one hydrogen atom. Aldehydes are particularly reactive due to their high polarity, and are commonly associated with strong smells and tastes.
- Ketones are carbonyls in which the carbon atom makes single bonds with two other carbon atoms. Ketones are less reactive than aldehydes and are a common component in nail polish removers and paint strippers.
- Carboxylic acid is a carbonyl in which in which the carbon atom is bonded to an OH group on one side and either a carbon or hydrogen atom on the other. Carboxylic acids are weak acids, for example, vinegar.
- Esters are similar to carboxylic acids but contain a second oxygen rather than the acidic hydrogen that is in a carboxylic acid. Esters create the pleasant aroma associated with many fruits and flowers.
- Amides are carbonyls attached to one nitrogen atom and one carbon or hydrogen atom. Amides are used in materials such as crayons and inks, as well as in paper rubber products.

Lesson Review Questions

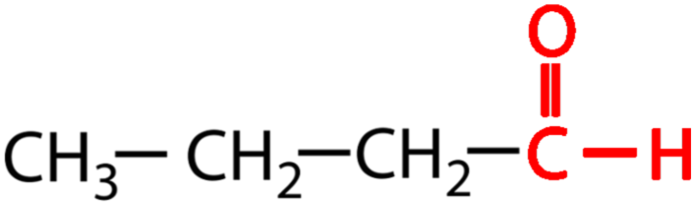
1. Draw structures for the following functional groups:
   a. ether
   b. ester
   c. ketone
   d. alkene
2. Name the following functional groups (in color):

a.



$$\begin{array}{ccccc} & H & & H & \\ & | & & | & \\ H- & C & - & C & -OH \\ & | & & | & \\ & H & & H & \end{array}$$

b.

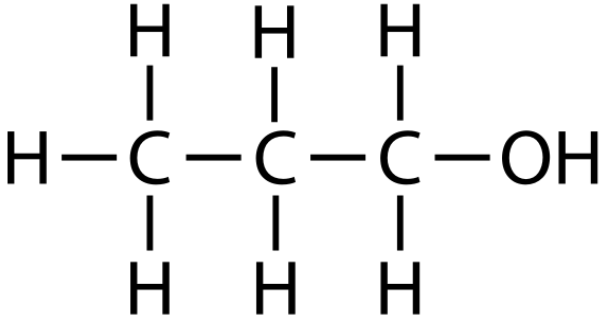


$$CH_3-CH_2-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-H$$

c. $CH_3-C\equiv C-CH_2-CH_3$

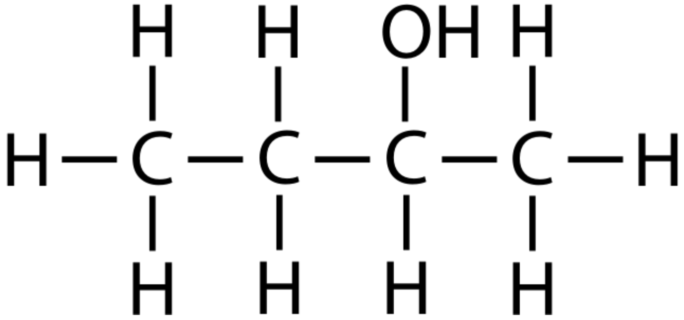
3. Designate the following alcohols as primary, secondary, or tertiary:

a.



$$\begin{array}{ccccccc} & H & & H & & H & \\ & | & & | & & | & \\ H- & C & - & C & - & C & -OH \\ & | & & | & & | & \\ & H & & H & & H & \end{array}$$

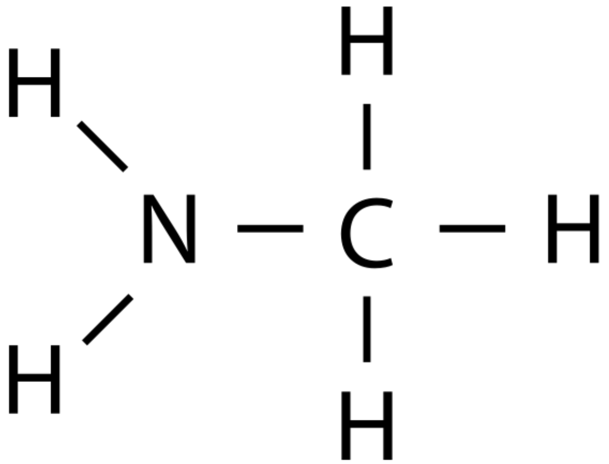
b.



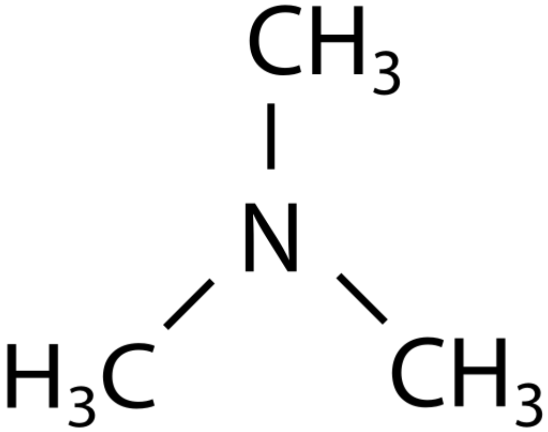
$$\begin{array}{ccccccccc} & H & & H & & OH & & H & \\ & | & & | & & | & & | & \\ H- & C & - & C & - & C & - & C & -H \\ & | & & | & & | & & | & \\ & H & & H & & H & & H & \end{array}$$

4. Designate the following amines as primary, secondary, or tertiary:

a.



b.



Further Reading/Supplementary Tasks

- Table of functional groups and reactions: http://academic.pgcc.edu/~ssinex/MolVis/FuncGroups.pdf
- Functional group practice: http://chemed.chem.purdue.edu/genchem/topicreview/bp/2organic/function.html
- Video about functional groups: http://www.youtube.com/watch?v=C5ZK6nPPAbo

Points to Consider

How to different functional groups react in organic molecules?

25.3 Organic Reactions

Lesson Objectives

- Be able to write reactions for:
  - Hydrogenation of an alkene or alkyne.
  - Halogenation of an alkene.
  - Dehydrohalogenation of an alkene.
  - Dehydration of an alcohol.
  - Oxidation of an alcohol.
  - Ester synthesis and hydrolysis.
  - Amide synthesis and hydrolysis.
  - Addition reactions leading to the formation of polymers.
  - Condensation reactions leading to the formation of polymers.
- Be able to list some common polymers and describe their uses.

Lesson Vocabulary

- **dehydration**: A type of elimination reaction that involves the loss of a water molecule.
- **dehydrohalogenation**: A reaction between an alkyl halide and an alcoholic alkali resulting in an alkene.
- **halogenation**: A reaction in which one or more of the hydrogen atoms in an organic compound is replaced by a halogen.
- **hydrogenation**: A reaction in which a hydrogen atom is added to a molecule, yielding a saturated compound when added to an organic molecule.
- **hydrolysis**: A type of decomposition reaction in which water is used to break chemical bonds, often the formation of an acid or a base from a salt and water.
- **monomer**: A chemical structure that represents building blocks used to construct more complex compounds.
- **polymer**: A chemical structure built from a number of combined monomers.

Check Your Understanding

Recalling Prior Knowledge

- Which parts of an organic molecule are considered functional groups, and why?

Introduction

With over twenty million organic compounds to keep track of, we need some way to organize information other than simply memorizing reactions for each substance. The presence of functional groups allows us to group together similar modes of chemical reactivity. Instead of learning the reactions that can be performed with a given compound, we learn the reactions that can be performed on a given functional group. Although there are always special cases, specific sets of reaction conditions tend to cause the same changes to a certain functional group regardless of what the rest of the reactant molecule looks like.

Although there are thousands of different types of organic reactions, many of the more complex ones can be broken down and understood in terms of simpler processes, such as addition, elimination, and substitution reactions. We will look at a small sampling of the most common processes that occur during organic reactions. In each case, we will focus on how one functional group is changed into another under a certain set of conditions.

Additions Across a Double Bond

There are two types of double bonds we will look at in terms of reactions, the C=C double bond and the C=O double bond. Because one of these bonds is polarized and the other is not, they differ quite a bit in terms of the conditions under which they are reactive. However, the overall change from reactant to product has the same form in either case; the double bond becomes a single bond, and a new atom or group of atoms is attached to each of the two atoms originally involved in the double bond.

Addition of Hydrogen

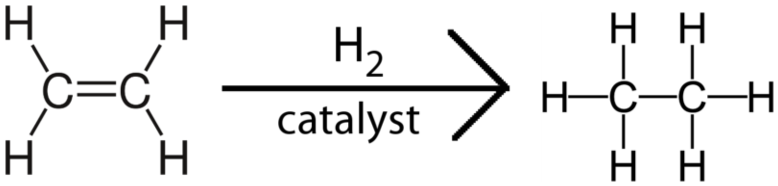


FIGURE 25.22

Hydrogenation is a very common addition reaction that involves the net addition of H_2 across a double bond. Although the actual reaction mechanism for such a process can be quite complicated, the overall transformation is relatively simple. Each atom involved in the double bond is attached to a new hydrogen atom, and the double bond becomes a single bond.

For alkenes and alkynes (unpolarized multiple bonds), this process is generally accomplished by mixing the starting material and H_2 gas in the presence of a metal catalyst (often Pt or Pd, although some cheaper metals can also be effective under certain conditions). An alkene can combine with one equivalent of H_2 gas to form an unfunctionalized alkane. Similarly, an alkyne can combine with two equivalents of H_2 (one for each pi bond) to make an alkane.

C=O bonds can also undergo a net addition of H_2, but the reactants are often quite different. In fact, many conditions for adding hydrogen to an alkene will not affect a C=O bond at all, and vice versa. Complementary reactivity patterns like this allow chemists to selectively change one portion of a molecule without altering the rest.

In our chapter on *Oxidation-Reduction Reactions*, we learned that one definition of reduction is the addition of hydrogen atoms. The addition of H_2 across a double bond is an example of this type of reduction reaction.

Addition of Halogens

Halogenation is analogous to hydrogenation, except that instead of adding a hydrogen atom to each side of the double bond, we add a halogen atom instead. In **Figure** 25.23, we see that adding molecular bromine to an alkene results in the formation of a dibrominated product. Unlike hydrogenation, no catalyst is required for this reaction to occur. Again, using these same conditions on a C=O double bond will *not* produce the analogous addition product due to the different reactivity of these two functional groups.

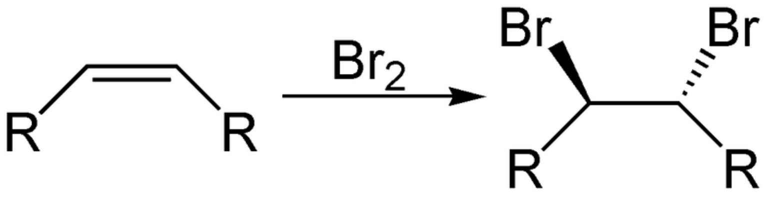


FIGURE 25.23
Halogenation of an alkene.

Formation of Double Bonds

Formation of C=C bonds

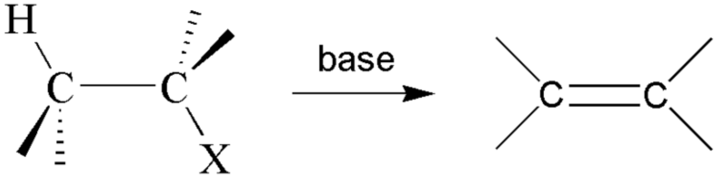


FIGURE 25.24
Dehydrohalogenation of an alkane.

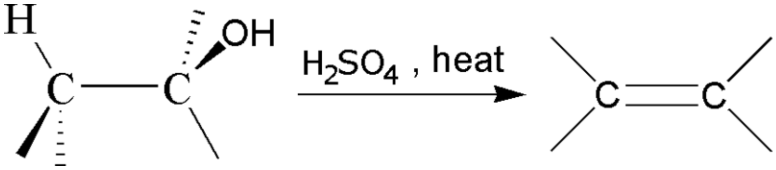


FIGURE 25.25
Dehydration of an alcohol.

Formation of C=O bonds

Recall that one definition of oxidation is the loss of hydrogen atoms. Oxidation of a primary alcohol will first lead to the formation of an aldehyde. This process is the net removal of H_2 (one from oxygen and one from carbon), leaving behind a double bond. In other words, this oxidation is the opposite of the hydrogenation (reduction) reaction that we looked at previously. If water is present, or if we use a strong enough oxidizing agent, the aldehyde will be further oxidized to the carboxylic acid. This fits with the idea that some oxidation reactions involve the literal addition of oxygen atoms to the molecule.

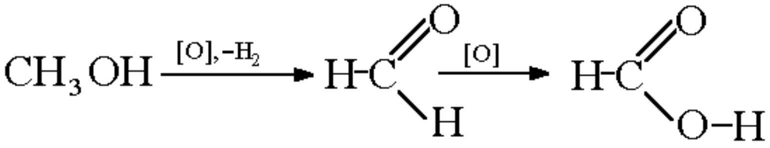


FIGURE 25.26

Oxidation of a primary alcohol.

A secondary alcohol forms a ketone when oxidized. The secondary alcohol cannot be further oxidized to produce a carboxylic acid. Tertiary alcohols cannot be oxidized in this way, because the carbon atom bonded to the OH group is not also bonded to any hydrogens.

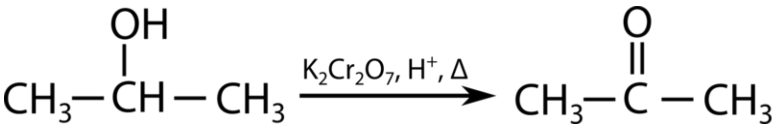


FIGURE 25.27

Oxidation of a secondary alcohol.

Formation and Hydrolysis of Carboxylic Acid Derivatives

Esters

In the presence of a strong acid catalyst, such as sulfuric acid, an alcohol and a carboxylic acid can combine to form an ester and water.

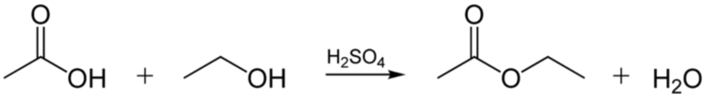


FIGURE 25.28

Ester formation from a carboxylic acid and an alcohol.

This reaction is reversible. The reverse reaction, in which water adds to an ester in order to form an acid and an alcohol, is referred to as **hydrolysis** of the ester. Because the reverse reaction happens so readily, we need to manipulate this equilibrium in order to achieve a high yield of the ester product. For example, if we increase the amount of one of the starting materials, the reaction will be shifted in the direction of ester formation according to Le Chatelier's Principle. Usually, the less expensive starting material would be used in excess.

Conversely, we can also remove one of the products (generally water) in order to drive the reaction forward. If the reaction is run above the boiling point of water, the H_2O product will leave the system as a gas, shifting the equilibrium to the right. Chemical drying agents also provide ways to remove water from active participation in the equilibrium.

Amides

A similar reaction can occur between a carboxylic acid and an amine:

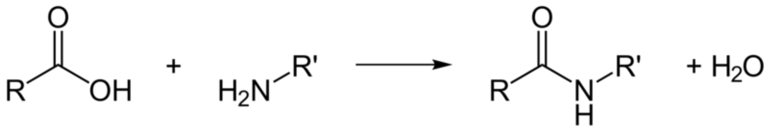


FIGURE 25.29

Amide synthesis.

We can see from the diagram that the –OH of the carboxyl group and a hydrogen from the amine form water as a byproduct. The nitrogen will attach to the carboxyl carbon in the same way the oxygen atom of the alcohol did in the ester synthesis. The reaction shown above uses a primary amine, which has two hydrogen atoms that could potentially be removed to form the final product. The same process can also occur with a secondary amine, which still has one hydrogen attached to the nitrogen. Tertiary amines will not form amides, because the new bond to the carbonyl carbon must replace an existing N-H bond.

The reverse reaction (amide hydrolysis) is very useful in the study of protein structure. Proteins are long chains of amino acids (each amino acid contains an amine group and a carboxyl group, both attached to a central carbon atom). The amino acids are linked together by amide bonds to form the long protein chain. One of the techniques for looking at protein structure is to break those amide linkages so we can learn the identity of the amino acids in the chain. We do this through a hydrolysis reaction:

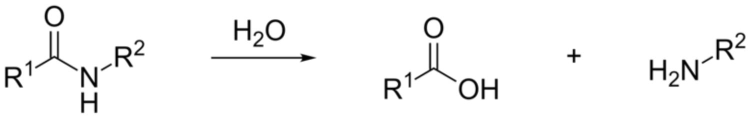


FIGURE 25.30

Hydrolysis of an amide linkage.

Usually, an acid such as HCl is used for the hydrolysis. The amino acids can then be separated and identified. More complex reaction conditions allow the amino acids to be broken off one by one, allowing the amino acid sequence of an unknown protein to be determined. The three-dimensional structures and functions of large protein molecules are ultimately determined by the sequence of amino acids from which they are constructed.

Organic Polymers

What Are Polymers?

Polymers are a pervasive part of modern life. It is very likely that at least some part of your clothing is made of nylon, rayon, or polyester. The milk or juice that you have for breakfast often comes in a polyethylene container. If you don't have breakfast at home, you might get coffee from a fast food establishment, where your order is delivered to you in a Styrofoam® container. While getting out of your car, you bang the door on another vehicle. One reason you may not have dented the door is the fact that it could be made out of a polymeric plastic material that resists deformation more than simple metallic structures. Elsewhere on your car, both synthetic and natural rubber are probably present in the tires. All these materials are examples of organic polymers.

Polymers are long-chain organic molecules made up of many smaller subunits (called **monomers**) that are connected together in a repeating pattern. Some polymers are constructed by living organisms, such as starch, cellulose, proteins, and DNA. These natural polymers are covered in the following chapter on *Biochemistry*. In this section, we will focus on synthetic polymers that are made in the laboratory.

Important Synthetic Polymers

One widely used polymer is polystyrene:

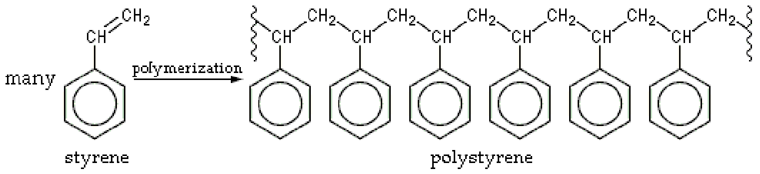


FIGURE 25.31

Polystyrene structure.

This polymer is used for many purposes. We find it in Styrofoam® packaging materials, plastic cutlery, CD "jewel cases", laboratory ware, and a wide variety of other applications. Polystyrene can take on many forms, depending on how it is manufactured. It is inexpensive, easy to work with, and fairly durable.

Polyethylene can come in two forms. The low-density form is used for squeeze bottles, insulation for wiring, and flexible pipes. The high-density form is employed in bottles, pipes, and plastic bags.

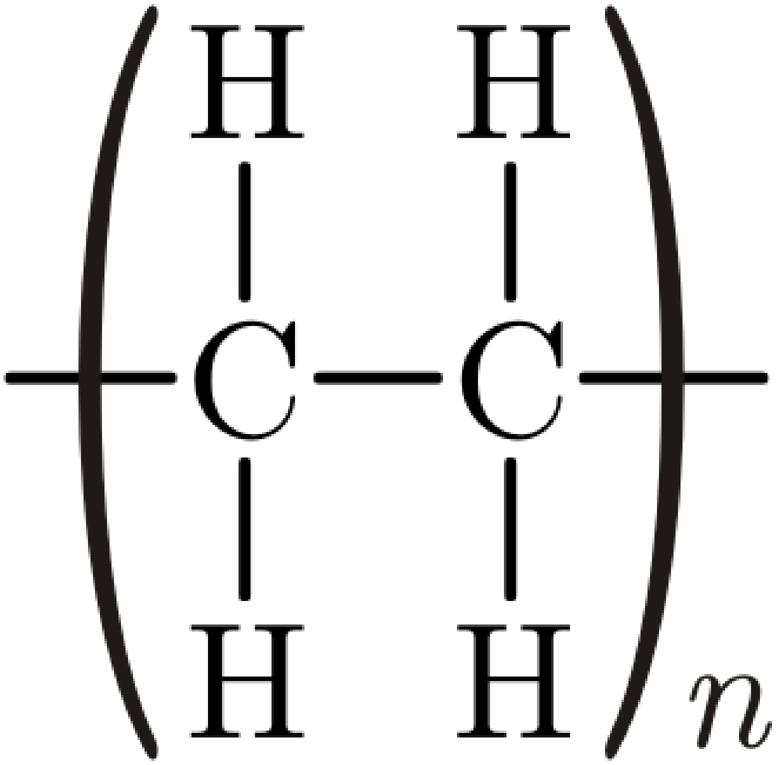


FIGURE 25.32

Repeating unit of polyethylene.

Polyethylene has the simplest structure of all the polymers; it is essentially just a very long linear alkane. Its repeating unit is shown above.

Polytetrafluoroethylene (Teflon®) is very chemically inert and non-wettable –water does not stick to it. This polymer has found broad applications in cookware because materials do not stick to it. Since it does not react with other materials, Teflon storage containers are used to package highly reactive or corrosive chemicals.

All of these polymers (and many more) are referred to as homopolymers, because they are composed of a single repeating unit. There is another class of polymers called copolymers. This group contains two different repeating

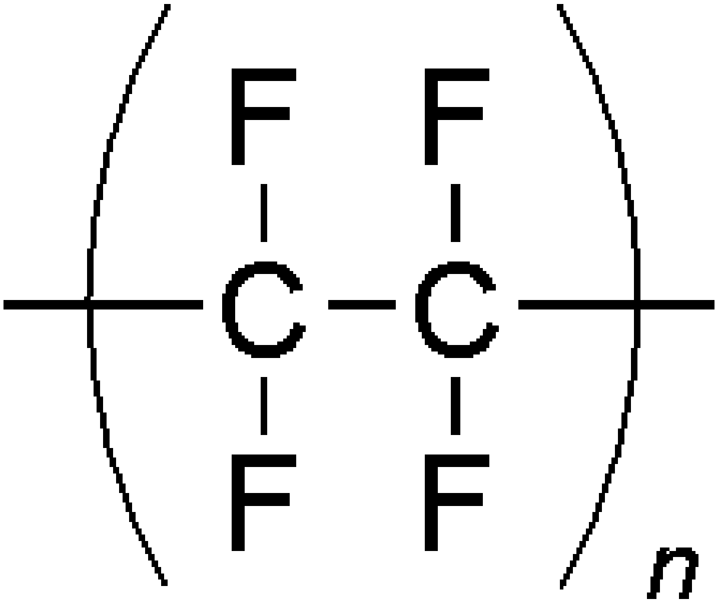


FIGURE 25.33

Repeating unit of polytetrafluoroethylene.

units in its structure. Kevlar®, used in body armor, is one such copolymer:

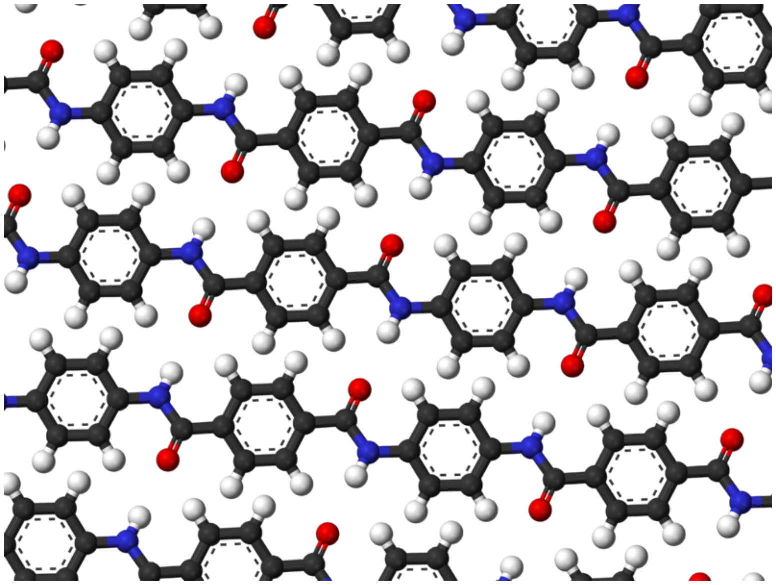


FIGURE 25.34

Structure of Kevlar®.

One of the repeating units is a substituted benzene ring with attached amine groups, while the other repeating unit contains carbonyl groups connected to the benzene ring. In addition to the strong covalent bonds that link these monomers together, the polymeric chains interact with one another via hydrogen bonds, further increasing the strength of the material.

Synthesis of Polymers

We will now look at two of the reactions that are commonly used to create synthetic polymers. One way to form polymers is through addition reactions. If each monomer contains an alkene or alkyne, various methods can be used to connect each side of the multiple bond with one of the other monomers, resulting in a long chain.

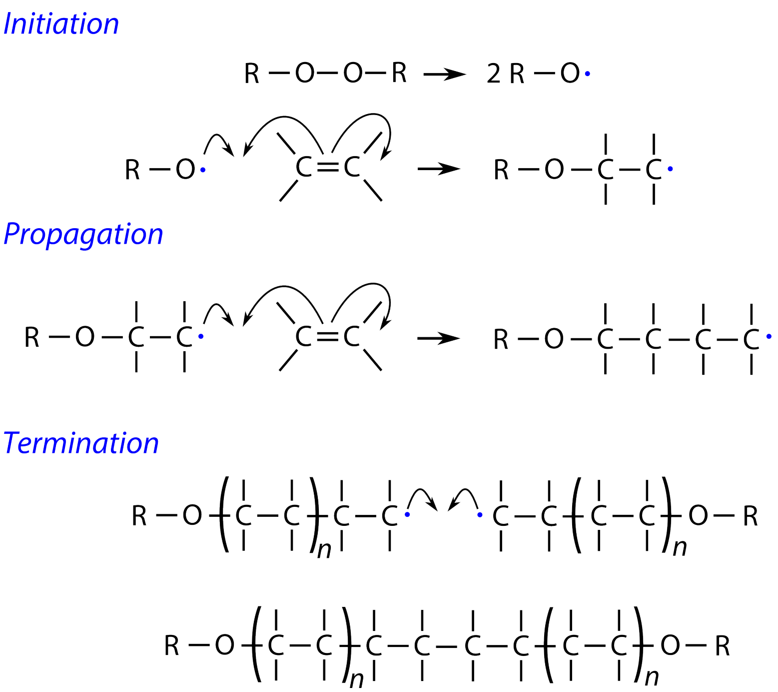


FIGURE 25.35

Steps in addition reaction.

One way to form an addition polymer is through a radical chain reaction. The steps in this process are as follows:

1. A free radical initiator attacks the carbon-carbon double bond. The initiator can be something like hydrogen peroxide, which can be split with light or heat to form two radical species, each of which contains a reactive, unpaired electron (H-O-O-H → 2 H-O). This free radical attacks a carbon-carbon double bond. The initiator binds to one of the carbon atoms using its unpaired electron and one of the pi electrons from the double bond. The other pi electron forms a new free radical on the other carbon atom.
2. The new free radical adds to another alkene, generating yet another unpaired electron and continuing the process of chain growth.
3. Termination occurs whenever two free radicals meet. The two unpaired electrons form a covalent bond, ending the chain reaction.

The other general category of polymer synthesis reactions are the condensation reactions. In these situations, a reaction occurs between two different functional groups with the expulsion of water. For example, polyesters and polyamides can be formed via the condensation reactions discussed earlier in this lesson.

Another condensation reaction can be seen in the synthesis of Kevlar®:

In this case, we see the formation of amide bonds between amines and acyl halides (which can be thought of as "activated" carboxylic acids). Note that each molecule must have two functional groups in order for this type of polymerization to occur.

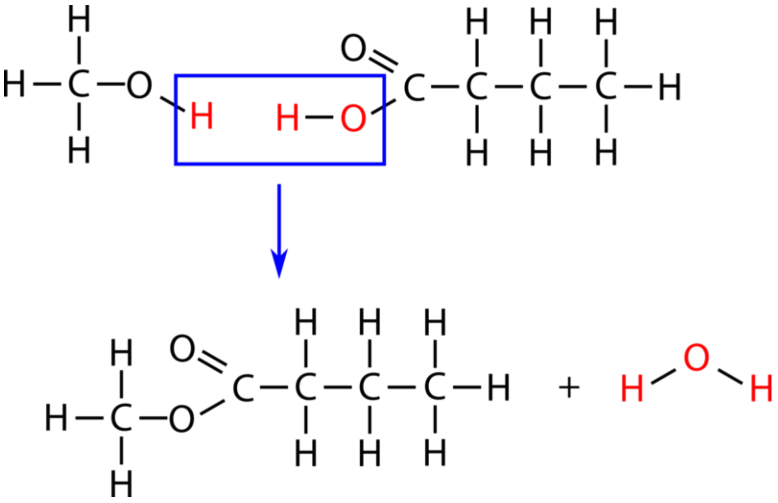


FIGURE 25.36

A condensation reaction.

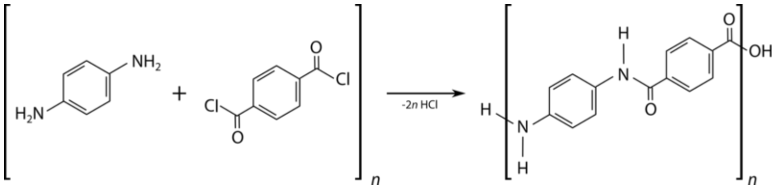


FIGURE 25.37

Synthesis of Kevlar®.

Lesson Summary

- Alkenes and alkynes can be reduced with hydrogen gas to form alkanes.
- Alkenes can react with halogens to form dihalides.
- Alkenes can react with water to form alcohols.
- Alcohols can lose water to form alkenes.
- Alcohols can be oxidized to aldehydes or ketones.
- Aldehydes can be oxidized to carboxylic acids.
- Carboxylic acids can form esters with alcohols.
- Carboxylic acids can form amides with amines.
- Polymers are long-chain materials with useful properties.

Lesson Review Questions

1. Name the product (class of compound) formed in the following reactions:
    a. alcohol + carboxylic acid
    b. primary alcohol + oxidizing agent
    c. ketone + oxidizing agent
    d. alkene + hydrogen + metal catalyst
2. What class of compound(s) would be used to form the following product:
    a. amide

   b. ketone
   c. halogenated alkane
   d. alcohol

3. Draw the structure of the product formed in the following reactions:
   a. $CH_3CH_2CH{=}CHCH_3 + Cl_2$
   b. $CH_3CH_2CHOHCH_3$+ oxidizing agent

Further Reading/Supplementary Links

- Summaries of organic reactions: http://pages.towson.edu/ladon/orgrxs/reactsum.htm
- Polymer addition reactions: http://www.materialsworldmodules.org/resources/polimarization/3-addition.html

Points to Consider

- What do reactions in living cells have in common with these organic reactions? How are they similar and how are they different?

25.4 References

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CHAPTER 26 Biochemistry

Chapter Outline

26.1 CARBOHYDRATES

26.2 AMINO ACIDS AND PROTEINS

26.3 LIPIDS

26.4 NUCLEIC ACIDS

26.5 REFERENCES

The primary role of red blood cells in the circulatory system is to transport oxygen to the tissues. The actual carrier of oxygen molecules is the protein hemoglobin, which binds to the oxygen and moves it throughout the body, releasing it in areas where the concentration of dissolved oxygen is low. A certain mutation in the gene for hemoglobin causes a slight change in the structure of this crucial protein, resulting in a disease called sickle-cell anemia. For people with this mutation, the hemoglobin produced by their red blood cells has a tendency to clump together, distorting the shape of the red blood cells and giving rise to the crescent-shaped cells seen above. By understanding the changes in structure that are the underlying cause of this disease, we have developed various ways to treat and manage this illness.

Biochemistry is the study of chemical processes in living systems. In this chapter, we will explore some of the basic chemical components of biological systems and develop an understanding of the roles played by each major type of biomolecule.

United States, National Human Genome Research Institute. commons.wikimedia.org/wiki/File:Sicklecells4.jpg. Public Domain.

26.1 Carbohydrates

Lesson Objectives

- Draw open-chain and cyclic structures for carbohydrates.
- Classify carbohydrates by chain length.
- Classify carbohydrates as monosaccharides, disaccharides, or polysaccharides.
- Describe the digestion and utilization of carbohydrates in the body.

Lesson Vocabulary

- **carbohydrate**: A class of organic compounds with a chemical formula of the form $C_n(H_2O)_n$, or a derivative of such a compound.
- **monosaccharide**: The simplest basic unit of carbohydrates.
- **disaccharide**: A simple carbohydrate made up of two monosaccharides.
- **polysaccharide**: A carbohydrate made of many monosaccharides.
- **glycogen**: A polysaccharide composed of long chains of glucose units.
- **glycolysis**: The "splitting of glucose" to form products used in biochemical energy production.
- **gluconeogenesis**: The process of generating glucose from other chemical components in the body.

Check Your Understanding

Recalling Past Knowledge

- What are the structures for each of the following functional groups:
  - alcohol
  - aldehyde
  - ketone

Carbohydrate Structure

Carbohydrates are a class of organic compounds in which each carbon in the chain is bonded to an oxygen atom, either through a single bond to an OH group or through a double bond, making a carbonyl. The name comes from the fact that the chemical formula for a carbohydrate can be written in the form $C_n(H_2O)_n$, where n is some integer. However, carbohydrates are not actually "hydrates of carbon." No water molecules are actually present, and each oxygen in the formula is bonded to at least one carbon atom.

One of the most important carbohydrates is glucose, shown in the **Figure** 26.1.

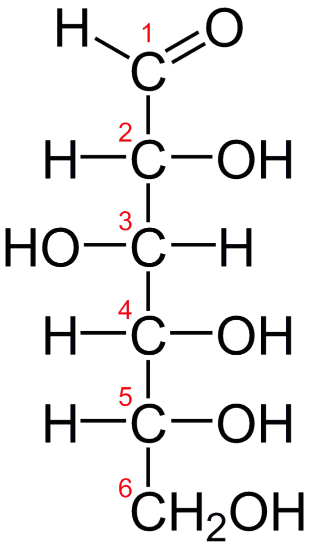

FIGURE 26.1

Structure of glucose, a typical carbohydrate.

The glucose molecule illustrated in the **Figure** 26.1 has a carbonyl on C-1 and –OH groups on each of the other carbons. This way of representing the structure is known as a Fischer projection, named after the German chemist Emil Fischer (1852-1919), who studied carbohydrate chemistry.

When dissolved in water, most of the glucose molecules are not actually present in the form represented above. Instead, one of the oxygen atoms near the end of the chain becomes bonded to the carbonyl carbon, and a subsequent transfer of hydrogen results in the cyclic structure shown in **Figure** 26.2.

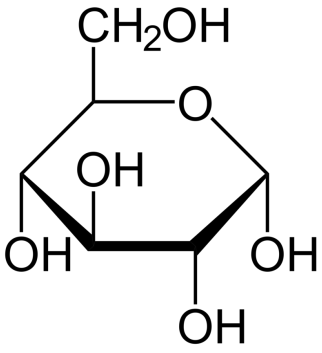

FIGURE 26.2

Cyclic structure of glucose.

Because six-membered rings are particularly stable, the oxygen atom used to form the ring will generally be on a carbon atom that is five away from the carbonyl. If such a situation is not possible, five-membered rings can also be formed. Rings of other sizes are generally less favorable than the open-chain form and will not be present in large amounts.

Classes of Carbohydrates

There are several methods of classifying the various possible carbohydrates. The simplest carbohydrates consist of a short chain or a single ring. These structures can be classified by the number of carbons in the chain. The terms used for simple carbohydrates with 3-6 carbon atoms in their primary chain are shown below:

triose –three carbons
tetrose –four carbons
pentose –five carbons
hexose –six carbons

Some of the most important simple carbohydrates studied in biochemistry include ribose and deoxyribose (pentoses involved in the structure of nucleic acids) and glucose, fructose, and galactose (hexoses that make major contributions to our diet).

The simple carbohydrates discussed above are used as the building blocks for complex carbohydrates. **Monosaccharides** like glucose or fructose can be linked together to form larger structures. When two monosaccharides are bound together, the result is a **disaccharide**. Some common disaccharides are shown in the **Table** 26.1.

TABLE 26.1:

Disaccharide	Made up of
sucrose	glucose + fructose
lactose	glucose + galactose
maltose	glucose + glucose

Longer chains of monosaccharides are referred to as **polysaccharides**. Starch, glycogen, and cellulose are three extremely common polysaccharides made entirely out of glucose molecules. The differences lie in the types of bonds between the glucose units and the extent of branching in the carbohydrate chain. Starch is found in plants and is consumed as part of our diet. **Glycogen** is made by the body and is a storage form of glucose for when the cells need extra energy. Cellulose is another long-chain polysaccharide found in plants. Unlike starch and glycogen, the human body cannot break cellulose down into molecules of glucose. Although cellulose does not have any nutritional value in terms of calories, it is a major component of dietary fiber, which has other digestive benefits.

Carbohydrate Intake and Utilization

Dietary Consumption and Digestion of Carbohydrates

There are several dietary sources of carbohydrates. Starch is found in many vegetables (especially potatoes) and baked goods. Sucrose (table sugar) is included as part of many prepared foods. Lactose is found in milk products, and maltose is present in some vegetables.

A small amount of starch digestion will occur in the mouth, but the bulk of this process occurs in the small intestine. Amylase, an enzyme produced in the pancreas and released into the interior of the small intestine, breaks complex carbohydrates like starch into disaccharides and trisaccharides. These molecules are then cleaved into their corresponding monosaccharides by specific enzymes located in the interior wall of the small intestine.

TABLE 26.2:

Disaccharide	Enzyme	Products
sucrose	sucrase	glucose + fructose
lactose	lactase	glucose + galactose
maltose	maltase	glucose + glucose

Many people have very low levels of the lactase enzyme. As a result, lactose (found in most dairy products) accumulates in the small intestine, since it cannot be fully digested. This can result in bloating, cramps, abdominal distress, and nausea. Reduction or elimination of lactose in the diet is the most effective treatment.

Cellular Utilization of Carbohydrates

What happens after complex carbohydrates have been broken down into simple monosaccharides? When energy is needed, glucose is broken down further via a multi-step process called **glycolysis**, which means "splitting of glucose." All common monosaccharides can be converted by the body to glucose or to some other intermediate along the glycolytic pathway. The key "splitting" reaction occurs when the enzyme aldolase splits fructose-1,6-disphosphate into two three-carbon compounds. These two compounds then interconvert and form two molecules of pyruvate, the end-product of the glycolytic pathway.

Pyruvate then enters an intracellular organelle called the mitochondrion (plural: mitochondria). Through a complex series of processes including two separate pathways, the cell uses O_2 and pyruvate to form, among other things, a molecule known as ATP. This compound is essential for many biochemical reactions as well as for processes such as muscle contraction and movement of materials across cell membranes.

Formation of Glucose in the Body

Shortly after eating, there is a surplus of glucose in the body. Some of it will be used immediately, but the rest is stored in the form of glycogen. Between meals, when the level of glucose in the blood drops below a certain point, a signal is sent to the liver that says “make more glucose.” In response, the glycogen in the liver is broken down and the resulting glucose is released into the bloodstream.

Alternatively, the body can make glucose molecules from simpler components in a process known as **gluconeogenesis**. In addition to carbohydrates, fats and proteins can also be broken down into the starting materials for gluconeogenesis, so they are indirect sources of glucose. As a result, any of these classes of compounds can be used by the body to produce energy.

Lesson Summary

- Carbohydrates have a chemical formula that can be written in the form $C_n(H_2O)_n$.
- Simple carbohydrates can be classified in terms of chain length.
- Monosaccharides can be linked together to form disaccharides or polysaccharides.
- Digestion of polysaccharides and disaccharides in the small intestine produces glucose and other monosaccharides.
- Glucose undergoes a lengthy series of reactions that ultimately results in the formation of ATP.
- Glycogen breakdown and gluconeogenesis are two complementary pathways used by the body to produce glucose when the concentration of glucose in the blood is low.

Lesson Review Questions

1. What is the origin of the term "carbohydrate"?
2. Name the term used for carbohydrates with the following chain lengths:
    a. four carbons
    b. six carbons

   c. five carbons

3. Classify each of the following carbohydrates as a monosaccharide, a disaccharide, or a polysaccharide:
   a. lactose
   b. ribose
   c. glycogen
   d. galactose
   e. sucrose
   f. starch
4. How many pyruvate molecules can be formed from the metabolism of three molecules of glucose?
5. What relationship is there between glucose metabolism and ATP formation?
6. Explain how glycogen and amino acids (components of proteins) can both be used to produce glucose in the bloodstream.

Further Reading/Supplementary Links

- Carbohydrates as nutrients: http://www.fao.org/docrep/field/003/AB470E/AB470E04.htm

- Carbohydrates and diet: http://www.umm.edu/ency/article/002469fod.htm

26.2 Amino Acids and Proteins

Lesson Objectives

- Draw the structure of a generic amino acid.
- Define the following aspects of protein structure:
  - Primary
  - Secondary
  - Tertiary
  - Quaternary
- List and describe the functions of proteins.
- Describe how an enzyme catalyzes a biochemical reaction.
- List the six classes of reactions catalyzed by enzymes.
- Describe the structure of hemoglobin and its role in oxygen transport.
- Describe the molecular problems that lead to sickle cell disease.

Lesson Vocabulary

- alpha helix
- amino acid
- beta sheet
- enzyme
- secondary structure
- primary structure
- protein
- quaternary structure
- tertiary structure

Check Your Understanding

Recalling Past Knowledge

- What is the structure of a carboxylic acid?
- What is the structure of an amine?
- What is the structure of an amide?

Amino Acids

Amino acids are a class of molecules that contain both the carboxylic acid and amine functional groups. Amino acids are key building blocks in biological systems. The most common biologically relevant amino acids have the generic structure shown in the **Figure** 26.3, in which a central carbon atom is connected to an NH_2 group, a CO_2H group, and a variable R group.

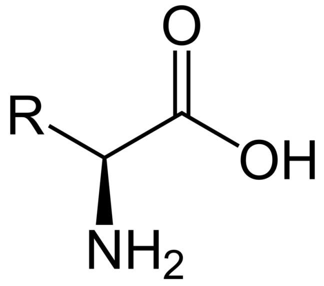

FIGURE 26.3

Generic amino acid.

The only difference between one amino acid and another is the structure of the R group. In the simplest amino acid, glycine, the R group is just a hydrogen atom. However, other common amino acids may involve alcohols, amines, carboxylic acids, or aromatic rings.

Many amino acids can be linked together to form a long chain known as a **protein**. These linkages are formed when the carboxylic acid of one amino acid reacts with the amine of another to produce an amide (see **Figure** 26.4).

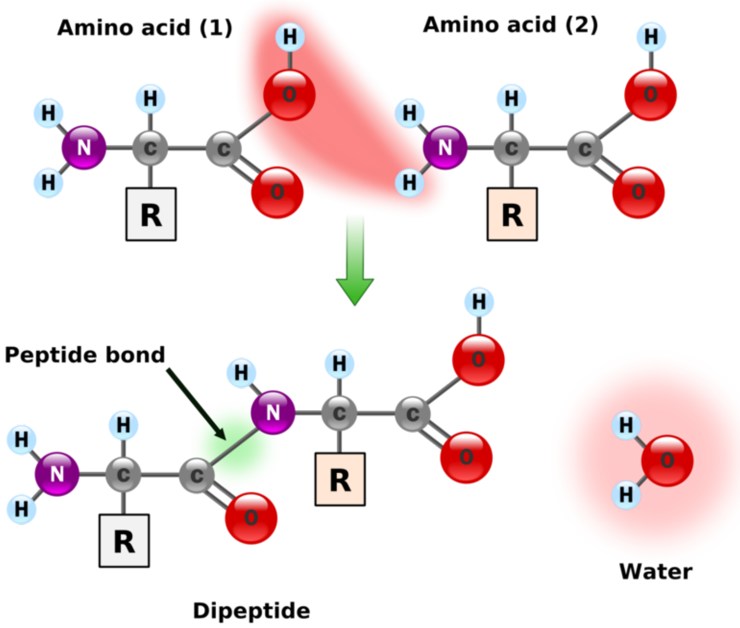

FIGURE 26.4

Peptide bond in protein.

In the context of proteins, the newly formed bond between the carboxyl carbon and the amine nitrogen is referred to as an amide bond or a peptide bond.

Nearly all biological proteins are constructed from a set of just 20 common amino acids. The names, abbreviations, and other information for each of these amino acids are presented in the **Table** 26.3:

TABLE 26.3:

Amino Acid	3-Letter	1-Letter	Side Chain Polarity	Side Chain Charge (pH 7.4)
Alanine	Ala	A	nonpolar	neutral
Arginine	Arg	R	polar	positive
Asparagine	Asn	N	polar	neutral
Aspartic acid	Asp	D	polar	negative
Cysteine	Cys	C	nonpolar	neutral
Glutamic acid	Glu	E	polar	negative
Glutamine	Gln	Q	polar	neutral
Glycine	Gly	G	nonpolar	neutral
Histidine	His	H	polar	positive (10%) neutral (90%)
Isoleucine	Ile	I	nonpolar	neutral
Leucine	Leu	L	nonpolar	neutral
Lysine	Lys	K	polar	positive
Methionine	Met	M	nonpolar	neutral
Phenylalanine	Phe	F	nonpolar	neutral
Proline	Pro	P	nonpolar	neutral
Serine	Ser	S	polar	neutral
Threonine	Thr	T	polar	neutral
Tryptophan	Trp	W	nonpolar	neutral
Tyrosine	Tyr	Y	polar	neutral
Valine	Val	V	nonpolar	neutral

Protein Structure

The structural features of complete proteins can be broken down into four levels, referred to as primary, secondary, tertiary, and quaternary structures. These levels are illustrated in the **Figure** 26.5.

The **primary structure** of a protein is simply the sequence of amino acids from which it is constructed. By convention, this sequence is written starting with the N-terminal amino acid, which has a free –NH_2 group, and ending with the C-terminal amino acid, which has a free carboxylic acid. Because protein sequences can be very long, the abbreviations listed in the table above are commonly used. For example, the sequence lysine-histidine-threonine-valine can be written as either Lys-His-Thr-Val or KHTV.

The **secondary structure** of a protein refers to local coiling or folding. This aspect of the structure applies only to a section of the protein, not the entire structure. The two basic forms of secondary structure are the **alpha helix** and the **beta sheet**. Because they have to do with the ways that multiple amides pack together, one or both of these substructures show up in most long protein strands. The appearance of alpha helices and beta sheets can be predicted fairly well (by computers) from the primary sequence of amino acids.

Tertiary structure refers to the overall three-dimensional shape of an entire protein chain. Because of the ways that proteins can fold in on themselves, tertiary structure often involves interactions between amino acids that are very far apart in the primary sequence. Ultimately, this is also dependent on the primary sequence of the protein, but because of these long-range interactions, predicting tertiary structures from sequences of amino acids is still very difficult.

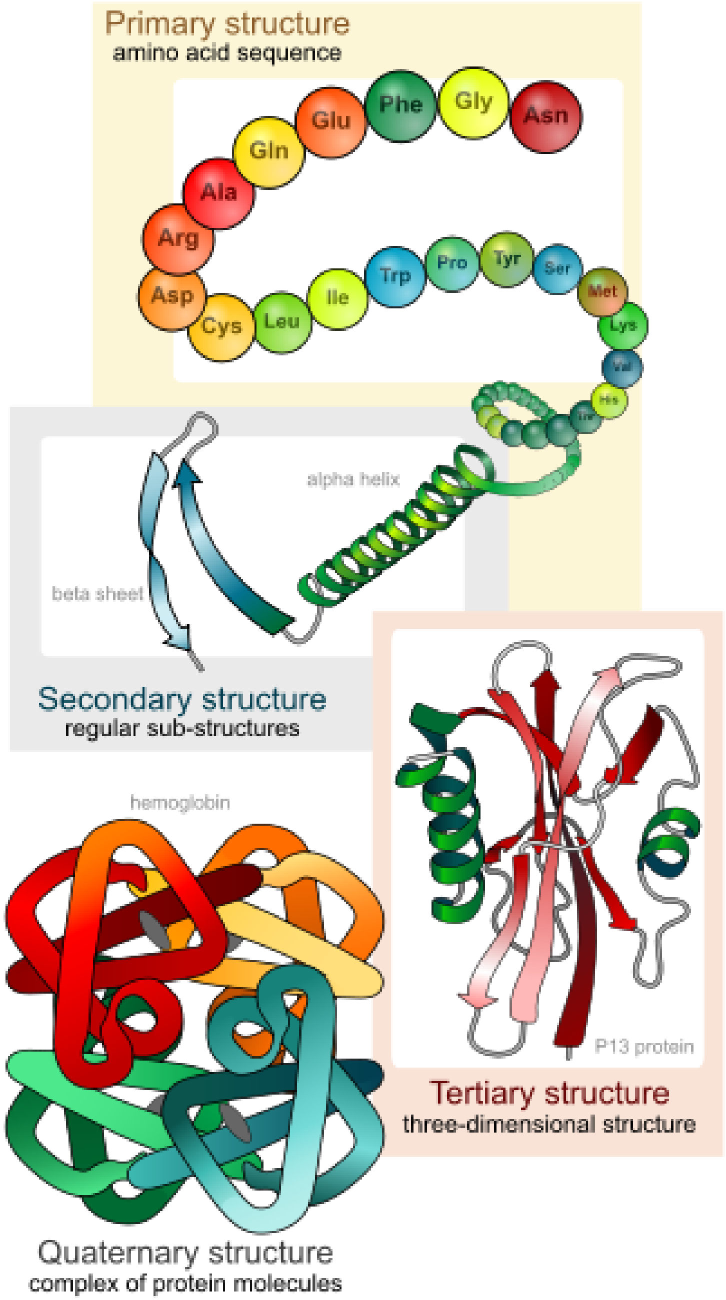

FIGURE 26.5

Hierarchy of protein structure.

Quaternary structure refers only to proteins in which more than one chain of amino acids interact to form a single functional structure. If a protein consists of only a single chain, it does not have any quaternary structure. The separate subunits in such a protein are held together by ionic bonds and various types of intermolecular forces, especially hydrogen bonds. They are not covalently bonded to one another, so the individual chains can be separated and studied individually. These subunits can also be recombined to form the original protein.

In the **Figure** 26.6, we see the quaternary structure of an enzyme called succinate dehydrogenase. Four different peptide chains, each drawn in a different color, combine to form the fully functional protein. Again, the four chains are not covalently bound to one another, but they are held together by various other attractive forces. A number of alpha helix groups can also be seen in this structure, especially in the orange and blue subunits.

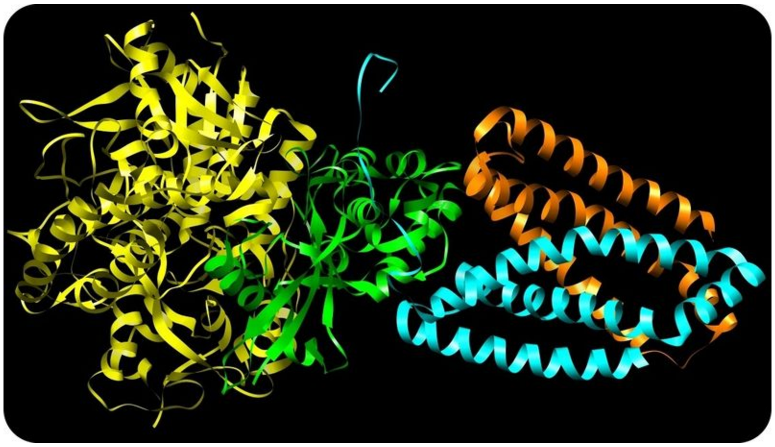

FIGURE 26.6

Structure of succinate dehydrogenase.

Protein Functions

Proteins play a variety of important roles in biochemical systems. Some of the most common protein functions are listed below:

1. Structural –Support for tissues is provided by structural proteins. For example, collagen is a structural protein that provides a matrix in which bones can develop. Calcium phosphate deposited on a collagen scaffold provides the basis for forming strong bones.
2. Enzymes –Enzymes are used to catalyze biochemical reactions. We will look more at this class of proteins in the following section.
3. Hormones –Hormones are molecular signals that help regulate a number of biochemical processes. Single amino acids and short protein chains are very common types of hormones. For example, insulin is a protein hormone that regulates the amount of glucose present in the bloodstream.
4. Antibodies –These proteins recognize and combine with harmful materials, including both toxic chemicals and invasive microorganisms (such as bacteria and viruses). When an antibody binds to its target, it is tagged for destruction. This tag is recognized by white blood cells, which complete the process. Some antibodies also partially or completely deactivate their targets while waiting for further help from white blood cells.
5. Transport –Some proteins bind to specific materials and carry them around the body through the bloodstream to a place where they are currently needed. For example, transferrin shuttles iron in and out of cells. Hemoglobin is an extremely important protein that binds to molecular oxygen and carries it throughout the body. We will discuss hemoglobin further in its own section.
6. Storage –The body does not like to get rid of materials that it might find useful later. Storage proteins such as albumin preserve amino acids until they are needed.

Enzymes

Enzymes are biochemical catalysts, which means that they speed up the rate of a specific chemical reaction. A process that might take weeks in the absence of an enzyme can occur in milliseconds if the proper enzyme is present. A generic enzyme-catalyzed reaction could be represented as follows:

$\text{Substrate} \overset{enzyme}{\rightarrow} \text{Product}$

The mechanism of the reaction above is somewhat more complicated. In general, the first step involves the enzyme binding to a substrate (the reactant or reactants in the process), forming an enzyme-substrate complex. The enzyme then undergoes a shift in its conformation to produce the product or products, which are then released from the enzyme active site.

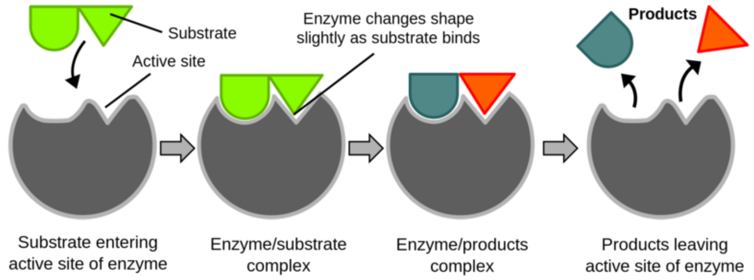

FIGURE 26.7

Typical enzyme-substrate interaction.

Over 1,500 enzymes are known. In order to keep track of all these compounds, a classification system was developed based on the type of reaction catalyzed by each enzyme. Six broad families of enzymes are defined as follows:

1. Oxidoreductase –This type of enzyme moves electrons from one compound to another, usually accompanied by hydrogen atoms (one proton + one electron).
2. Transferase –These enzymes transfer functional groups (such as $–NH_2$ or $-PO_4$) from one molecule to another.
3. Hydrolase –A hydrolase splits a molecule into two fragments by using water. The catalyzed reaction is referred to as a hydrolysis.
4. Lyase –These enzymes split a molecule into fragments without using water.
5. Isomerase –Isomerases catalyze rearrangements of their substrates but do not add or subtract material.
6. Ligase –These enzymes catalyze the formation of various covalent bonds between separate molecules.

Hemoglobin

Hemoglobin is a large iron-containing protein that binds to oxygen molecules and transports them around the body. There are four subunits (separate chains) in the hemoglobin complex –two alpha subunits and two beta subunits. Each subunit contains one iron ion. Its oxidation state changes back and forth between +2 and +3, depending on whether it is bound to oxygen.

The yellow subunits are identical in structure, as are the gray subunits. A smaller organic structure called a porphyrin ring is attached to each protein subunit and contains the iron ion used to bind oxygen.

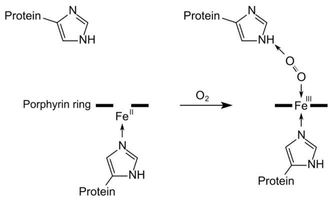

FIGURE 26.9

Oxygen binding to iron in hemoglobin.

When the oxygen binds to the iron, the three-dimensional shape of the molecule changes. Upon release of the oxygen to the cells, the shape changes back.

Some individuals have a specific mutation in the primary sequence of their hemoglobin molecules that causes them to aggregate, resulting in a deformation of their red blood cells. This abnormality is genetic in nature. A person may inherit the gene from one parent and have sickle cell trait (only some of the hemoglobin is hemoglobin S), which is usually not life-threatening. Inheriting the gene from both parents will result in sickle cell disease, which is a very

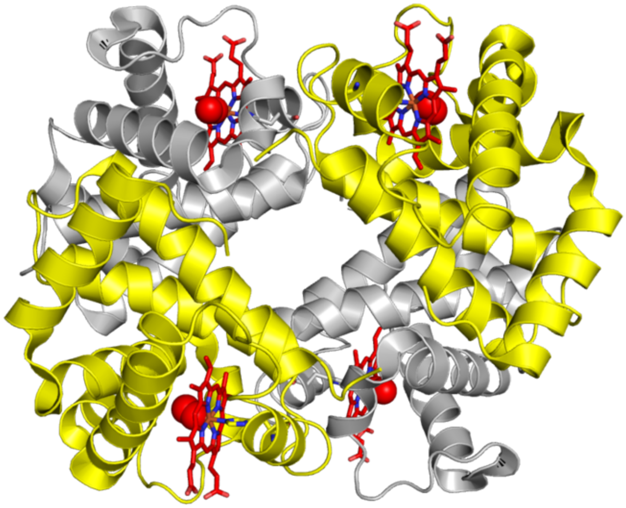

FIGURE 26.8

Hemoglobin molecule.

serious condition.

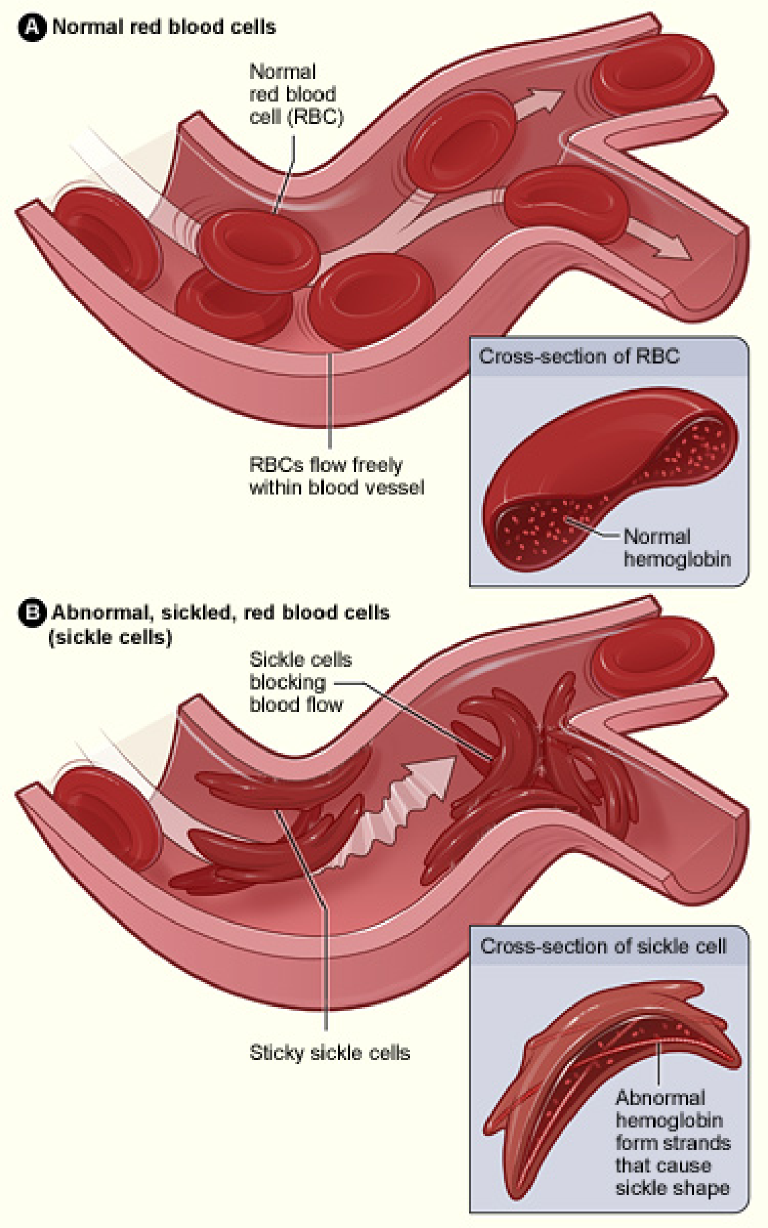

FIGURE 26.10

Sickling in red cells due to presence of hemoglobin S.

Lesson Summary

- Amino acids contain both a carboxylic acid group and an amine group.
- Proteins are formed by the linkage of amino acids with amide (peptide) bonds.
- There are four levels of protein structure: primary, secondary, tertiary, and quaternary.
- Proteins serve numerous functions in the body, including structural support, catalysis, and molecular transportation.
- Enzymes catalyze biochemical reactions.
- Enzymes are classified by the types of reactions that they catalyze.
- Hemoglobin is a protein containing four subunits that transports oxygen throughout the body.
- In sickle-cell disease, an abnormal hemoglobin structure causes aggregation (clumping) of that protein, which

results in deformation of the red blood cells.

Lesson Review Questions

1. Draw a generic amino acid.
2. Draw a structure showing how two amino acids form a peptide bond.
3. Define the following aspects of protein structure:
    a. primary
    b. secondary
    c. tertiary
    d. quaternary
4. List six common functions of proteins.
5. Write the generic form for an enzyme-catalyzed reaction.
6. Describe the structure of the hemoglobin molecule.
7. Describe the molecular defect that causes sickle-cell disease.

Further Reading/Supplementary Links

- Protein structure: http://www.chemguide.co.uk/organicprops/aminoacids/proteinstruct.html
- Levels of protein structure: http://lectures.molgen.mpg.de/ProteinStructure/Levels/index.html
- Sickle cell disease: http://www.webmd.com/a-to-z-guides/sickle-cell-test

26.3 Lipids

Lesson Objectives

- List various classes of lipids and explain their functions.
- Describe the digestion of lipids in the small intestine.
- List various classes of lipoproteins and explain their functions.
- Describe the utilization of stored triglycerides for biochemical energy.
- Explain the relationship between cholesterol and heart disease.

Lesson Vocabulary

- cholesterol
- chylomicron
- fatty acid
- glycerol
- lipid
- lipoprotein
- steroid
- triglyceride

Check Your Understanding

Recalling Prior Knowledge

- What is the structure of a carboxylic acid?
- What is the structure of an ester?
- What do enzymes do?

Classes of Lipids

In the lesson on carbohydrates, we saw that monosaccharides all have a similar structure, but with slight variations. Many monosaccharides can then be linked together to form long polysaccharide chains. Similarly, amino acids all share some of the same structural features, and linking many amino acids together results in the formation of proteins. In contrast, lipids constitute a much broader class of compounds. A **lipid** is a biological molecule that is soluble in nonpolar solvents. This also means that lipids are generally not very soluble in polar solvents, such as water. Because of this characteristic, lipids in the body generally cluster together in order to minimize contact with water, and transportation of lipid molecules throughout the body requires that they be reversibly attached to various transport proteins. A lipid bonded to a protein is referred to as a **lipoprotein**.

In the **Figure** 26.11, we see the structures of some common classes of lipids. Free **fatty acids** are carboxylic acids that contain long hydrocarbon chains. Saturated fatty acids are alkanes with a single carboxylic acid, whereas unsaturated fatty acids contain one or more C-C double bonds. Fatty acids often form esters with one of the alcohol functional groups on **glycerol**, a three carbon chain in which each carbon is bonded to one OH group. **Triglycerides** are common structures, in which all three of these OH groups are esterified with a fatty acid. The three fatty acids in a triglyceride may be the same or different. Another common structure is a phospholipid, in which two of the alcohols in glycerol form esters with fatty acids, and the third is connected to a very polar phosphorus-containing group.

Cholesterol is also considered to be a lipid, even though its structure is very different from the ones we have discussed so far. Cholesterol belongs to a broader class of lipids called **steroids**, all of which possess the same four-ring hydrocarbon core. Other common steroids include cortisol, testosterone, and estrogen.

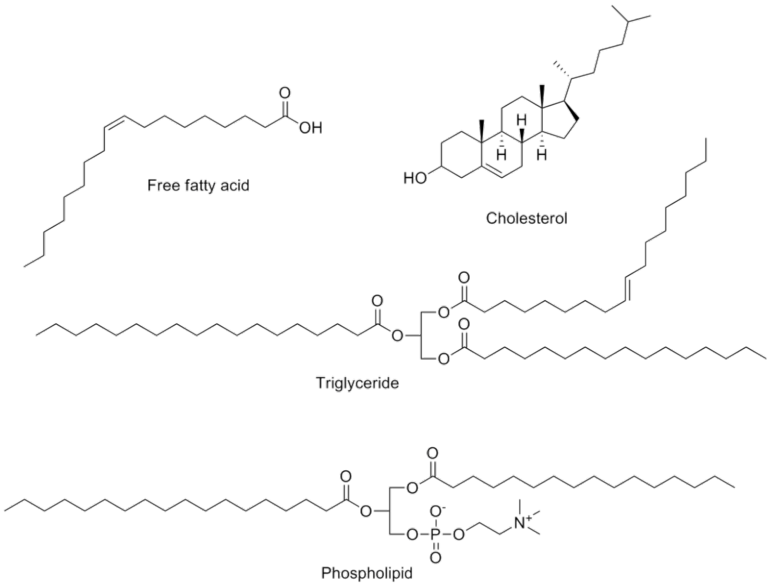

FIGURE 26.11

Classes of lipids.

In addition to the categories of lipids listed above, various vitamins are also classified as lipids, including vitamins A, D, E, and K. You may sometimes hear these referred to as "fat-soluble" vitamins, because they are nonpolar structures that are more soluble in other lipids than in water.

Functions of Lipids

Lipids play several important roles in the body. Triglycerides are stored in fat cells until the body needs to break them down for chemical energy. These stored triglycerides also help insulate the body against extreme temperatures and cushion organs against physical jostling. Phospholipids and cholesterol are important constituents of the cell membrane. These compounds provide structural integrity to the cell wall, since they are not water-soluble. Other steroids are used as chemical messengers in the body, and the fat-soluble vitamins serve a variety of other functions.

Digestion of Lipids

Lipids are consumed in the diet from a variety of foods. Animal products contain several different types of lipids, including saturated fats, unsaturated fats, and cholesterol. The degree of unsaturation in the fatty acids found in food (usually as part of a triglyceride) is thought be associated with lowering the body's stores of cholesterol.

Triglycerides in the diet are digested in the small intestine. Since lipids are not water-soluble, they are emulsified with the help of bile acids, which are produced by the liver and stored in the gall bladder. Bile acids are cholesterol-derived steroids that also contain a water-soluble component. The nonpolar region of these acids can interact with triglycerides, and the water-soluble portion allows the entire complex to dissolve in the aqueous environment within the body.

The pancreas releases the enzyme lipase to hydrolyze at least two of the ester linkages of each triglyceride. The fatty acids and glycerol esters then pass across the intestinal membrane and are resynthesized into triglycerides on the other side. The re-formed triglycerides (along with cholesterol and other lipids) are not water-soluble, so they will not dissolve in the aqueous environment of the bloodstream. Instead, the newly digested lipids will reassemble as lipoproteins known as **chylomicrons** in order to move throughout the body.

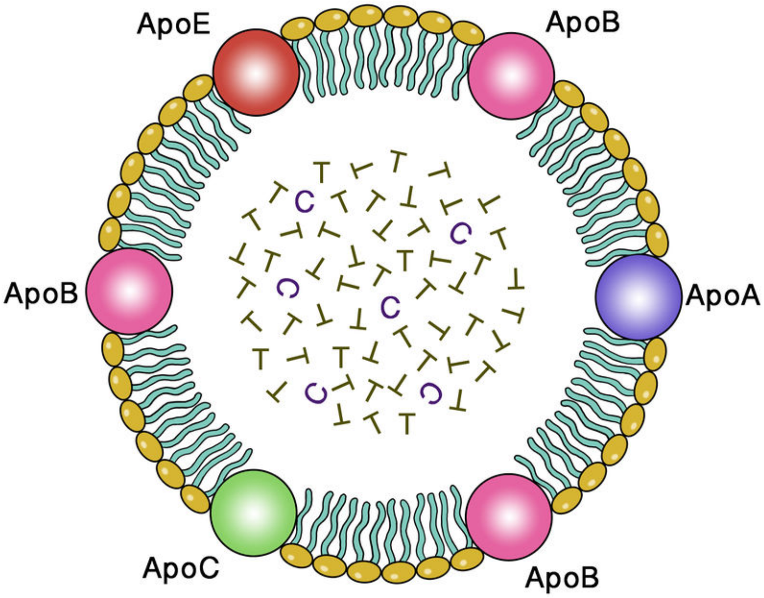

FIGURE 26.12

The outer shell of the chylomicron consists primarily of phospholipids (green), in which the polar phosphorus-containing groups point outward towards the surrounding water, allowing these structures to be relatively water-soluble. Also in the outer shell are various proteins, labeled in the figure above as apo A, B, C, and E. Triglycerides (T) and cholesterol (C) are sequestered on the inside of the chylomicron, along with the nonpolar portions of the phospholipids. As the chylomicrons circulate, the inner triglycerides are transported to certain regions of the body, such as the liver and adipose tissue, where they are unloaded.

Other lipoproteins also transport lipids throughout the body, but different types of lipoproteins tend to serve different functions. We will discuss some of these differences in the section below on cholesterol and heart disease. Lipoproteins are often classified into five different groups based on their densities. In increasing order of density, these groups include chylomicrons, very-low-density lipoproteins (VLDL), intermediate-density lipoproteins (IDL), low-density lipoproteins (LDL), and high-density lipoproteins (HDL).

Lipids and Biochemical Energy

Triglycerides in the body function as a long-term method for storing biochemical potential energy. Changes in the levels of the hormones insulin and epinephrine in the blood lead to the release of triglycerides from adipose tissue. The triglycerides are then broken down by lipase enzymes into glycerol and fatty acids. After being transported into the mitochondria, fatty acids are broken down further into two-carbon fragments, called acetyl CoA. Finally, acetyl CoA molecules can be used to generate ATP, which functions as a kind of universal biochemical energy source within the cell. A normal fatty acid might contain approximately 16 carbons, which would result in the formation of 8 molecules of acetyl CoA. Each acetyl CoA can then be used to generate 12 molecules of ATP. Thus, a single fatty acid might be used to produce nearly 100 ATP molecules.

Regular exercise will increase the demand for ATP and help lower the amount of triglycerides (stored fat) in the body, as will a decrease in the consumption of materials that contain triglycerides or other metabolic energy sources (such as carbohydrates).

Overview of Metabolism

The metabolism of fatty acids is highly interconnected with the breakdown of other dietary energy sources, such as carbohydrates and protein. Recall that glucose and amino acids can both be broken down to form the pyruvate molecule. Pyruvate can then be converted into acetyl CoA, which is then further metabolized to produce ATP. Eventually, all sources of biochemical energy are funneled into the same overall reaction pathways.

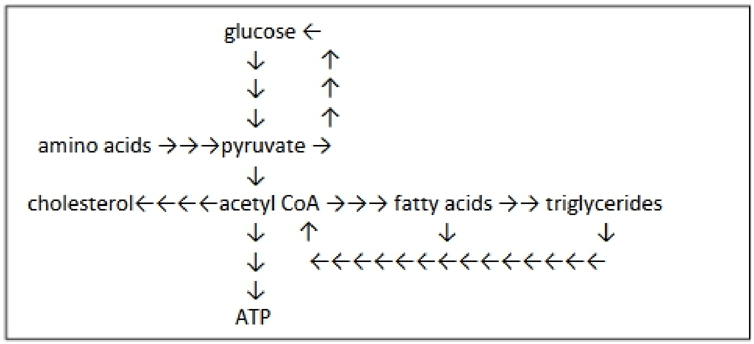

FIGURE 26.13

Overview of energy metabolism.

Additionally, all of these processes are reversible. The breakdown or rebuilding of biomolecules is directed by specific environmental cues in various parts of the body. Because all of these types of molecules can be broken down to the same common intermediates, they are all interconvertible using our biochemical machinery. For example, say the body needs to produce more steroids, but only complex carbohydrates are available as a source of material. The carbohydrates can be successively broken down into disaccharides, monosaccharides, pyruvate, and finally molecules of acetyl CoA. Then, the acetyl CoA can be assembled into cholesterol, which is then modified to produce the necessary steroid. Fatty acids, triglycerides, and other lipids can be generated in a similar way.

Cholesterol and Heart Disease

Because of the link between high levels of cholesterol and heart disease, it is commonly seen by the general public as a "bad" molecule. However, cholesterol plays a vital role in the body, as both a structural component of cell membranes and a metabolic precursor to various steroid hormones. Only about 30% of the cholesterol in our bodies comes from our diet; the rest is synthesized in the liver, intestines, adrenal glands, and reproductive organs. The same acetyl CoA molecule that provides biochemical energy can also be used by the body to synthesize cholesterol. There are approximately twenty-two steps involved in the formation of cholesterol from acetyl CoA.

Cholesterol has been implicated in heart disease for decades. Atherosclerosis is a disorder of the arteries in which cholesterol and other materials are deposited on the interior of the arterial wall. These deposits lead to the formation of plaques that can restrict or even block the flow of blood through these blood vessels (see **Figure** 26.14). A decrease in the flow of blood can lead to high blood pressure and a lowered oxygen supply to the heart muscle. A complete blockage of blood flow to parts of the heart (a heart attack) can cause significant damage due to oxygen deprivation, in some cases leading to death.

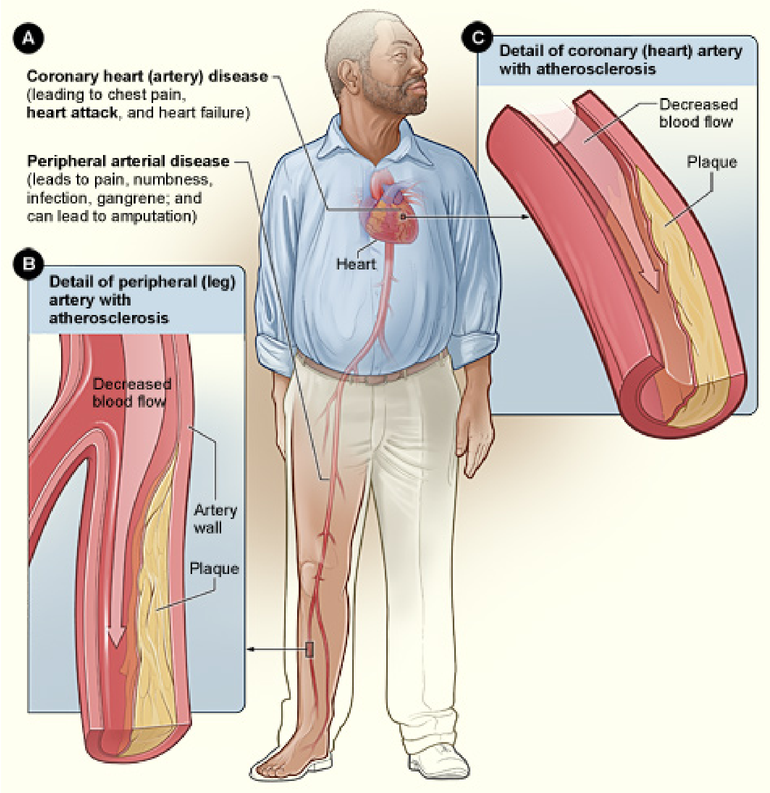

FIGURE 26.14

Plaque formation in artery leading to narrowing of artery.

The growth of plaques in the arteries is facilitated by a high level of low-density lipoproteins (LDL), which transport cholesterol from the liver to various parts of the body. The opposite process, moving cholesterol back to the liver, is carried out by high-density lipoproteins (HDL). Once back in the liver, the cholesterol can be converted to bile acids, which are either excreted or used in the digestion of dietary lipids.

When you get your cholesterol tested, they are measuring not only the total amount of cholesterol in the blood, but also whether it is being transported by LDL or HDL. All of these values are important for assessing the likelihood of a heart attack. Total cholesterol gives an idea of the overall cholesterol load in the body. The LDL cholesterol (sometimes referred to as “bad” cholesterol) is more likely to be incorporated into a cell or a plaque, so it is important that these levels be low. Conversely, since cholesterol being carried by HDL (“good” cholesterol) is being transported away from the rest of the body and into the liver for disposal, higher HDL levels are generally considered beneficial.

High levels of cholesterol in the blood can be treated by medications. The statins (a class of cholesterol-lowering drugs) inhibit the production of cholesterol. One enzyme in the twenty-two step process is rate-limiting –this enzyme catalyzes the slowest reaction in the sequence. Blockage of cholesterol synthesis at this step is currently the most effective way of decreasing cholesterol formation in the body.

Lesson Summary

- Lipids are a diverse class of relatively nonpolar biomolecules that generally do not dissolve well in water. Common types of lipids include fatty acids, triglycerides, phospholipids, and steroids.
- Lipoproteins transport lipids in the bloodstream.
- Triglycerides can be broken down into fatty acids, which can be further metabolized to produce acetyl CoA.
- Acetyl CoA acts as a common intermediate for many metabolic pathways. It can be broken down further as a source of energy or used as a building block to generate more complex molecules.
- Elevated levels of cholesterol in the blood can cause arterial damage, which may lead to a heart attack.

Lesson Review Questions

1. List four classes of lipids and their functions in the body.
2. How are triglycerides digested in the small intestine?
3. What are the functions of LDL and HDL?
4. How can stored triglycerides be used for biochemical energy?
5. How does high cholesterol contribute to a heart attack?

Further Reading/Supplementary Links

- Tutorial on lipid metabolism: http://nfs.uvm.edu/nfs-new/activities/tutorials/lipid.html

- Cholesterol and heart disease: http://www.webmd.com/heart-disease/guide/heart-disease-lower-cholesterol-risk

26.4 Nucleic Acids

Lesson Objectives

- Describe the structure of DNA.
- Describe the structures of messenger RNA and transfer RNA.
- Describe the process of protein synthesis.

Lesson Vocabulary

- DNA
- nucleotide
- RNA
- transcription
- translation

Check Your Understanding

Recalling Prior Knowledge

- What do we mean when we refer to the primary structure of a protein?

Classes of Nucleic Acids

The final type of biomolecules that we will be looking at are the nucleic acids. Like carbohydrates and proteins, nucleic acids are complex polymers of a few simple building blocks. Nucleic acids provide the molecular blueprints for all proteins produced in living systems. We will explore the process by which this information is translated into functional structures later in this lesson. First, we will look at the structures of nucleic acids.

Nucleotides

The subunits from which nucleic acids are generated are referred to as **nucleotides**. A nucleotide consists of a pentose molecule connected to a nitrogen-containing base and one or more phosphate groups. Biological systems make use of two different pentoses for the construction of nucleic acids: ribose and deoxyribose. Long polymers of ribose-derived nucleotides are referred to as ribonucleic acids (**RNA**), and and polymers of deoxyribose nucleotides are referred to as deoxyribonucleic acids (**DNA**).

In a given strand of DNA or RNA, the only difference between each subunit is the choice of base. The five common bases are shown in the **Figure** 26.15. Based on the number of rings, they are classified as either purines or pyrimidines.

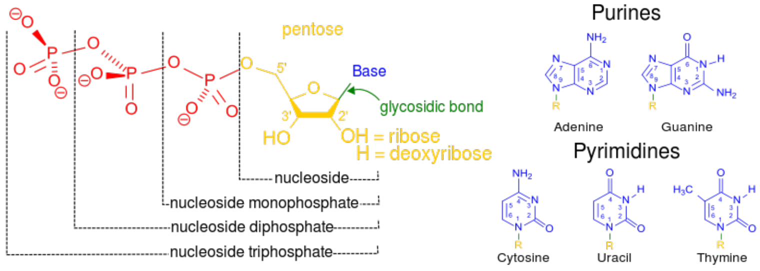

FIGURE 26.15
Nucleotide structures.

In general, DNA does not make use of the uracil base, and RNA does not contain thymine. As a result, each strand of a nucleic acid will use only four of these bases.

DNA

Individual nucleotides can be linked together through their phosphate groups to form nucleic acid polymers. Once constructed, DNA generally exists as two strands that are linked together by hydrogen bonds, producing a double-helical structure (see **Figure** 26.16).

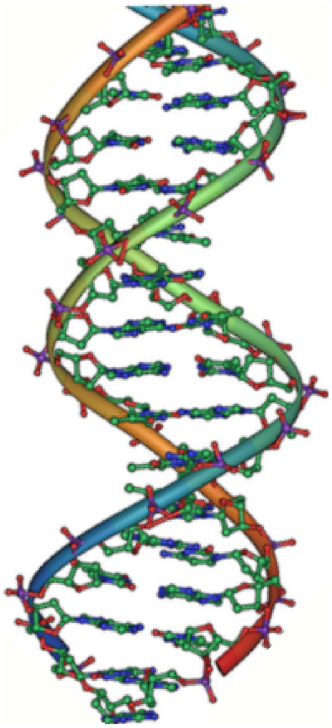

FIGURE 26.16
DNA structure.

In order for the structure in **Figure** 26.16 to form, the bases that line up across from each other must be complementary to one another. Based on their structures, adenine will make favorable hydrogen bonding interactions with thymine, and vice versa. Guanine and cytosine form another complementary pair. Mismatched bases will form unfavorable interactions in the center of the helix.

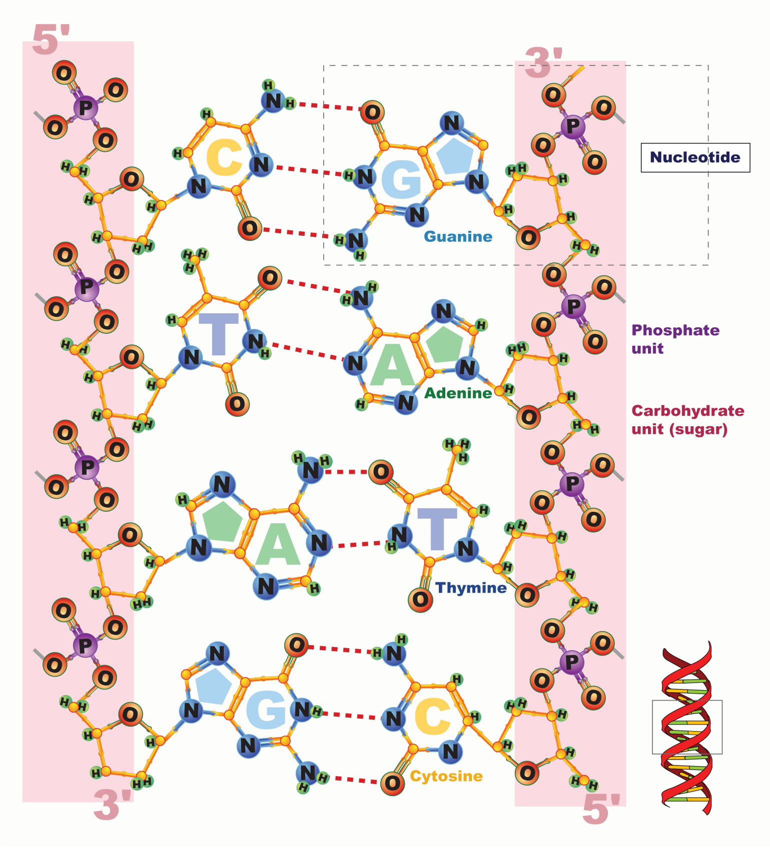

FIGURE 26.17
Base pairing in DNA.

If we know the sequence of one strand in a DNA double helix, we can predict the sequence of the opposite strand based on the required pairings.

RNA

RNA is nearly identical to DNA, except that the sugar has an extra OH group and uracil is used instead of thymine. Due to the additional hydrogen bonding opportunities generated by the extra OH group, RNA is found more often as a single strand that is folded in on itself. However, RNA can still form a double helix with a strand of either DNA or RNA if the bases form a complementary sequence.

RNA is sometimes classified based on the function that it is performing. The types most relevant to the production of proteins are messenger RNA (mRNA), transfer RNA (tRNA), and ribosomal RNA (rRNA). We will look at the role of each type of RNA in the following section.

Protein Synthesis

The process of protein synthesis is summarized in the **Figure** 26.19. DNA produces an RNA template that directs the amino acids to be introduced into the growing protein chain in the proper sequence. A specific transfer RNA attaches to each amino acid and brings it to the RNA for incorporation.

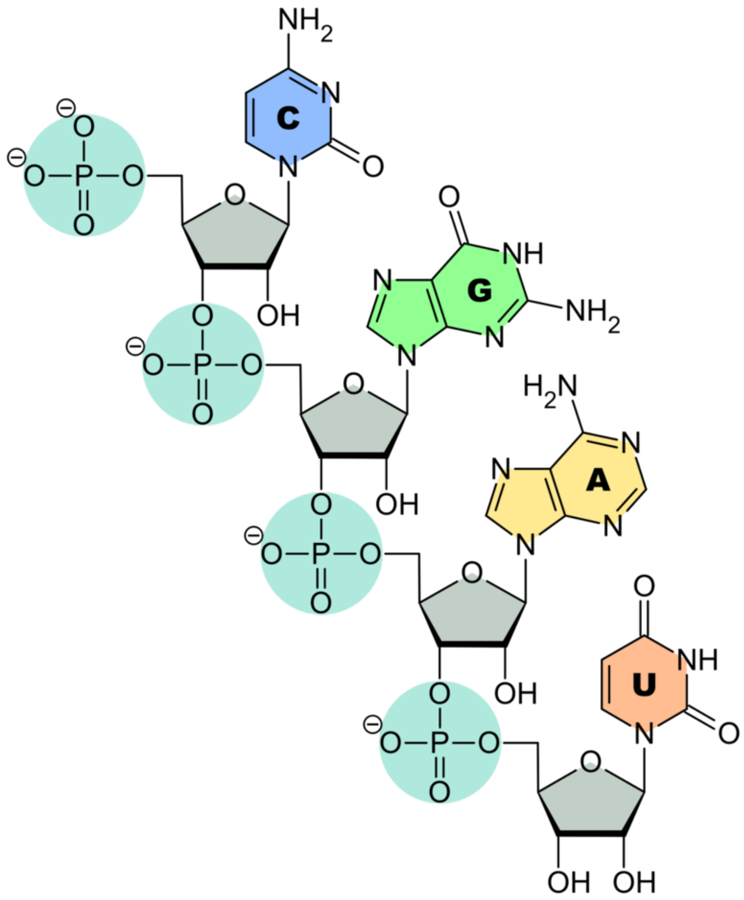

FIGURE 26.18

RNA structure.

The first step in the process is **transcription** - the unfolding of DNA and the production of an mRNA strand. This step takes place in the nucleus of the cell.

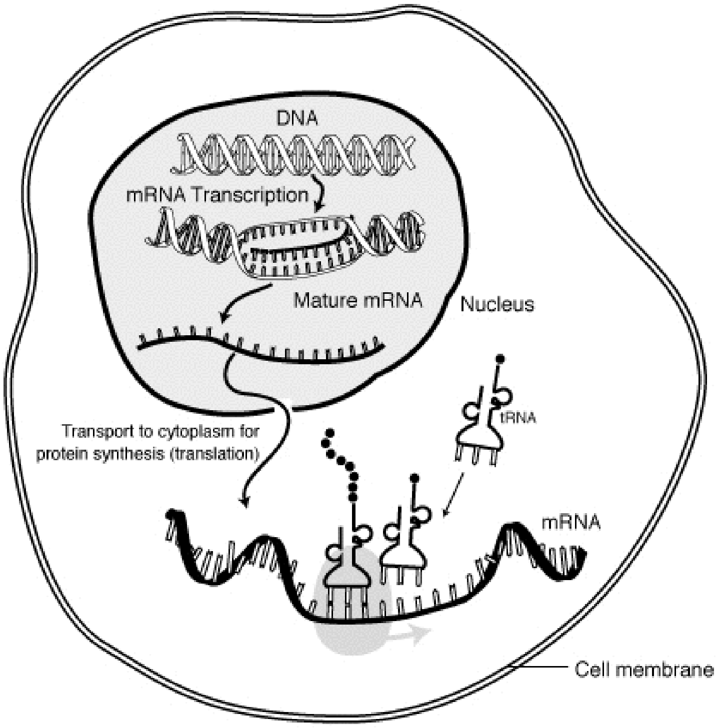

FIGURE 26.19
Overview of protein synthesis.

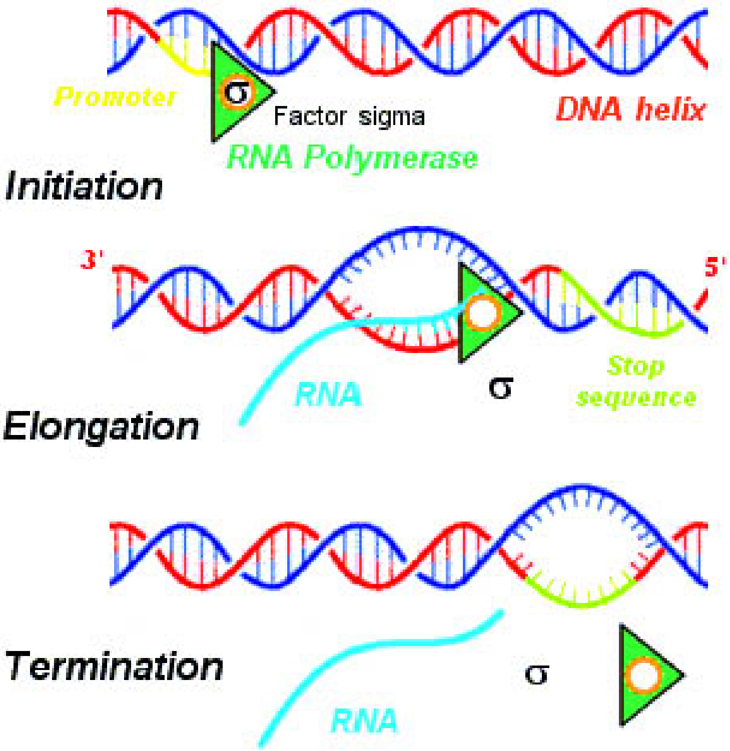

FIGURE 26.20
Formation of RNA from DNA.

The DNA uncoils and provides the pattern for the formation of a single strand of mRNA. After production of the

RNA, the DNA refolds into the original double helix. The mRNA is exported to the cytoplasm (outside the nucleus) for further processing.

Amino acids will link with specific transfer RNA molecules for proper placement in the protein chain. The tRNA is a small coiled molecule that accepts an amino acid on one end and matches up to a specific three-base portion of the mRNA on the other end. The tRNA interacts with the mRNA so as to put the amino acids in the proper sequence for the developing protein. After adding the amino acid to the sequence, the tRNA is cleaved from the amino acid and recycled for further participation in the process. Because we are converting from one "language" to another (a sequence of mRNA bases into a sequence of amino acids), this part of the process is referred to as **translation**.

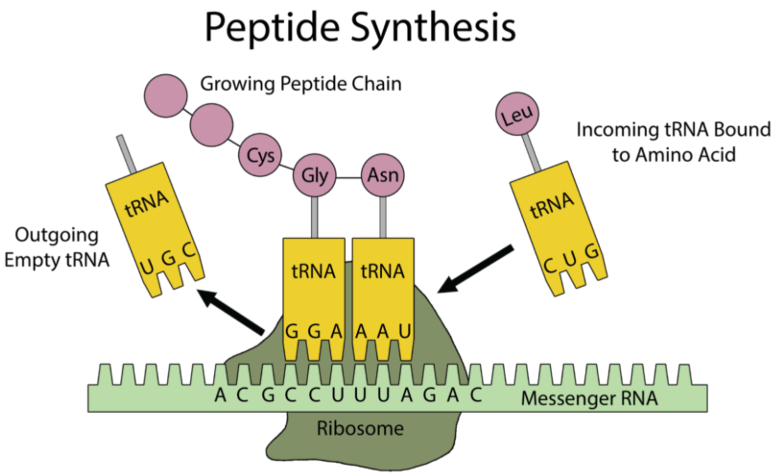

FIGURE 26.21

The process of assembling amino acids into a protein takes place in the ribosome. This structure consists of two subunits, each of which is composed of both proteins and ribosomal RNA (rRNA). The two subunits clamp together on the mRNA and catalyze the formation of the amide linkages in the growing protein. When protein synthesis is complete, the two subunits dissociate and release the completed protein chain.

The process of protein synthesis is fairly fast. Amino acids are added to the growing peptide chain at a rate of about 3-5 amino acids per second. A smaller protein (100-200 amino acids) can be produced in a minute or less.

Lesson Summary

- Nucleotides contain a pentose sugar, a nitrogen-containing base, and one or more phosphate groups.
- Nucleic acids, such as DNA and RNA, are composed of long strands of nucleotides bonded together through their phosphate groups.
- DNA generally exists as two complementary strands connected by hydrogen bonds into a double helix structure.
- DNA contains the genetic information for the production of proteins.
- The transcription process produces a strand of messenger RNA from DNA.
- During translation, messenger RNA interacts with the ribosome and transfer RNA to produce a protein.

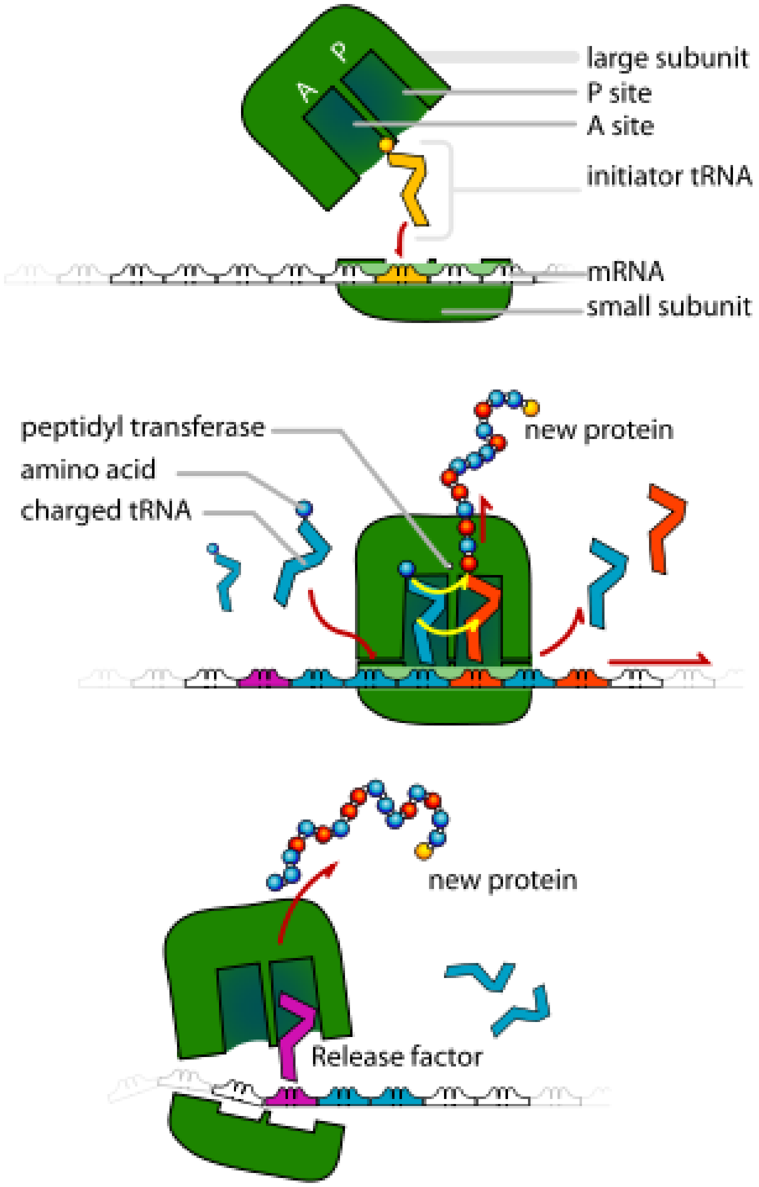

FIGURE 26.22

Role of ribosome in protein synthesis.

Lesson Review Questions

1. Describe the differences in structure between DNA and RNA.
2. Describe the process of transcription.
3. Describe the structure of transfer RNA.
4. Describe how translation leads to synthesis of a new protein.

Further Reading/Supplementary Links

- Structures of nucleic acids: http://www.ncbi.nlm.nih.gov/books/NBK21514
- Animation of the translation process in protein synthesis: http://www.youtube.com/watch?v=Ikq9AcBcohA
- Animation of protein synthesis: http://en.wikipedia.org/wiki/File:Translation.gif

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17. Mariana Ruiz Villarreal (LadyofHats) for CK-12 Foundation. CK-12 Foundadtion . CC BY-NC 3.0
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CHAPTER 27

Glossary

Chapter Outline

27.1 A
27.2 B
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27.26 Z

27.1 A

absolute zero

In 1848 Lord Kelvin observed what happened to the volume of a gas as its temperature fell. For every 1°C drop in temperature, the gas contracted almost uniformly by 1/273th of its volume at 0°C. He interpreted this to mean that the volume must fall to zero at -273°C, absolute zero.

accuracy

Describes how close a given set of data is to the "real" value.

acid

Any compound that produces hydrogen ions (H^+) in water.

activation energy

The energy that is needed to get reactants close enough together for a reaction to occur.

activity series

The electromotive series (or activity series) ranks metals in terms of their ability to participate in oxidation-reduction reactions.

adhesion

Ability to stick to other substances.

alchemist

A practitioner of the medieval science of alchemy, which aimed mainly to transform everyday metals into gold.

alcohol

The alcohol functional group is R-OH where R can represent any specific carbon structure. Alcohols can be primary, secondary, or tertiary.

aldehyde

Has a double-bonded carbon-oxygen bond (one sigma bond and one pi bond). The carbon to which the oxygen is attached has one hydrogen atom connected to it.

alkane

Contains only carbon-carbon single bonds.

alkene

Contains one or more carbon-carbon double bonds.

alkyne

Contains one or more carbon-carbon triple bonds.

allotrope

Multiple physical forms where one element can exist.

alloy

A solid solution either of two or more metals, or of a metal or metals with one or more nonmetals.

alpha helix

One basic form of secondary structure.

alpha particle

This emission consists of a helium nucleus.

amalgam

Special type of alloy used for a variety of purposes, including dentistry and gold extraction.

amide bond

Links individual acids together.

amide

Forms between a carboxylic acid and an amine.

amine

Functional group consists of a C attached to a N. There can be three different classes of amines: primary, secondary, and tertiary.

amorphous solid

Solid that lacks an ordered internal structure.

anion

Negatively charged ion.

anode

The electrode at which oxidation occurs.

Arrhenius acid

Produces a proton in solution.

Arrhenius base

Produces a hydroxide ion in solution.

atmospheric pressure

The force exerted by a hypothetical column of gas that stretches from sea level to the outer reaches of the atmosphere.

atom

Matter is composed of these tiny indivisible particles.

atomic mass

The weighted average of the atomic masses of the naturally occurring isotopes of that element.

atomic number
Is equal to the number of protons in its nucleus.

atomic radius
The distance from an atom's nucleus to the outermost orbital of electron.

Aufbau Principle
States that as protons are added one by one to the nucleus of an atom to build up the elements, electrons are similarly added to the atomic

orbitals.

Avogadro's number
Defined as 6.022×10^{23}. It is a number used to describe amounts of atoms and molecules.

A-Z notation
The composition of any atom can be illustrated with this shorthand notation.

27.2 B

balanced chemical equation
The number of each specific atom that exists as a reactant must equal the number of that atom in the products.

barometer
Instrument that measures pressure.

base unit
Measurements that have their own independent scale and cannot be expressed in terms of other base units.

base
Compounds which contain hydroxide ions .

battery
Used oxidation-reduction reactions to generate electron flow which can be employed for useful work.

beta particle
This emission involves the conversion of a neutron to a proton (which remains in the nucleus) and an electron (beta particle) which is ejected from the nucleus.

beta-pleated sheet
One basic form of secondary structure.

bimolecular reaction
Two different reactants interact to form products.

binary acid
Acids in which the acidic hydrogen atom(s) are bound directly to an atom other than oxygen.

binding energy
Energy that is released that holds the nucleus together.

boiling point elevation
If we dissolve a known amount of solute in a known amount of water and measure the boiling point of the solution, the boiling point will be elevated.

boiling point
Temperature at which liquid transitions to gas.

Boyle's Law
For a fixed amount of gas at constant temperature, the volume is inversely proportional to its pressure.

brittleness
Can break or shatter without deformation.

Brønsted-Lowry acid
Donates a proton.

Brønsted-Lowry base
Accepts a proton.

27.3 C

calibration

A method of setting or correcting a measuring device by matching it to known measurement standards.

cancer

These cells have an abnormal structure due to the damaged DNA. In addition, they usually grow rapidly since the normal control processes regulating cell growth have been changed by the altered composition of the DNA.

carbohydrate

Has the general structure $C_n(H_2O)_n$. Can be classified in terms of chain length. Can be classified as monosaccharides, disaccharides, or polysaccharides.

catalyst

Material that speeds up the rate of reaction without undergoing any change itself.

cathode

The electrode at which reduction occurs.

cation

Positively charged ion.

Celsius scale

Defines the normal freezing point and boiling point of water as 0°C and 100°C, respectively.

Charles's Law

States that the volume of a given mass of a gas, with constant pressure, is proportional to temperature.

chemical change

A change during which the chemical identity of a substance is altered. Chemical changes are often accompanied by a change in color, temperature, or odor, or the production of a gas or precipitate.

chemical equilibrium

The study of the forward and reverse nature of chemical processes.

chemical property

A property that describes the ability of a substance to undergo a specific chemical change.

chemical species

Atoms, ions, elements, compounds, etc that take place in a chemical reaction.

chemistry

The science of the properties, reaction, composition, and structures of matter.

cholesterol
Contains a four-ring system with a hydrocarbon side chain.

chromatography
The separation of a mixture by passing it through a medium in which the components move at different rates. This can be done as a liquid solution, a suspension, or a vapor (as in gas chromatography).

combustion
Occurs when a hydrocarbon reacts in the presence of oxygen to produce water and carbon dioxide.

cohesion
Ability to stick to itself.

colligative properties
Affected strictly by the amount of solute added and not the type of solute added.

collision theory
Molecules need to collide in order for a reaction to take place.

colloid
A mixture that is not totally homogeneous, nor totally heterogeneous.

combination reaction
Two chemical species combine to produce a new compound. The general expression for this reaction is A + B → C.

compounds
Substances with a constant composition that can be broken down into two or more elements by chemical processes.

continuous theory of matter
It was thought that matter could be divided and subdivided into smaller and smaller pieces without limit.

conversion factor
Used in solving problems in which a certain measurement must be expressed with different units.

copper cycle
A series of chemical reactions where an initial amount of copper reacts with nitric acid, goes into solution, and disappears. Then a series of reactions proceed, only to have the copper metal recovered. The copper cycle is a good illustration of how mass is conserved in a given chemical reaction.

corrosion
Involves the formation of an oxidized form of a metal by an electrochemical process.

covalent bond
Forms when two or more elements share electrons.

covalent compounds
Nonionic (not composed of cations and anions) substances that are comprised of nonmetals.

crystal lattice

A geometric arrangement of points in space at which the atoms, molecules, or ions of a crystal occur.

crystalline solid

Arranged in a geometric, organized, three-dimensional structure. Has definite melting point and shape.

27.4 D

Dalton's law of partial pressures
States that the total pressure of the mixture is the sum of the partial pressures of each gas component.

decomposition reaction
The exact opposite of a combination process. A chemical species breaks down to produce two new chemical species. The general expression for this reaction is C → A + B.

deductive reasoning
Takes a general principle and then draws a specific conclusion from the general concept.

dehydration
Chemical reaction that results in a loss of water.

dehydrohalogenation
When an alkene is acquired by an alkyl halide during an organic reaction. An example of elimination reaction.

density
An expression of the amount of space occupied by a given mass of a substance.

derived unit
Combinations of base units.

dew point
Temperature needed for water vapor to condense into water.

diatomic gas
Where two nitrogen atoms are held together by triple bonds.

diffusion
The rate at which two gases mix. Inversely proportional to the density of the gas.

dilution
Process requires adding more solvent to the initial concentrated solution.

dimensional analysis
A technique that uses the units (dimensions) of the measurement in order to correctly solve problems.

disaccharide
Composed of two monosaccharides

discontinuous theory of matter
Believed matter was actually finite and not limitless.

dispersed phase

A substance in the colloidal stage.

dispersion force

Attractive forces that arise as a result of temporary dipoles induced in atoms or molecules. Also referred to as van der Waals forces or interactions.

dispersion medium

The medium where a disperse phase is distributed.

dissociate

When ions break apart from a lattice and go into solution.

dissolution

The process where water interacts with the ions within the crystal lattice, causing the lattice to break apart.

dissolving

When one substance dissolves in another. This process requires there be a solvent and a solute that interact to produce a homogeneous solution.

distillation

A purification process where the components of a liquid mixture are vaporized and then condensed and isolated.

DNA

Deoxyribonucleic acid. Consists of two chains of nucleotides that connect to one another in a double helix. Contains the genetic information for the accurate production of proteins.

double displacement

Typically includes two soluble salts that react with one another in aqueous media. The general form of this reaction is $AB + CD \rightarrow AD + CB$.

dry cell battery

Uses a paste in a casing containing two different metals.

ductility

Can be stretched, bent, or twisted without breaking.

27.5 E

effective nuclear charge
When an electron is in a multi-electron atom, it produces this net positive charge.

effusion
Rate at which a gas escapes through a pinhole into a vacuum. Inversely proportional to the molar mass of the gas.

elastic collision
Collisions are elastic. Momentum is conserved. No energy is lost through collisions.

electrolysis
Is a process that uses electrons to cause certain chemical reactions to occur.

electron configurations
Arrangement of all the electrons of that atom.

electron shielding
As more electrons are added to a nucleus, the outer electrons become shielded from the nucleus by the inner shell electrons.

electron
Negatively charged and has a very small mass compared to the mass of other subatomic particles. Electrons were initially called cathode rays.

electronegativity
Electronegativity (EN) is a measure of the relative tendency of an atom to attract electrons to itself when chemically combined with another atom.

elements
Substances that cannot be decomposed into simpler substances by chemical or physical means.

empirical formula
The smallest whole number ratio of the numbers of atoms in a compound.

emulsifying agent
A substance that inhibits coagulation of colloidal particles and covers the particles of the dispersed phase.

emulsion
If there are liquid-dispersed particles in liquid phase.

endothermic reaction
A reaction that requires heat for the reaction to take place.

enthalpy
A thermodynamic function of a system, equivalent to the sum of the internal energy of the system plus the product of its volume multiplied by the pressure exerted on it by its surroundings. The symbol for enthalpy is H.

enthalpy of reaction
When a mole of matter is altered by a chemical reaction under standard conditions, a change of enthalpy takes place.

entropy
A thermodynamic function that describes the number of arrangements that are available to a system existing in a given state. A measure of randomness or disorder. The symbol of entropy is S.

enzyme
Catalyzes biochemical reactions.

equilibrium constant
Relates the concentrations of materials on both sides of the reaction arrow at equilibrium.

equilibrium expression
Can be used to describe changes for a chemical reaction.

equivalence point
The point in a neutralization reaction where the number of moles of hydrogen ions is equal to the number of moles of hydroxide ions.

ester
Formed from a reaction between an alcohol and a carboxylic acid.

estimate
As used in measurement, is the process of referencing a physical quantity in terms of a calibration or reference point.

ether
The ether functional group consists of an oxygen atom which forms single bonds with two carbon atoms.

evaporation
The process whereby atoms or molecules in a liquid state (or solid state, if the substance sublimes) gain sufficient energy to enter the gaseous state. This can be used as a technique to separate the liquid component of a homogeneous mixture from its dissolved solids.

exothermic reaction
A reaction that releases heat during the course of the reaction.

extensive properties
Properties that depend on the amount of a substance that is present. Examples include mass, volume, and length.

27.6 F

Fahrenheit scale

The most commonly used scale in the United States, defines the normal freezing point and boiling point of water as 32°F and 212°F, respectively.

fatty acid

Are cleaved from triglycerides in the small intestine.

filtration

A method used to separate substances in mixtures where at least one component has particles that are large enough in size to be captured by a porous material.

first law of thermodynamics

Energy can be converted from one form to another, but cannot be created or destroyed.

first-order reaction

The rate is dependent upon the reactant concentration raised to the first power.

fission

Nuclear fission reactions involve collision of a slow neuron with an element, usually uranium. The products of a fission reaction are two smaller isotopes, more neutrons, and heat energy.

force

Ability to do work.

formula mass

The sum of masses of all the atoms represented in a chemical formula.

free element

Uncombined state where each atom has an oxidation number of zero.

freezing point depression

The addition of solute to a pure solvent will decrease the freezing point of the solution by a measurable amount.

frequency

Inversely proportional to wavelength. Photons with high frequency light have more energy than photons with low frequency light (Zukav 1979).

frost

A solid form of water.

fuel cell

Employ oxidation-reduction reactions of hydrogen and oxygen gases ad a platinum catalyst.

functional group

In a compound, a group of atoms that define the behavior of the compound.

fusion

This reactions are a potential source of power. Involves the collision of smaller atoms to form larger ones. Nuclear fusion reactions occur in stars.

27.7 G

galvanic cell

Otherwise known as a voltaic cell.

gamma emission

The release of energy.

Gay-Lussac's Law

Gas law which states that the pressure of a given mass of a gas varies directly with the absolute temperature of the gas when the volume is kept constant.

glycolysis

Means splitting of glucose.

Gibbs free energy

A thermodynamic quantity that combines enthalpy and entropy into a single value that has been named after Josiah Gibbs, an American physicist. This value can be used to determine equilibrium constants.

gluconeogenesis

Process that breaks down proteins and provides needed glucose for the cells.

glycogen

Made up of long chains of glucose units.

gold foil experiment

Ernest Rutherford discovered the presence of a positively charged nucleus with this experiment. He used a radioactive source to direct alpha particles toward a very thin sheet of gold foil. Surrounding the foil was a screen that fluoresced when struck by the alpha particles.

Graham's law of effusion

States that the rate of effusion or diffusion of a gas is inversely proportional to the square root fo the molar mass of the gas.

27.8 H

half-reaction

Contains only half the entire redox process. One half-reaction illustrates the oxidation component while the other half-reaction illustrates the reduction component.

halogenation

Chemical reaction where a halogen atom is included in a molecule.

heat capacity

The amount of heat need to raise a specified amount of material one degree Celsius. Can be calculated using the formula C=ms.

heat energy

Chemical reactions involve a transfer of heat energy. Measured in joules.

Heisenberg's Uncertainty Principle

Heisenberg described mathematically the phenomena revealed by Young's double slit experiment. He showed that it is impossible to determine simultaneously both the exact location and exact velocity of an electron or any other particle.

Henry's Law

Describes mathematically the relationship between the vapor pressure of the solution in terms of solute concentration.

Hess's law

States that regardless of the multiple stages or steps of a reaction, enthalpy change overall encompasses the sum of all changes.

heterogeneous mixtures

Mixtures that include two or more distinct phases, which contain nonequivalent proportions of the mixture components.

homogeneous mixtures

Mixtures that have a constant composition throughout.

humidity

Quantity of water vapor in the air.

Hund's Rule

The rule states that orbitals of equal energy are each occupied by one electron before any orbital is occupied by a second electron, and all electrons in singly occupied orbitals must have the same spin.

hybridization

The mixing of atomic orbitals in an atom (usually a central atom) to generate a set of hybrid orbitals.

hydrocarbon
Contains only carbon and hydrogen.

hydrogen bond
A “special case” dipole-dipole interaction.

hydrolysis
When molecules of water are split into hydroxide anions and hydrogen cations (protons). Useful in the study of protein structure.

27.9 I

ideal gas law

PV=nRT.

ideal gas

Gases that conform to the basic principles of kinetic-molecular theory.

immiscible

Molecules don't mix well together, and form a heterogeneous mixture- exhibiting a noticeable bilayer.

indicator

Used to measure pH. Changes color depending on the pH of the solution.

inductive reasoning

Involves getting a collection of specific examples and drawing a general conclusion from them.

initial rate of reaction

The rate at the very beginning where the reactant concentration has not changed appreciably and the product concentration is negligible.

insoluble

It does not dissolve, and it does not dissociate in water.

intensive properties

Physical properties that do not depend on amount. Examples include color, taste, melting point, boiling point, density, luster, and hardness.

ion

Formed when elements either gain or lose electrons.

ion-product constant

An equilibrium constant. $K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$ at 25°C

ionic bond

An electrostatic attraction between two ions that have exchanged electrons.

ionic compounds

A compound formed by ions bonded together through electrostatic forces.

ionic equation

An equation in which dissolved ionic compounds are shown as free ions.

ionic radius
The radius exhibited by an ion in an ionic crystal where the ions are packed together to a point where their outermost electronic orbitals are in contact with each other.

ionization energy
The energy required to remove an electron from a specific atom. It is measured in kJ/mol, which is an energy unit, much like calories.

isoelectric
Having equal numbers of electrons or the same electronic configuration.

isotopes
Atoms that have the same atomic number but different mass numbers due to a change in the number of neutrons.

27.10 J

27.11 K

Kelvin scale

Which is also referred to as the absolute temperature scale, defines absolute zero as the lowest theoretically possible temperature, which means that temperatures expressed in Kelvin cannot be negative numbers.

kernel electrons

Interior electrons.

ketone

Has a structure similar to that of aldehydes, except the ketone has two R groups attached to the carbon containing the C=O bond. Reactions of aldehydes and ketones are sometimes similar.

kinetic energy

The energy of motion. Kinetic energy increases as the molecular mass increases and as the velocity of the particle increases.

kinetic-molecular theory

Makes the following assumptions: 1. Gas particles are in constant, random motion. 2. The volume of gas particles is negligible in comparison to the volume of the container. 3. There are no attractive forces involved between gas particles. 4. Collisions of gas particles are elastic –no energy is lost. 5. The speed of a gas particle is proportional to the temperature of the system.

27.12 L

lattice energy

Lattice energy of an ionic solid is a measure of the strength of bonds in that ionic compound.

law of conservation of mass

For a closed system, the mass of the reactants must equal the mass of the products for any chemical process.

law of definite proportions

Joseph Proust found that compounds always contain the same proportion of elements by mass, regardless of amount.

law of mass action

A general expression that can be applied to any chemical reaction.

law of multiple proportions

This law states that if two elements form more than one compound between them, then the ratios of the masses of the second element that combine with a fixed mass of the first element will be ratios of small whole numbers.

Le Chatelier's Principle

Describes how a chemical system will change to maintain equilibrium when a stress is applied.

Lewis acid

Accepts an electron pair.

Lewis base

Donates an electron pair.

Lewis structure

A simple way of representing covalent bonds. Each dot in the structure represents one electron in the compound. Also known as Lewis dot structures.

light

Behaves both as a particle and as a wave.

limiting reactant/reagent

The reactant that is used up first in a reaction; the limiting reactant determines the amount of product that can be formed in a chemical reaction.

linear

Molecule with atoms organized so the bond angle is 180 degrees between each of them.

line-emission spectrum

Frequencies of electromagnetic radiation given off by a compound's molecules or element's atoms.

lipid
Does not possess a unique structure. Lipids are better defined by the fact that they are not particularly soluble in water. Classes include fatty acids, triglycerides, phospholipids, and cholesterol.

lipoprotein
Transports lipids in the bloodstream.

lone pair
A couple of opposite spin valence electrons that are accountable for the development of coordinate bonds and are not shared between atoms.

lustrous
Glowing.

27.13 M

malleability
Can be stamped, hammered, forged, pressed or rolled into thin sheets.

mass
Measure of the amount of matter that an object contains.

mass number
The total number of protons and neutrons in an atom.

mass spectrometer
An instrument developed in 1918 by Arthur Jeffrey Dempster. Determines the masses of atoms, molecules, and molecular fragments.

matter
Anything that has mass and takes up space.

melting point
Temperature at which solid transitions to liquid.

meniscus
In a standing body of liquid, this is the curve in the top surface of the liquid.

miscible
Molecules mix well with one another, and form a homogeneous mixture.

mixtures
A physical combination of two or more pure substances. The proportions of the individual components may vary, and these components can be separated by physical methods.

molality
The mass of the solution. Moles of solute per kg of solvent. Abbreviated as "m."

molar heat of fusion
The heat absorbed by one mole of a substance as it is converted from a solid to a liquid.

molar heat of vaporization
The heat absorbed by one mole of a substance as it is converted from a liquid to a gas.

molar mass
The mass of one mole of any given substance.

molar solubility

Molar solubility of a gas is expressed by taking the inverse of Henry's Law constant (kH) and multiplying it by the partial pressure of the gas above the solution.

molarity

Total volume of solution. Moles of solute per liter of solution. Abbreviated as "M."

mole fraction

Expressed as x. It is the amount of a component n_i divided by the total amount of all components in a mixture n_{tot}.

mole ratio

When we express the moles of reactants and products in terms of one another in a ratio.

molecular formula

A formula indicating the numbers and types of atoms in a molecule.

molecular orbital

The result of interactions of the atomic orbitals of the bonding atoms and are associated with the entire molecule.

monatomic

Ions that consist of a single atom with either a positive or negative charge.

monoprotic acid

Has one available hydrogen to react.

monosaccharide

One basic unit or one molecule.

27.14 N

net ionic equation

For a reaction that includes only the species involved in the reaction.

neutralization

This reaction involves H^+ + OH^- $\rightarrow$ salt + water.

neutron

A particle with a mass similar to that of the proton, but has no electrical charge. Neutrons also reside in the nucleus.

27.15 O

octahedral
Six atoms are evenly organized around a central atom.

octet rule
States that atoms will lose, gain or share electrons to achieve the electron configuration of the nearest noble gas (8 valence electrons except for He with 2).

orbital
A three-dimensional region around the nucleus that indicates the probable location of the electron.

oxidation number
Used to describe the state of an element's electrons as it undergoes a chemical change.

oxidation
Involves the loss of hydrogen, the gain of oxygen, or the loss of electrons.

oxidation-reduction reaction
Oxidation and reduction both occur within the same reaction- one or more atoms are oxidized while one or more different atoms are reduced. Simply referred to as a redox reaction. There are 4 types of reactions are combination, decomposition, displacement, and combustion.

oxidizing agent
Causes the oxidation of another species in the reaction.

oxyacid
Compounds comprised of at least one oxygen atom as part of their molecular structure.

27.16 P

partial pressure
The pressure that each individual gas exerts.

Pauli exclusion principle
No two electrons in same atom can have the same set of four quantum numbers.

percent abundance
The percentage of atoms in a naturally occurring sample of the pure element that are a particular isotope.

percent error
An expression of the accuracy of a measurement, standardized to how large the measurement is.

percent uncertainty
The ratio of the uncertainty to the measured value, multiplied by one hundred.

percent yield
The ratio of the actual yield to the theoretical yield, expressed as a percentage.

periodic law
States that when elements are arranged in order of increasing atomic number, there is a periodic repetition of their chemical and physical properties.

periodicity
Repetitive variations or trends in element properties.

PET
Positron emission tomography (PET), often referred to as a PET scan. One of the more useful approaches to radioisotope use in medicine. This technique is useful in studying the processes in the brain.

pH
The negative logarithm of the hydrogen ion concentration.

philosopher's stone
A substance that could cause the transmutation of lead into gold.

phlogiston
Substance previously thought to be a unstable component of all combustible substances.

photoelectric effect
Under the right conditions, light can be used to eject electrons from a solid material.

photoemissive
Materials that eject electrons when illuminated with light, such as potassium.

photon
A particle of light.

physical change
A change that affects the form of a chemical substance but does not change its chemical composition.

physical properties
Those properties that can be observed or measured without changing the composition of the matter. Physical properties of matter include mass, weight, volume, and density.

pi bond
Not connected directly between the two atoms, but above and below them.

plum pudding model
J. J. Thomson postulated that the atom was comprised of negatively charged particles in a disperse field of positive charge (positively charged particles had not yet been discovered). This proposed arrangement was compared to the arrangement of plums in plum pudding.

polarity
Polar molecules contain one or more atoms which possess either a partial positive or a partial negative charge.

polyatomic
Charged molecules comprised more than two elements.

polymer
Are long-chain materials with useful properties.

polyprotic acid
Has two or three available hydrogen to react.

polysaccharide
Made up of many monosaccharides.

positron
This emission involves the conversion of a proton in the nucleus to a neutron (remaining the in the nucleus) and an ejected positron (positive electron).

precision
Describes how close estimates are to one another.

pressure
Applied force per unit area on a surface.

primary structure
The amino acid sequence.

product-favored equilibrium
At the equilibrium, the concentration of products is large and the concentration of reactants is small.

proton

Positively charged and has a relatively large mass compared to electrons. They can be found in the nucleus of the atom.

pure substances

Substances with a constant composition that can only be broken down to their constituent parts by chemical means.

pyramidal

Geometry of an molecule with an equilateral triangle of 3 atoms and one atom right above.

27.17 Q

quantum (plural - quanta)

Minimum quantity of energy that can either be lost or gained by an atom.

quantum numbers

We use these series of specific numbers to describe the location of an electron in an associated atom.

quantum theory

Describes the allowed energies of molecules and atoms.

quaternary structure

Only possessed by proteins that have more than one subunit.

27.18 R

radioactivity

Involves the release of particles and/or energy from the nucleus of an atom.

Raoult's Law

States that vapor pressure of a solution equals the product of the vapor pressure of the pure solvent and the mole fraction of solvent, as described by: $P = x_{solvent}P°$.

reactant-favored equilibrium

At the equilibrium, the concentration of products is small and the concentration of reactants is large.

reaction mechanism

Follows a reaction pathway going from initial reactants to final products. Describes the intermediate steps in a reaction.

reaction quotient

A function of the actions of a chemical species in a chemical reaction. The symbol for this is Q.

reaction rate

The change in concentration of a reactant or product with time.

reaction yield

The amount of product that is actually produced in a given chemical reaction.

reactor

Nuclear reactors heat water to steam to drive a turbine for generation of electricity.

reducing agent

Causes a reduction of another species in the reaction.

reduction

The gain of hydrogen, the loss of oxygen, or the gain of electrons.

RNA

Ribonucleic acid. The single-stranded polymer is also composed of bases linked by phosphate bridges.

27.19 S

saturated
When no more solid dissolves.

scientific method
Developed mainly by Francis Bacon (1561-1626), a British scholar. Uses inductive reasoning and involves the following steps: 1. Ask a question. 2. Make observations. 3. Propose an explanation. 4. Design and carry out ways to test the hypothesis.

scientific notation
A way to express numbers as the product of two numbers, such as a coefficient and the number 10 raised to a power.

second law of thermodynamics
In any spontaneous process, there is always an increase in the entropy of the universe.

secondary structure
The local coiling or folding of biopolymers.

sigma bond
Made up of two overlapping electron orbitals and fills the space directly between the two atoms.

significant figures
Figures associated with uncertainty of a measurement.

single displacement
Includes a metal as one of the reactants and an acid or salt solution for the other reactant. The general form of this reaction is $AB + C \rightarrow AC + B$.

solubility
The degree to which a solute dissolves in a solvent.

soluble
Can dissolve.

solute
The substance that comprises the smaller amount in solution.

solution
Has at least two components- the solute and solvent.

solvent
The substance which comprises the larger component of the solution.

specific heat
The amount of heat needed to raise the temperature of one gram of material by one degree Celsius.

spectator ion
Ions that do not participate in the overall reaction.

spontaneous
Occurs without outside intervention.

standard enthalpy of formation
For any element in its most stable form it is zero. Can be calculated indirectly if the ΔH_f values for each reactant and product are not known.

standard temperature and pressure (STP)
The number of moles of a gas was related to volume at a specific temperature and pressure. The temperature was established at 25°C and the pressure at one atmosphere –these conditions are known as STP. Under these conditions, it was determined that 22.4 liters of a gas comprised one mole of that gas. With this information, we can determine amounts of a gas given the volume at STP.

steroid
Organic compound that has a precise organization of four joined cycloalkane rings.

stoichiometric coefficient
In the formula $aA+bB \rightarrow cC+dD$, letters a, b, c, d are stoichiometric coefficients. This formula can describe any chemical reaction, where A and B are reactants and C and D are products.

Stoichiometry
Area of chemistry that deals with the calculation of amounts of substances in a chemical reaction based on the balanced equation.

strong acid
Ionizes completely in solution.

strong base
Ionizes completely in solution.

supersaturated
When the amount of solute dissolved exceeds the solubility of the solute. Occurs when a solution is saturated and the temperature slowly drops.

surface tension
The amount of energy required to increase the surface of a liquid.

suspension
A heterogeneous mixture in which some of the particles settle out of the mixture upon standing.

system
The chemical reaction in a container.

systeme international (SI)
An international governing body developed this metric system of units of measurement for scientists.

27.20 T

termolecular reaction
Require the collision of three particles simultaneously.

tertiary structure
Refers to the overall three-dimensional shape of the entire protein. Determined by the sequence of amino acids in the protein chain.

tetrahedral
The four bonds take on a tetrahedral shape, again with each electron pair as far away as possible from other electron pairs.

theoretical yield
The amount of substance that is calculated to be produced.

thermochemistry
The study of energy relationships in chemical reactions.

titrant
Reagent in a titration experiment.

titration
An experiment where a volume of a solution of known concentration is added to a volume of another solution in order to determine its concentration.

toughness
Ability to withstand shock and to be deformed without rupturing.

transcription
The unfolding of DNA and the production of an mRNA strand. This step takes place in the nucleus of the cell.

translation
Messenger RNA interacts with the ribosome and transfers RNA to produce a protein.

trigonal bipyramid
One atom at the center with 5 at the corners. Bond angles around the atom are not the same.

trigonal planar
The three fluorine atoms lie in a plane with the central boron atom.

triple point
Point where all three states of matter can exist simultaneously.

Tyndall Effect
The phenomenon in which light is scattered by very small particles in its path.

27.21 U

uncertainty

Expressed as one-half of the smallest difference between calibration marks. It can also be expressed as a percent. All measurements have an associated uncertainty.

universal gas constant

A constant used with thermochemical equations. The symbol for this is R.

unsaturated

There is a predictable amount of solute that can be dissolved at a specific temperature.

27.22 V

valence electrons

Electrons in the outermost shell (highest principal quantum number) of an atom and are those involved in chemical bonding.

valence

Described by associating atomic volume with atomic mass.

van't Hoff Factor

Describes the number of moles of particles that dissociate from an ionic solid.

vapor pressure

A measure of the force exerted by a gas above a liquid in a sealed container.

viscosity

A measure of the fluid's resistance to flow –the higher the viscosity, the slower the flow of the material.

voltag

An electromotive force or potential difference.

volume

Measure of the space occupied by a sample of matter.

VSEPR

The basic premise of the valence-shell electron-pair repulsion (VSEPR) model is that electron pairs will align themselves as far apart from one another as possible.

27.23 W

wavelength

The distance between two crests of a wave of light. The color of light is related to its wavelength. This is inversely proportional to frequency.

weak acid

Not ionized completely. Usually organic acids containing a carboxyl group.

weak base

Not ionized completely.

weight

Measure of force that is equal to the gravitational pull on an object.

weight percent

The weight of solute divided by weight of solution.

27.24 X

27.25 Y

27.26 Z

zero-order reaction

The rate is independent of the concentration of the reactant.