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CK-12 Chemistry Concepts - Intermediate

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Donald F. Calbreath, Ph.D.
Wade Baxter, Ph.D.

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AUTHORS

Donald F. Calbreath, Ph.D.
Wade Baxter, Ph.D.

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CHAPTER 1

Introduction to Chemistry

Chapter Outline

1.1 Defining Chemistry

- Define the term "chemistry."
- List modern items produced by chemistry.

Chemistry affects every area of our lives. Here is just one example of chemistry in action – the making of soaps. Soap was once made by boiling animal fat in ashes – the product was hard on the skin and not very pleasant to use. Today, soap manufacture involves complicated chemical processes to provide a wide variety of soaps for different skin types. Colors and odors can be custom-made for that individual experience.

Defining Chemistry

What is this made of? How can we produce this material quicker and at lower cost? Will this product harm us or help us? All of the questions can be answered using the science 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 certainly accurate, but does not give a good picture of the scope of chemistry or of the many interesting 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.

What is the World Made of?

Questions about matter have been asked for centuries. The ancient Greek philosophes spent a lot of time trying to figure out what matter was. Different philosophers debated whether matter was earth, water, air, fir, or some combination. They argued, but did not do any experiments at that time.

It took many centuries for humans to develop a better concept of what matter really is. Even today, we have an incomplete picture of exactly what this stuff is that we can touch and see. Chemistry involves the study of these substances, both in terms of basic properties and also learning all the things we can do with matter.

Chemists look at the world in two ways, often simultaneously. The two worlds of the chemist are the **macroscopic** world and the **microscopic** world. Macroscopic refers to substances and objects that can be seen, touched, and measured directly. Microscopic refers to the small particles that make up all matter. Chemists must observe matter and do experiments macroscopically and then make generalizations and propose explanations that are microscopic in nature. For example, anyone can observe the physical change in appearance that occurs as an iron object such as a tractor that is left out in the elements gradually turns to rust. However, a chemist looks at the rusting tractor and thinks about what is going on with the individual atoms that make up the iron and how they are changing as a result of exposure to oxygen in the air and water from rain. Throughout your study of chemistry, you will often switch back and forth between the macroscopic and microscopic worlds.

FIGURE 1.1

Rusting artillery shells.

Summary

- Chemistry is the study of matter and the changes it undergoes.
- Chemistry considers both macroscopic and microscopic information.

Practice

1. 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.
2. 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.

Review

1. How did ancient philosophers study the world around them?
2. What is the macroscopic world?
3. What is the microscopic world?

- **chemistry:** The study of matter and the changes it undergoes.
- **macroscopic:** Substances and objects that can be seen, touched, and measured directly.
- **matter:** Composes all physical objects (what we can touch and see).
- **microscopic:** The small particles that make up all matter.

1.2 Events in Chemistry History

- Name famous chemists and the contributions they made to the science of chemistry.

Where did chemistry come from? Early "chemists" focused on practical questions – how to make dyes and perfumes, soap manufacture, uses of metals, and glass production among others. The goal was not to understand the physical world – that came later. People just wanted to make things that would improve their lives in some way.

History of Chemistry

The **history** of chemistry is an interesting and challenging one. Very early chemists often were motivated mainly by the achievement of a specific goal or product. Making perfume or soaps did not need a lot of **theory**, just a good recipe and careful attention to detail. There was no standard way of naming materials (and no periodic table that we could all agree on). It is often difficult to figure out exactly what a particular person was using. But the science 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 the basic ideas for the behavior of gases. We could then describe gases mathematically. Boyle also helped develop the idea that small particles could combine to form molecules. John Dalton used these ideas to develop the atomic theory a number of years later.

FIGURE 1.2

Robert Boyle.

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

Chemistry in the 1800s continued the discovery of new compounds. The science also began to develop a more theoretical foundation. John Dalton (1766-1844) put forth his atomic theory in 1807. This idea allowed scientists to think about chemistry in a much more systematic way. Amadeo Avogadro (1776-1856) laid the groundwork for a more quantitative approach to chemistry by calculating the number of particles in a given amount of a gas. A lot of effort was put forth in studying chemical reactions. These efforts led to new materials being produced. Following the invention of the battery by Alessandro Volta (1745-1827), the field of electrochemistry (both theoretical and applications) developed through major contributions by Humphry Davy (1778-1829) and Michael Faraday (1791-1867). Other areas of the discipline also progressed rapidly.

It would take a large book to cover developments in chemistry during the twentieth century and up to today. One major area of expansion was in the area of the chemistry of living processes. Research in photosynthesis in plants, the discovery and characterization of enzymes as biochemical catalysts, elucidation of the structures of biomolecules such as insulin and DNA – these efforts gave rise to an explosion of information in the field of biochemistry.

The practical aspects of chemistry we not ignored. 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, allowing a stable rubber product to be produced for the tires of all the vehicles we have today. 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. Leo Baekeland (1863-1944) developed the first synthetic resin, widely used for inexpensive and sturdy dinnerware.

Summary

- Many civilizations contributed to the growth of chemistry.
- A lot of early chemical researched focused on practical uses.
- Basic chemistry theories were developed during the nineteenth century.
- New materials and batteries are a few of the products of modern chemistry.

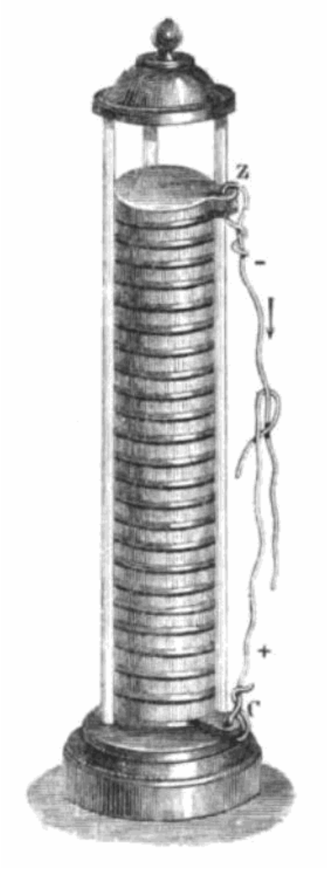


FIGURE 1.3

Battery developed by Volta.

FIGURE 1.4

Practice

Use this resource http://www.columbia.edu/itc/chemistry/chem-c2507/navbar/chemhist.html to answer the following questions:

1. Who published the atomic theory?
2. What elements are proposed by Aristotle?
3. Who discovered the proton?
4. What new elements did Marie Curie discover?
5. Who is called the "Father of Modern Chemistry"?

Review

1. Who invented the first battery?
2. What contribution to chemistry did Robert Boyle make?
3. Who invented dynamite?
4. What was the first synthetic resin used for?

- **history:** The study of events the occurred in the past.
- **research:** To systematically investigate materials to obtain facts and new information.
- **theory:** Ideas used to describe something.

1.3 Areas of Chemistry

- List and define the five areas of chemistry.

In talking with guitar players, it is not enough to say "I play the guitar." The next question is always "Oh, what do you play?" In the picture above, we see several types of guitars by style. There are two acoustic guitars (non-electric, non-amplified) and three different electric guitars. Not shown are instruments such as a classical guitar (six nylon strings instead of steel strings), a bass guitar (usually four strings, but some have five), a resonator guitar for slide blues (uses open tunings), an electric steel guitar (for country music) and a Hawaiian guitar. Guitar players specialize in terms of type of instrument and style of music. The same is true of chemistry and other sciences.

Areas of Chemistry

The study of modern chemistry has many branches, but can generally be broken down into five main disciplines, or areas of study:

- **physical chemistry**
- **organic chemistry**
- **inorganic chemistry**
- **analytical chemistry**
- **biochemistry**

Physical Chemistry

Physical chemistry is the study of the both the macroscopic and the atomic properties and phenomena in chemical systems. A physical chemist may study such things as the rates of chemical reactions, the energy transfers that occur in reactions, or the physical structure of materials at the molecular level.

Organic Chemistry

Organic chemistry is the study of carbon-containing chemicals. Carbon is one of the most abundant elements on Earth and is capable of forming a tremendously vast number of chemicals (over twenty million so far). Most of the chemicals found in all living organisms are based on carbon.

Inorganic Chemistry

Inorganic chemistry is the study of chemicals that do not, in general, contain carbon. Inorganic chemicals are commonly found in rocks and minerals. One current important area of inorganic chemistry deals with the design and properties of materials involved in energy and information technology.

Analytical Chemistry

Analytical chemistry is the study of the composition of matter, focusing on separating, identifying, and quantifying chemicals in samples of matter. An analytical chemist may use complex instruments to analyze an unknown material in order to determine its various components.

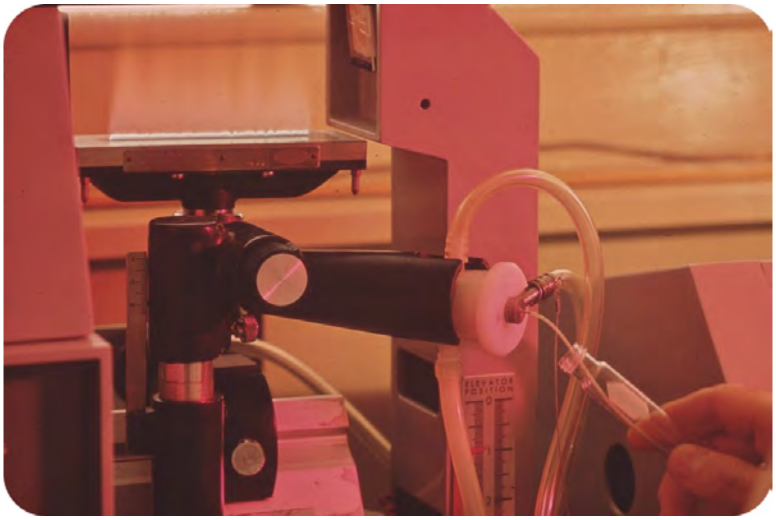


FIGURE 1.5

Measurement of trace metals using atomic absorption spectroscopy.

Biochemistry

Biochemistry is the study of chemical processes that occur in living things. Research may cover basic cellular processes up to understanding disease states so better treatments can be developed.

In practice, chemical research is often not limited to just one of the five major disciplines. A particular chemist may use biochemistry to isolate a particular chemical found in the human body such as hemoglobin, the oxygen carrying

FIGURE 1.6

Measuring hormone concentrations.

component of red blood cells. He or she may then proceed to analyze the hemoglobin using methods that would pertain to the areas of physical or analytical chemistry. Many chemists specialize in areas that are combinations of the main disciplines, such as bioinorganic chemistry or physical organic chemistry.

Summary

- Five areas of chemistry are described:
  - physical chemistry
  - organic chemistry
  - inorganic chemistry
  - analytical chemistry
  - biochemistry

Practice

Do an internet search using one of the five chemistry areas as a search term. List two significant contributions made to chemistry by that area.

Review

Match the project with the proper chemistry discipline

TABLE 1.1:

a. measuring mercury in seawater	1. biochemistry
b. studying enzymes in cells	2. organic chemistry
c. measuring the electrical properties of solutions	3. inorganic chemistry
d. synthesizing new carbon compounds	4. physical chemistry
e. making new compounds for energy processes	5. analytical chemistry

- **physical chemistry:** The study of the both the macroscopic and the atomic properties and phenomena in chemical systems.
- **organic chemistry:** The study of carbon-containing chemicals. Carbon is one of the most abundant elements on Earth and is capable of forming a tremendously vast number of chemicals (over twenty million so far).
- **inorganic chemistry:** The study of chemicals that do not, in general, contain carbon.
- **analytical chemistry:** The study of the composition of matter, focusing on separating, identifying, and

1.4 Pure and Applied Chemistry

- Define pure and applied research.
- Explain the differences between the two.
- Give examples of pure and applied research.

How did chemistry develop? What is happening in the field of chemistry today? What can I do with a chemistry degree? All of these are good questions and they should be asked by students interested in chemistry. Research in chemistry (or any other field, for that matter) is interesting and challenging. But there are different directions a person can take as they explore research opportunities.

Types of Research

In science, we usually talk about two types of research: pure and applied. **Pure research** is said to be done to answer a basic question such as how do gases behave? **Applied research** would be involved with developing a specific preparation for a gas so that it can be produced and delivered efficiently and economically. This division sounds like it would be easy to make, but sometimes we cannot draw a clear line between what is "pure" and what is "applied."

Examples of "Pure" Research

A lot of "pure" research is of the "what is this?" or "how does it work?" variety. The early history of chemistry contains many examples. The ancient Greek philosophers debated the composition of matter (earth? air? fire? water? all of the above?). They weren't going to do anything with their knowledge – they just wanted to know.

Studies on the elements (especially after Mendeleev's periodic table was published) were primarily "pure" research types of experiments. Does this element exist? What are its properties? The scientists did not have any practical application in mind, but were curious about the world around them.

FIGURE 1.7
Ancient Greek philosophers.

Examples of "Applied" Research

There is a great deal of "applied" research taking place today. In general, no new science principles are discovered, but existing knowledge is used to develop a new product. Research on laundry detergents will probably not give us any new concepts about soap, but will help us develop materials that get our clothes cleaner, use less water, and create lower amounts of pollution.

A lot of research is done by petroleum companies. They want to find better ways to power vehicles, better lubricants to cut down on engine wear, and better ways to lower air pollution. These companies will use information that is readily available to come up with new products.

FIGURE 1.8
Gasoline pump.

Some "In-Between" Examples

Sometimes it is hard to differentiate pure and applied research. What may start out as simply asking a question may result is some very useful information. If scientists are studying the biochemistry of a microorganism that causes a disease, they may soon find information that would suggest a way to make a chemical that would inactivate the microbe. The compound could be used to learn more about the biochemistry, but could also be used to cure the disease.

Hemoglobin is a protein in red blood cells that transports oxygen in the bloodstream. Scientists studied hemoglobin simply to learn how it worked. Out of this research came an understanding of how the protein changes shape when oxygen attaches to it. This information was then applied to help patients with sickle cell anemia, a disorder caused by an abnormal hemoglobin structure that makes hemoglobin molecules clump up when oxygen leaves the protein. Basic knowledge of protein structure led to an improved understanding of a wide-spread disease and opened the door for development of treatments.

Summary

- Pure research focuses on understanding basic properties and processes.
- Applied research focuses on the use of information to create useful materials.
- Sometimes there is no clear line between pure and applied research.

Practice

Use this resource to answer the following questions:

http://www.ornl.gov/sci/techresources/Human_Genome/posters/chromosome/sca.shtml

1. What happens to red cells in sickle cell patients when the hemoglobin loses oxygen?
2. What is the difference between sickle cell trait and sickle cell disease?
3. List some symptoms of sickle cell disease.
4. List three treatments used for sickle cell disease.

Review

1. What is pure research?
2. What is applied research?
3. Give one example of pure research.
4. Give on example of applied research.
5. Is it always easy to classify research as pure or applied? Explain your answer.

- **pure research:** Focuses on understanding basic properties and processes.
- **applied research:** Focuses on the use of information to create useful materials.

1.5 Energy in Chemistry

- Explain the source of chemical energy.
- Describe ways chemical energy is generated and used.

Some chemistry reactions can be very calm and boring, while other reactions release a great deal of energy. Dynamite is a chemical that can explode violently. Here we see dynamite being used to move boulders to clear a path for a road. The chemical reactions involved here release tremendous amounts of energy very quickly.

Dynamite was invented by Alfred Nobel in 1866. Nitroglycerin, a very unstable explosive, was already known. Nobel mixed the nitroglycerin with silica to stabilize it and form a solid material. He made a fortune with this discovery and established the Nobel Foundation, which funds the Nobel Prizes every year.

Energy in Chemical Bonds

Chemical reactions either require **energy** or release energy. The amount of energy needed or released depends upon the structure of the molecules that are involved in the reaction. Some reactions need to be heated for long periods in order for change to take place. Other reactions release energy, allowing heat to be given off to the surroundings.

This energy can be used in a variety of ways.

Heating

Coal, natural gas, oil – these materials can be burned to produce heat. The reaction with oxygen releases a great deal of energy that can warm homes and offices. Wood is another example of a chemical (yes, a very complicated one) that will release energy when burned.

Transportation

A major use for petroleum products is fuel for cars, trucks, airplanes, trains, and other vehicles. The chemical used are usually a mixture of compounds containing several carbon atoms in a chain. When the material is ignited, a massive amount of gas is created almost instantaneously. This increase in volume will move the pistons in an internal combustion engine to provide power. A jet plane works on a similar principle. Air comes into the front of the engine and mixes with the jet fuel. This mixture is ignited and the gases formed create a lot of pressure to push the plane forward. The idea can be seen even more clearly in the case of a rocket launch. The ignition of the fuel (either solid-state or liquid) creates gases produced under great pressure that pushes the rocket up.

FIGURE 1.9

Rocket launch.

Batteries

A major source of energy produced by chemical reactions involves batteries. There are many types of batteries that operate using a variety of chemical reactions. The general principle behind these reactions is the release of electrons that can then flow through a circuit, producing an electrical current.

FIGURE 1.10

Car battery.

Batteries are used in a wide variety of applications:

1. flashlights
2. watches
3. computers
4. cars
5. hybrid vehicles – provide some power to wheels
6. cell phones
7. many other uses

Batteries in cars, computers, cell phones, and other devices are usually rechargeable. An electric current is passed through the battery to provide electrons that reverse (at least partially) the chemical reactions originally used to create the electric current. However, eventually the system can no longer be recharged and the battery has to be discarded.

Hand-Warmers

Hikers, campers, and other outdoor folks take advantage of chemical reactions to keep their hands warm. Small containers of chemicals can undergo reaction to generate heat that can be used to avoid frostbite. Some products contain iron filings that will react with air to release thermal energy. These types of warmer cannot be reused. Other systems rely on heat being released when certain chemicals crystallize. If the warmer is placed in very hot water after use, the system can be regenerated.

Summary

- Some chemical reactions release energy.
- This energy can be used in a variety of ways.

Practice

Use the link below to answer the following questions:

http://reference.yourdictionary.com/word-definitions/define-chemical-energy.html

1. Define "chemical energy."
2. What is an exothermic reaction?
3. Give an example of an exothermic reaction.
4. What is an endothermic reaction?
5. Give an example of an endothermic reaction.

Review

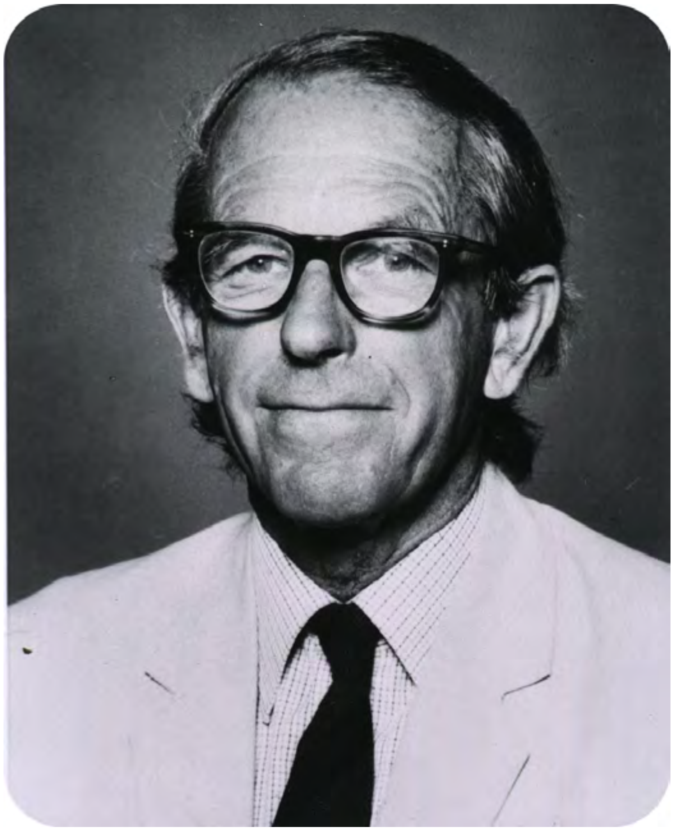
1. Who invented dynamite?
2. How was the nitroglycerin made more stable?
3. What kind of energy is released when we burn natural gas?
4. How does burning gasoline power a car?
5. How do batteries create energy?
6. Explain how a hand-warmer works.

- **energy:** The ability to perform work.

- **chemical reaction:** Chemical reactions either require energy or release energy. The amount of energy needed or released depends upon the structure of the molecules that are involved in the reaction.

1.6 Medicine

- Describe contributions chemistry has made to medicine.



Diabetes mellitus is a disease characterized by the body's inability to use glucose (a component of table sugar). Glucose is needed to provide biochemical energy for all the cells of the body. When the body cannot make energy using glucose, it begins to break down fat and protein to provide the needed energy, eventually leading to death. Diabetes is the result of the pancreas losing the ability to make insulin, a protein that helps glucose enter the cells and be used for biochemical energy. A key piece of the puzzle surrounding our understanding of diabetes came when Frederick Sanger, a British biochemist, carried out experiments that gave him the structure of the **insulin** molecule. Sanger 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.

Chemistry in Medicine

Major contributions to health care have been made by chemistry. The development of new drugs involves chemical analysis and synthesis of new compounds. Many recent television programs advertise the large number of new drugs produced by chemists.

The development of a new drug is long and complicated. The chemistry of the disease must be studied, as well how the drug affects the human body. A drug may work well in animals, but not in humans. Out of a hundred drugs that look like they help treat a disease, only a small handful actually turns out to be both safe and effective.

FIGURE 1.11

Drug for treatment of disease.

Chemistry contributes to the preparation and use of materials for surgery (sutures, artificial skin, and sterile materials). The sutures used in many surgeries today do not have to be removed, because the simply dissolve in the body after a period of time. Replacement blood vessels for heart and other types of surgery are often make of chemicals that do not react with the tissues, so they will not be rejected by the body. Artificial skin can be used to replace human skin for burn patients.

FIGURE 1.12

Surgical procedure.

Clinical laboratory testing (is your cholesterol too high? do you have diabetes?) uses a wide variety of chemical techniques and instrumentation for analysis. Some of the laboratory tests use simple techniques. Other processes involve complex equipment and computer analysis of the data in order to perform measurements on large numbers of patient samples.

Laboratory testing has come to the local drug store or grocery store because of developments in chemistry. You can test your blood glucose using a simple portable device that runs a chemical test on the blood sample and tells you how much glucose is present, allowing a diabetic patient to regulate how much insulin to administer (chemistry is

FIGURE 1.13
Blood samples for laboratory testing.

also used to produce the insulin and the disposable syringe that administers the drug).

FIGURE 1.14
Blood glucose testing device.

Summary

1. Chemistry finds many applications in the healthcare field.
2. Development of medicines involves many complicated chemistry processes.
3. Chemistry is used to create materials used in surgery.
4. Much laboratory testing is based on chemistry techniques.

Practice

Use this resource to answer the following questions:

http://www.scribd.com/doc/2187/Chemistry-and-medicines

1. What is an antibiotic?
2. What does an analgesic do?
3. How is an antiseptic different from an antibiotic?

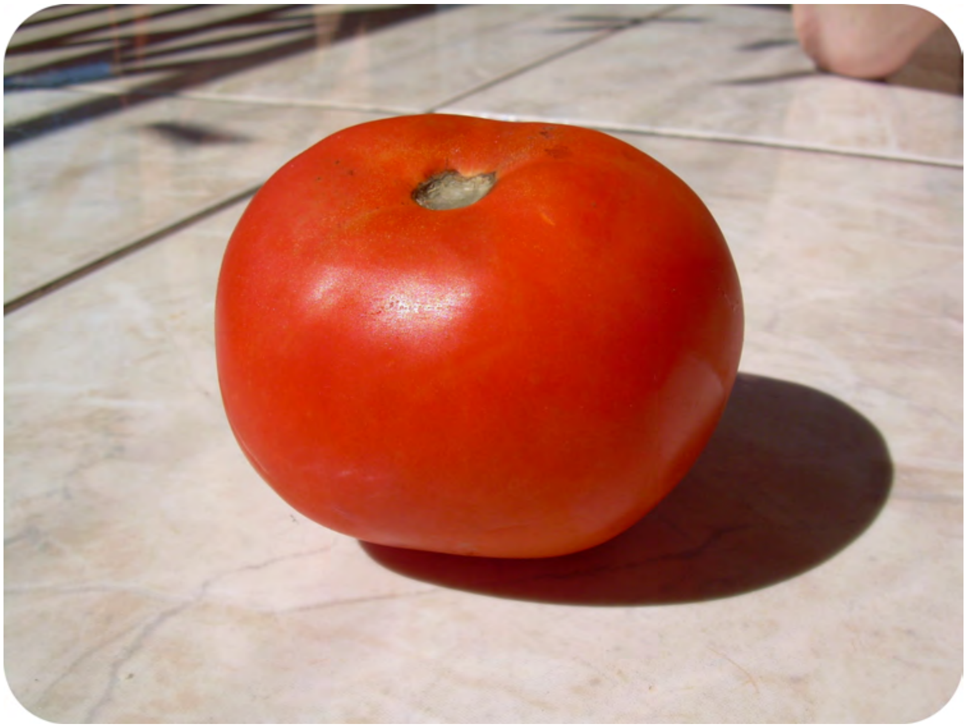
Review

1. What chemical is missing in the diabetic patient?
2. Who discovered the structure of insulin?
3. What two things need to be studied to develop a new drug?
4. List two areas where chemistry has helped surgical patients
5. What blood test can be run using material purchased from your local drugstore?

- **diabetes mellitus:** A disease characterized by the body's inability to use glucose (a component of table sugar).
- **insulin:** A protein that helps glucose enter the cells and be used for biochemical energy.

1.7 Agriculture

- Describe ways chemistry has contributed to the success of modern agriculture.



In the spring, many people begin to plant their gardens. They see ads in catalogs or shop the gardening section of a local store to get ideas. The right place in the garden is selected, seeds or plants are put in the soil, and then the wait. Whether it is a small home garden or a large thousand acre farm, chemistry contributes greatly to the success of the crop.

Agriculture

Crops need three things for good growth: water, **nutrients** from the soil, and protection from predators such as insects. Chemistry has made major contributions in all three areas. Water purification uses a number of chemical and physical techniques to remove salts and contaminants that would pollute the soil. Chemical analysis of soil allows the grower to see what nutrients are lacking so they can be added. In the spring, grocery stores, hardware stores, and gardening centers have high stacks of bags containing fertilizers and weed killers that enrich the soil and keep down unwanted plants. These same stores also provide a number of sprays or solid treatments for insects that might otherwise have a snack on the plants.

Water Purification

Fresh water is essential for good crops. In some areas of the world, there is enough rain to accomplish this task. In other locales, water must be provided so the crops will grow. Worldwide, irrigation covers about 18% of farm land and produces some 40% of crops. A major source of cleaner water in many parts of the world is provided by the process of **desalinization**.

FIGURE 1.15

Idaho wheat field.

FIGURE 1.16

Desalinization equipment.

Sea water is treated to remove salts and the resulting water can then be used for irrigation without contaminating the soil with materials that harm the growing plants.

Soil Nutrients

In many areas of the world, the soil is deficient in essential nutrients. A number of minerals such as phosphorus, potassium, calcium, and magnesium may not be present in large enough amounts to cause good plant growth. Nitrogen is extremely important for good crops.

Soil analysis is available from a variety of labs. Local university extension services can provide valuable information as to the composition of a soil and will also make suggestions as to the types and amounts of needed nutrients. Fertilizers can be purchased and added to the soil to enrich it and ensure better yield of crops.

FIGURE 1.17
Man spreading chemicals on soil.

Insect Control

Even if the crop grows well, there is still the real possibility of insect or pest damage. The insect/pest can consume the crop or can damage it to the point where it will not grow well. Infestations of armyworms can do major damage to corn and grain crops. Aphids and boll weevils are major predators of cotton crops. Failure to control these pests will result in widespread crop damage and financial loss to the farmer.

FIGURE 1.18
Potato pests.

Watch an armyworm video at http://www.youtube.com/watch?v=b1SlOWeMkNQ (3:39).

MEDIA
Click image to the left for more content.

A wide variety of **pesticides** have been developed by chemists and other scientists to deal with all these pests. The basic approach is to have the pesticide interfere with some biochemical process in the pest. Ideally, the pesticide will not affect other living organisms, but this is not always the case. It is very important to read the labels and observe all precautions when using pesticides.

Summary

- Plant nutrients are very important for good plant growth.
- Chemical analysis of soil can tell he farmer or gardener what nutrients are needed.
- Chemists have developed many pesticides that will kill plant predators such as the army worm and the boll weevil.

Practice

Use this resource http://www.ncagr.gov/cyber/kidswrld/plant/nutrient.htm to answer the following questions:

1. What is a macronutrient?
2. What is a micronutrient?
3. List two examples of each kind of nutrient
4. What does each one of these nutrients do for the plant?

Review

1. List three things crops need for good growth.
2. How much of the water used in farming is provided by irrigation?
3. What fraction of crops are grown using irrigation?
4. Why do nutrients need to be added to the soil?
5. How do pesticides work?

- **desalinization:** A major source of cleaner water in many parts of the world is provided by this process.
- **nutrient:** Vitamins and Minerals that enable an organism to grow.
- **pesticide:** Chemicals that will kill plant predators. Developed to preserve plant growth, without the interference of plant predators.

1.8 Materials

- List ways chemistry has contributed to the development of materials.

Chemistry research is often full of surprises. One such surprise came to Stephanie Kwolek of the DuPont chemical company. She was working on a type of material known as polymers. These chemicals had been around for a while and were being used for new types of textiles. Kwolek was looking for a strong and rigid petroleum product. She came up with a material that did not look like your average polymer. But she played a hunch and had it made into threads. This new material had stiffness about nine times that of any of the known polymers of the time. Further research and development led to the production of Kevlar, a material now widely used in body armor (see figure above). In addition, Kevlar has found wide application in racing sails, car tires, brakes, and fire-resistant clothing worn by firefighters.

Materials

Electronics

Chemists are involved in the design and production of new materials. Some of the materials that chemists have helped discover or develop in recent years include polymers, ceramics, adhesives, coatings, and liquid crystals. Liquid crystals are used in electronic displays, as in watches and calculators. The silicon-based computer chip has revolutionized modern society and chemists have played a key role in their design and continued improvement. The calculator shown below uses both a liquid crystal display and chips inside the device.

FIGURE 1.19

Calculator with liquid crystal display.

Superconductors

Many chemists are currently working in the field of superconductivity. Superconductors are materials that are able to conduct electricity with 100% efficiency, meaning that no energy is lost during the electrical transmission, as happens with conventional conducting materials like copper cable. The challenge is to design materials that can act as superconductors at normal temperatures, as opposed to only being able to superconduct at very low temperatures.

Clothing

The fibers that compose the materials for our clothes are either natural or human-made. Silk and cotton would be examples of natural fibers. Silk is produced by the silkworm and cotton is grown as a plant. Human-made fabrics include nylon, orlon, and a number of other polymers. 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 more water-resistant and durable.

Materials originally developed as textiles are finding a wide variety of other uses. Nylon is found in a number of plastic utensils. Taking advantages of its strength and light weight, nylon is a component of ropes, fishing nets, tents, and parachutes.

Summary

- Chemists produce materials for electronics, superconducting, textile, and other applications.

Practice

Use the link below to answer the following questions:

http://library.thinkquest.org/C004179/nylon.htm

1. Who developed nylon?
2. What company did he work for?

FIGURE 1.20

Nylon spatula.

3. List three properties of nylon.

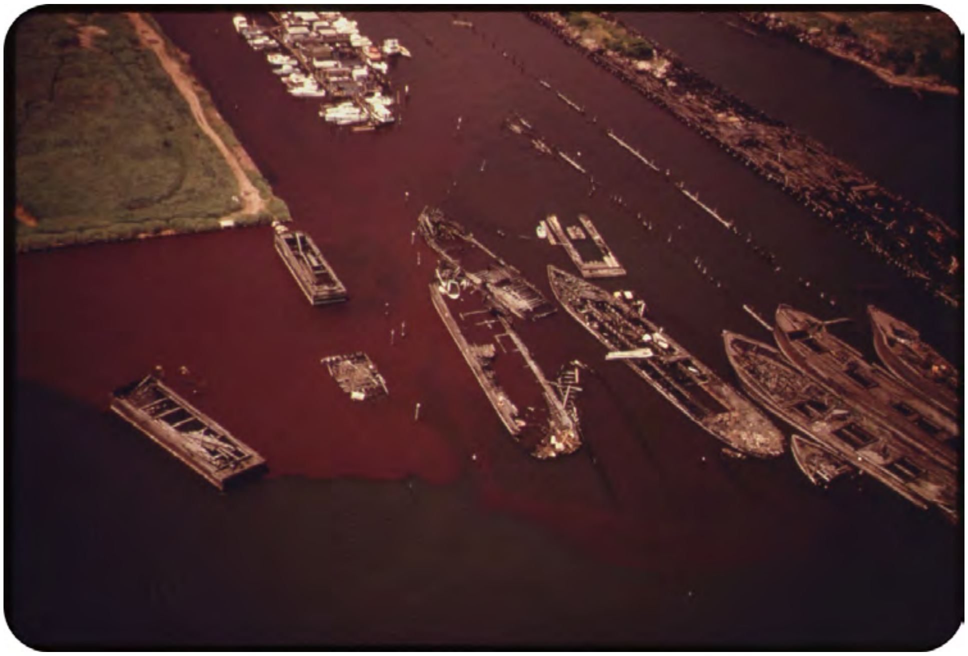
Review

1. Who developed Kevlar?
2. Where are liquid crystals used?
3. What is a superconductor?
4. What are synthetic polymers made from?

- **Kevlar:** A material now widely used in body armor. Also, has found wide application in racing sails, car tires, brakes, and fire-resistant clothing worn by firefighters.
- **liquid crystal:** Used in electronic displays, as in watches and calculators.
- **nylon:** Human-made fabric. Material is made from hydrocarbons found in petroleum products. It is found in a number of plastic utensils. Taking advantages of its strength and light weight, nylon is a component of ropes, fishing nets, tents, and parachutes.
- **superconductor:** Materials that are able to conduct electricity with 100% efficiency, meaning that no energy is lost during the electrical transmission, as happens with conventional conducting materials like copper cable.

1.9 Chemistry and the Environment

- List contributions made by chemistry to solving environmental contamination problems.



Where to dump the garbage? Where to put the waste materials we don't want after we have made what we do want? For many years we just dumped the waste in the nearest lake, river, empty spot of ground, and didn't worry about it. However, as we learn more about the effects of chemicals on living systems, we have become more concerned about the effects of all this dumping. In many cases, we just didn't know what the long-term effects would be. Today, dumpiong is generally illegal and offenders pay heavy penalties of fines and jail sentences.

Environment

Many chemicals that were once commonly used were later found out to be harmful to the **environment**, to human health, or both. The element **lead** was once a common additive to gasoline and to paint. Plumbing pipes were once typically made of lead. Only since the 1970s has the danger of lead become apparent. It causes brain damage and small children (who often chewed on objects painted with lead-based paint) are particularly susceptible. The use of lead in gasoline, paint, and plumbing pipes is now banned and new materials are being developed to replace the hazardous lead components.

Lead is still widely used in car batteries. In recent years, battery **recycling** is becoming very common - about 98% of car batteries a recycled today. The used batteries go to a processing plant where they are crushed and placed in a tank. The lead sinks to the bottom and can be separated, melted and used again. Plastic materials float to the top, are separated, and melted. The plastic can then be used in a number of applications. The battery acids are treated with chemicals to neutralize them before they are disposed of.

FIGURE 1.21

Batteries for recycling.

How Chemists Help the Environment

Chemists are involved in all aspects of environmental protection. In the case of lead, chemists measured the amount of lead in soil, paint, plumbing, blood, and other materials. Chemists studied the chemical processes in the body to see how lead did its damage. Methods for removal of lead from the body were developed with the help of chemists. New gasoline products were developed that gave good fuel efficiency and smooth running of the engine without the presence of lead.

Chemists continue to look for threats to our health and the environment and to search for alternatives so that harmful chemicals can be replaced with others that will do the job as effectively, but without the harm.

Summary

- Environmental **contamination** is a major problem today.
- Lead contamination has serious harmful effects on the body.
- Chemists contribute in many ways to helping with issues of lead contamination.

Practice

Use the link below to answer the following questions:

http://portal.acs.org/portal/acs/corg/content?_nfpb=true&_pageLabel=PP_ARTICLEMAIN&node_id=1188&content_id=CTP_003388&use_sec=true&sec_url_var=region1&__uuid=ba23e9e5-9a5b-4b9d-9e1e-5026ee802fdc

1. What do we mean by the “fate” of a chemical?
2. What do pollution abatement systems do?
3. What does a remediation system do?

Review

1. Where was lead found in products?
2. What is a hazard of lead?

3. What happens to the lead in used car batteries?
4. List two ways chemists help with issues related to lead contamination.

- **contamination:** When chemicals in the environment produce harmful effects.
- **environment:** An area or surroundings where organisms live.
- **lead:** An element that was once commonly used in gasoline and paint, is now found to have dangerous effects, such as brain damage. Lead contamination has many harmful effects on the body.
- **recycling:** Takes used items and materials and turns it into something new. For example, 98% of car batteries are recycled today. In the processing plant, the plastic materials are separated from the lead, so the plastic can then be used for many applications.

1.10 Alchemy

- Describe the efforts by the alchemists to make gold from lead.

What's the value of gold?

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

But mining for gold is a slow, dirty, and dangerous process. 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, not an individual or group. So there were few ways for most people to legally get any gold for themselves.

Alchemy

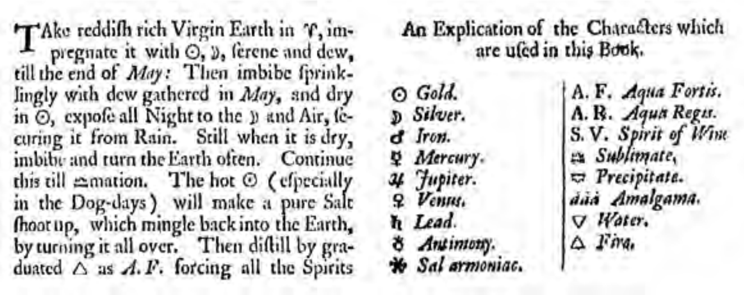
The alchemists were a varied group of scholars and charlatans whose goal was two-fold: to create the **Philosopher's Stone** (which caused the transmutation of lead into gold) and the discovery of the Elixir of Life (bestowing immortality on the person who possessed it). The origin of the term "**alchemy**" is uncertain. There are roots to Greek, Arabic, and ancient Egyptian words. Three major streams of alchemy are known – Chinese, Indian, and European, with all three streams having some factors in common. We will not focus on the philosophical or religious aspects of alchemy, but will look briefly at the techniques developed in the European stream 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 code for recording his data. The processes were kept secret so others could

FIGURE 1.22

Typical alchemist lab.

not profit from them. Different scholars developed their own set of symbols as they recorded the information they came up with. Many alchemists were not very honest, taking money from a nobleman by claiming to be able to make gold from lead, then leaving 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.*
☽ *Silver.*
♂ *Iron.*
☿ *Mercury.*
♃ *Jupiter.*
♀ *Venus.*
♄ *Lead.*
♁ *Antimony.*
✱ *Sal armoniac.*

A. F. *Aqua Fortis.*
A. R. *Aqua Regis.*
S. V. *Spirit of Wine*
🝞 *Sublimate,*
🝟 *Precipitate.*
ȧȧȧ *Amalgama.*
▽ *Water.*
△ *Fire.*

FIGURE 1.23

Alchemist recipe.

Alchemist Contributions to Chemistry

However, out of all this secrecy came several contributions to modern-day chemistry. Early acids and bases were discovered. 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 had not become well-established yet. But the groundwork was laid to the development of chemistry as a foundational science.

The alchemists were never successful in changing lead into gold. But modern nuclear physics can accomplish this task. Lead is subjected to nuclear bombardment in a particle accelerator. A small amount of gold can be obtained by this process. However, the cost of the procedure is far more than the amount of gold obtained. So the dream of the alchemists has never (and will never) come true.

Summary

- Gold has been considered valuably by all civilizations.

- The alchemists tried to find the philosopher's stone that would allow then to make gold from lead.
- Many dishonest schemes were created, but nobody ever made gold from lead.
- The alchemists did contribute many advances to the new science of chemistry.

Practice

Answer the following questions using information from this link:

http://www.economist.com/node/18226821

1. Where did the study of alchemy start?
2. Why did the medieval universities reject alchemy?
3. What was a major problem for alchemists?

Review

1. Why is gold considered to be valuable?
2. Who owned the gold mines during the ancient Egyptian and Roman civilizations?
3. What is the elixir of life?
4. What contributions to modern chemistry were made by the alchemists?

- **alchemy:** The alchemists were a varied group of scholars and charlatans whose goal was two-fold: to create the Philosopher's Stone (which caused the transmutation of lead into gold) and the discovery of the Elixir of Life (bestowing immortality on the person who possessed it). The origin of the term "alchemy" is uncertain. There are roots to Greek, Arabic, and ancient Egyptian words. Three major streams of alchemy are known – Chinese, Indian, and European, with all three streams having some factors in common.
- **philosophers stone:** Stone caused the transmutation of lead into gold. One of the main goals of the alchemists was to create this stone.

1.11 Nature of Science

- Describe teamwork involved in science research.
- Describe how science information is shared.

Most jobs to day involve a fair amount of meetings and team involvement. It doesn't matter what you do, you will spend a certain amount of time meeting with other people, sharing what you have done, planning projects, and organizing the work. Almost nobody works by themselves these days – everybody is part of a larger group.

The Nature of Science

Today's scientists rarely work alone. Rather, most scientists collaborate with one another as part of a group effort, no matter the setting. The majority of research scientists work either for a company such as DuPont Chemical Company in Wilmington, Delaware or for one of many universities, such as the California Institute of Technology. Working as part of a group has many advantages. Most scientific problems are so complex and time-consuming, that one person could not hope to address all of the issues by himself or herself. Instead, different members of a research group are each tasked with a particular small aspect of a larger research problem. Collaboration between members of the group is frequent. This occurs informally in the laboratory on an everyday basis. Research groups typically have regular meetings where one or more members of the group may give a presentation to the others on the status of the research that they are doing. Progress normally occurs in small steps rather than grand, sweeping discoveries, and that progress is helped along by the teamwork that comes from working as part of a group.

Modern scientific research is usually expensive. Lab equipment, chemicals, research space, and the upkeep of technical instrumentation all costs money. So research groups need to raise money in order to continue their research. Much of that money comes from government sources, such as the National Science Foundation or the National Institute of Health, especially in the case of research being done at universities. Private companies can fund their own research, but may also seek outside funding as well. Scientists write **grants** explaining the goals of their research along with projected costs, and funding agencies make decisions on which research projects they would like to fund. The long-term viability of most research labs depends on the ability to get and maintain funding.

Communicating Results

Suppose that your research is a success. What now? Scientists communicate their results to one another and to the public at large in several ways. One is to publish their research findings in one of many publications called scientific **journals**. There are many hundreds of scientific journals covering every field of science imaginable. In chemistry, there is the "Journal of the American Chemical Society," the "Journal of Physical Chemistry," and the "Inorganic Chemistry," to name just a few. Some journals have a very narrow scope while others publish articles from many different sciences and appeal to a wider audience. Examples of the latter include the journals "Science" and "Nature." Journal articles are often very complex and detailed. They must be accurate, since the research field as a whole uses these journal articles as a way to make scientific progress. Therefore, journal articles are only published after having been extensively reviewed by other professional scientists in the same field. Reviewers have the power to make suggestions about the research or possibly question the validity of the author's conclusions. Only when the reviewers are satisfied that the research is correct, will the journal publish the article. In this way, all scientists can trust the research findings that they read about in journals.

Scientists also communicate with one another by presenting their findings at international conferences. Some scientists are chosen to give a lecture at a conference, typically about research that has already been published. Many other scientists at the same conference will present their work at **poster sessions**. These poster sessions are more informal and may often represent research that is still in progress.

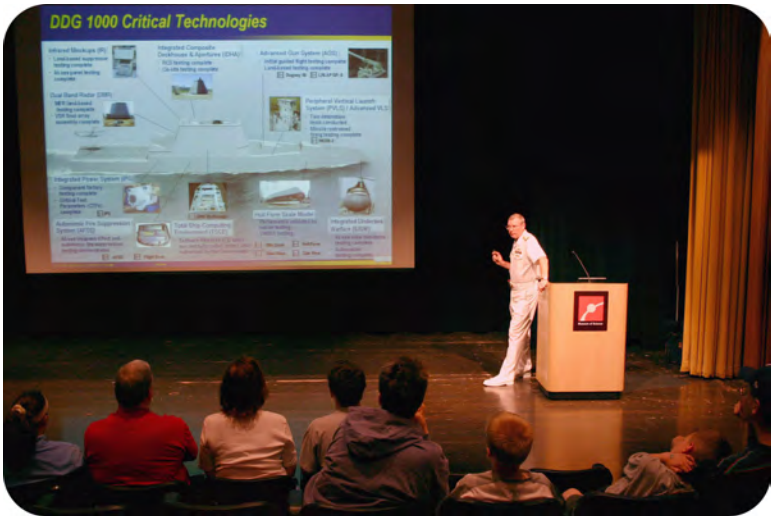


FIGURE 1.24

Scientific presentation.

Summary

- Scientific research today is a team effort.
- Support for research usually comes from grants.
- Findings are shared in meetings, conferences, and scientific publications.

Practice

Use the link below to answer the following questions:

http://umech.mit.edu/freeman/6.021J/2000/writing.pdf

1. What is the purpose of the abstract?

2. What does the introduction do?
3. What does the Results section do? What does it not do?

Review

1. How is most scientific research carried out today?
2. How is research usually supported?
3. How do scientists share their findings?

- **grant:** Scientists write grants explaining the goals of their research along with projected costs, and funding agencies make decisions on which research projects they would like to fund. The long-term viability of most research labs depends on the ability to get and maintain funding.
- **journal:** Scientists publish their research findings in one of many publications called scientific journals. They must be accurate, since the research field as a whole uses these journal articles as a way to make scientific progress.
- **peer review:** When colleagues assess your work.
- **poster session:** Some scientists are chosen to lecture at a conference (typically about research that has already been published), while others will present their work at poster sessions. These poster sessions are more informal and may often represent research that is still in progress.

1.12 Scientific Problem Solving

- Describe the approach of the ancient Greek philosophers to understanding the world around them.
- Define inductive and deductive reasoning.
- Describe the scientific method.

One day you wake up and realize your clock radio did not turn on to get you out of bed. You are puzzled, so you decide to find out what happened. You list three possible explanations:

1. There was a power failure and your radio cannot turn on..
2. Your little sister turned it off as a joke.
3. You did not set the alarm last night.

Upon investigation you find that the clock is on, so there is no power failure. Your little sister was spending the night with a friend and could not have turned the alarm off. You notice that the alarm is not set – your forgetfulness made you late. You have used the scientific method to find an answer to a question.

Scientific Problem Solving

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? Chemistry has been defined in various ways as the study of matter. What that 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.

The basic approach of these philosophers to questions about the world was discussion and debate. There was no gathering of information to speak of, just talking. As a result, several ideas about matter were put forth, but never resolved. The first philosopher to carry out the gathering of data was Aristotle (384-322 B.C.). He recorded many observations on the weather, on plant and animal life and behavior, on physical motions, and a number of other topics. Aristotle could probably be considered the first "real" scientist since he made systematic observations of nature and tried to understand what he was seeing.

FIGURE 1.25

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 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. Both are used in the development of scientific ideas.

Inductive reasoning first involves the collection of data. If I add sodium metal to water, I will observe a very violent reaction. Every time I repeat the process, I see the same thing happening. I draw a general conclusion from these observations: the addition of sodium to water results in a violent reaction.

In deductive reasoning, I make a specific prediction based on a general principle. One general principle is that acids turn blue litmus paper red. If I have a bottle of liquid labeled "acid," I expect the litmus paper to turn red when I immerse it in the liquid.

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. make new observations to test the hypothesis further

FIGURE 1.26

Sir Francis Bacon.

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. But this does provide a general idea of how scientific research is usually done.

When a hypothesis is confirmed repeatedly, it eventually becomes a theory – a general principle that is offered to explain natural phenomena. Note a key word – explanation. The theory offers a description of why something happens. A law, on the other hand, is a statement that is always true, but does not explain why. The law of gravity says a rock will fall when dropped, but does not explain why (gravitational theory is very complex and incomplete at present). The kinetic-molecular theory of gases, on the other hand, tells 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.

Summary

- The early Greek philosophers spend their time talking about nature, but did little or no actual exploration or investigation.
- inductive reasoning – developing a general conclusion from a collection of observations.
- deductive reasoning – making a specific statement based on a general principle.
- scientific method – a process of observation, developing a hypothesis, and testing that hypothesis.

Practice

Use the link below to answer the following questions:

http://cti.itc.virginia.edu/ meg3c/classes/tcc313/200Rprojs/lavoisier2/home.html

1. What was phlogiston?
2. State two observations the phlogiston theory explained?
3. How did Lavoisier disprove the phlogiston theory?

Review

1. What was the basic shortcoming of the Greek philosophers approach to studying the material world?
2. How did Aristotle improve the 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?

- **deductive reasoning:** Takes a general principle and then draws a specific conclusion from the general concept. Used in the development of scientific ideas.
- **inductive reasoning:** Involves getting a collection of specific examples and drawing a general conclusion from them. Used in the development of scientific ideas.
- **scientific method:** This approach was developed by Francis Bacon (1561-1626), a British scholar. Inductive reasoning is at the heart. of this method. The steps include: ask a question (identify the problem to be considered), make observations (gather data that pertains to the question), propose an explanation (a hypothesis) for the observations, make new observations to test the hypothesis further.

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CHAPTER 2

Matter and Change

Chapter Outline

2.1 Substances

- Define substance.

Have you ever had the experience of opening the refrigerator and seeing something you don't recognize?

Not an unfamiliar food, but something that has changed over the time period it was in the refrigerator. You are not sure just what it is, so you call it "stuff". Looking at it, you know it's not a good idea to eat it, so you throw it out. If you're not sure just what it is, you certainly don't want to put it in your body.

Substances

Silver and ordinary table salt are two examples of chemical **substances**. A substance is matter that has a uniform and definite composition. All samples of substances, sometimes called pure substances, have identical properties. When chemists run a chemical reaction, they want to use pure materials so they know exactly what they are dealing with. They know that the reaction involves a specific substance, so they expect the same reaction to give the same results each time it is run.

One of the characteristics of a substance is that it cannot be separated into components by physical separation techniques. The **compound** acetylsalicylic acid (the active ingredient in aspirin) is a substance because it is a chemical compound that cannot be further reduced to other materials by physical means. However, the aspirin that contains the acetylsalicylic acid is a mixture. In addition to the active pain-relieving ingredient, aspirin also may contain waxes, corn starch, and cellulose, among other ingredients. These added materials bind the tablet components into a solid pill and influence how rapidly the material dissolves.

Substances may be either **elements** or pure compounds. They may also be solid, liquid, or gas. Some of the elements (such as silver) exist in the solid form. Other elements (mercury) exist as liquids at room temperature. Elements such as helium and radon exist as gases at room temperature. A compound such as water will take the form of a solid, a liquid, or a gas, depending upon the temperature.

FIGURE 2.1
Aspirin tablets.

Summary

- A substance is a pure material with a uniform and definite composition.
- A substance cannot be separated into components using physical means.
- A substance can be a solid, a liquid, or a gas, depending on the temperature.

Practice

Use the link below to answer the following questions:

http://www.ivy-rose.co.uk/Chemistry/GCSE/What-is-a-substance.php

1. Is a solution a substance?
2. Why is water listed as a substance?
3. If neon were frozen into the solid state, would it still be a substance?

Review

1. Define substance.
2. Can salt be a substance?
3. Is aspirin a substance?

- **compound:** Made up of multiple elements.
- **element:** A substance that cannot be separated into smaller pieces. Defined by how many protons it has.
- **substance:** Matter that has a uniform and definite composition.

2.2 Physical Properties

- Define physical property.
- List and describe physical properties of matter.

Drag racing is a highly competitive (and expensive) sport. There are a variety of classes of vehicles, ranging from stock classes (depending on car weight, engine size, and degree of engine modification) all the way up to the Top Fuel class with weights of over two thousand pounds and capable of top speeds of well over 300 miles/hour at the end of the quarter-mile. The standards for each class are well-defined and frequent checks are made of engine dimensions and components to insure that the rules are followed.

Physical Properties

A **physical property** is a characteristic of a substance that can be observed or measured without changing the identity of the substance. Silver is a shiny metal that conducts electricity very well. It can be molded into thin sheets, a property called malleability. Salt is dull and brittle and conducts electricity when it has been dissolved into water, which it does quite easily. Physical properties of matter include color, hardness, malleability, solubility, electrical conductivity, density, **melting points**, and **boiling points**.

For the elements, color does not vary much from one element to the next. The vast majority of elements are colorless, silver, or gray. Some elements do have distinctive colors: sulfur and chlorine are yellow, copper is (of course) copper-colored, and elemental bromine is red.

Density can be a very useful parameter for identifying an element. Of the materials that exist as solids at room temperature, iodine has a very low density compared to zinc, chromium, and tin. Gold has a very high density, as does platinum.

Hardness helps determine how an element (especially a metal) might be used. Many elements are fairly soft (silver and gold, for example) while others (such as titanium, tungsten, and chromium) are much harder. Carbon is an interesting example of hardness. In graphite (the "lead" found in pencils) the carbon is very soft, while the carbon is a diamond is roughly seven times as hard.

FIGURE 2.2

Pencil.

FIGURE 2.3

Diamond ring.

Melting and boiling points are somewhat unique identifiers, especially of compounds. In addition to giving some idea as to the identity of the compound, important information can be obtained about the purity of the material.

Summary

- A physical property is a characteristic of a substance that can be observed or measured without changing the identity of the substance.
- Physical properties include color, density, hardness, and melting and boiling points.

Practice

Use the link below to answer the following questions:

http://www.slideshare.net/99tsu/physical-properties-of-matter-presentation

1. What is thermal conductivity?
2. Give an example of malleability.
3. Define ductility.

Review

1. What is a physical property?
2. What color are most metals?
3. Is titanium harder or softer than gold?

- **boiling point:** The temperature which causes liquid to boil.
- **density:** The concentration of a substance. Increases as its temperature decreases.
- **hardness:** Helps determine how an element (especially a metal) might be used.
- **melting point:** The temperature which causes solids to melt.
- **physical property:** A characteristic of a substance that can be observed or measured without changing the identity of the substance.

2.3 Extensive and Intensive Properties

- Define extensive property.
- Define intensive property.
- Give examples of extensive and intensive properties

I agree to mow someone's lawn for twenty dollars (it's a fairly big yard). When they pay me, they give me a $20 bill. It doesn't matter whether the bill is brand new or old, dirty, and wrinkled – all these bills have the same value of $20. If I want more $20 bills, I have to mow more lawns. I can't say, "This particular bill is actually worth more than $20." To get more bills, I have to put in more work.

Extensive and Intensive Properties

Extensive Properties

Some properties of matter depend on the size of the sample, while some do not. An **extensive** property is a property that depends on the amount of matter in a sample. The mass of an object is a measure of the amount of matter that an object contains. A small sample of a certain type of matter will have a small mass, while a larger sample will have a greater mass. Another extensive property is volume. The volume of an object is a measure of the space that is occupied by that object.

The figure below illustrates the extensive property of volume. The pitcher and glass both contain milk. The pitcher holds approximately two quarts and the glass will hold about 8 ounces of milk. The same milk is in each container. The only difference is the amount of milk contained in the glass and in the pitcher

Intensive Properties

The electrical conductivity of a substance is a property that depends only on the type of substance. Silver, gold, and copper are excellent conductors of electricity, while glass and plastic are poor conductors. A larger or smaller piece of glass will not change this property. An **intensive** property is a property of matter that depends only on the type of matter in a sample and not on the amount. Other intensive properties include color, temperature, density, and solubility.

The copper wire shown in the picture below has a certain electrical conductivity. You could cut off the small end sticking out and it would have the same conductivity as the entire long roll of wire shown here. The conductivity is a property of the copper metal itself, not of the length of the wire.

FIGURE 2.4
Milk pitcher and glass.

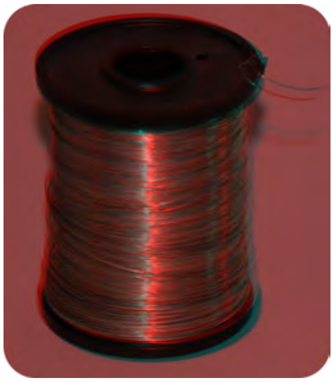


FIGURE 2.5
Copper wire.

Summary

- An extensive property is a property that depends on the amount of matter in a sample.
- Mass and volume are examples of extensive properties.
- An intensive property is a property of matter that depends only on the type of matter in a sample and not on the amount.
- Color, temperature, and solubility are examples of intensive properties.

Practice

Use the link below to answer the following questions:

http://www.reference.com/motif/science/extensive-and-intensive-properties

1. Is energy an extensive or intensive property?
2. Is density an extensive or intensive property?

Review

1. Define extensive property.
2. Give two examples of extensive properties,
3. Define intensive property.
4. Give two examples of intensive properties.

- **extensive property:** A property that depends on the amount of matter in a sample.
- **intensive property:** A property of matter that depends only on the type of matter in a sample and not on the amount.

2.4 Solid, Liquid, and Gas

- Define, solid, liquid, and gas.
- Explain differences among these three phases of matter.

Why is the state of water different in each picture?

Water can take many forms. At low temperatures (below 0°C), it is a solid. When at "normal" temperatures (between 0°C and 100°C), it is a liquid. While at temperatures above 100°C, water is a gas (steam).

The state the water is in depends upon the temperature. Each state (solid, liquid, and gas) has its own unique set of physical properties.

Matter and Its States

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

Note: Technically speaking a fourth state of matter called plasma exists, but it does not naturally occur on earth, so we will omit it from our study here.

Liquid

Liquids have the following characteristics:

- no definite shape (takes the shape of its container)
- has definite volume
- particles are free to move over each other, but are still attracted to each other

A familiar liquid is mercury metal. Mercury is an anomaly. It is the only metal we know of that is liquid at room temperature. Mercury also has an ability to stick to itself (surface tension) – a property all liquids exhibit. Mercury has a relatively high surface tension, which makes it very unique. Here you see mercury in its common liquid form.

If we were to heat liquid mercury to its boiling point of 357°C, and under the right pressure conditions, we would notice all particles in the liquid state go into the gas state.

Gas

Gases have the following characteristics:

- no definite shape (takes the shape of its container)
- no definite volume
- particles move in random motion with little or no attraction to each other
- highly compressible

FIGURE 2.6

Mercury.

Solid

Solids are defined by the following characteristics:

- definite shape (rigid)
- definite volume
- particles vibrate around fixed axes

If we were to cool liquid mercury to its freezing point of -39°C, and under the right pressure conditions, we would notice all of the liquid particles would go into the solid state.

The video below from http://www.youtube.com/watch?v=zKUl6gJhFZY shows this process.

MEDIA

Click image to the left for more content.

As you can see in the video, mercury can be solidified when its temperature is brought to its freezing point. However, when returned to room temperature conditions, mercury does not exist in solid state for long, and returns back to its more common liquid form.

Summary

- Three states of matter exist – solid, liquid, and gas.
- Solids have a definite shape and volume.
- Liquids have a definite volume, but take the shape of the container.
- Gases have no definite shape or volume.

Practice

Use the web site to answer the following questions:

http://www.miamisci.org/af/sln/phases/nitrogensolid.html

1. Which material is a gas at room temperature (25°C)?
2. Which material is a solid at room temperature?
3. Which material is a liquid at room temperature?
4. What happens to the motion of the particles as you increase the temperature?
5. What happens to the motion of the particles as you decrease the temperature?

Review

1. How many states of matter are there?
2. What is a solid?
3. What is a liquid?
4. What is a gas?

- **solid:** Has a definite shape and volume.
- **liquid:** Has a definite volume, but take the shape of the container.
- **gas:** Has no definite shape or volume.

2.5 Physical Change

- Define physical change.
- Give examples of physical changes.

Want to buy a car – cheap? Notice that the ad did not say "in good condition" or even "needs a little work." The car above is pretty beat up. The body is damaged, the windows are broken, and the interior is probably torn up. But this is still a car. It has all the components of a car, even though you would not want to buy it in the present condition. But change that condition and you have a (possibly) useable car.

Physical Change

As an ice cube melts, its shape changes as it acquires the ability to flow. However, its composition does not change. **Melting** is an example of a **physical change**. A physical change is a change to a sample of matter in which some properties of the material change, but the identity of the matter does not. Physical changes can further be classified as reversible or irreversible. The melted ice cube may be refrozen, so melting is a reversible physical change. Physical changes that involve a change of state are all reversible. Other changes of state include **vaporization** (liquid to gas), **freezing** (liquid to solid), and **condensation** (gas to liquid). Dissolving is also a reversible physical change. When salt is dissolved into water, the salt is said to have entered the aqueous state. The salt may be regained by boiling off the water, leaving the salt behind.

When a piece of wood is ground into sawdust, that change is irreversible since the sawdust could not be reconstituted into the same piece of wood that it was before. Cutting the grass or pulverizing a rock would be other irreversible physical changes. Fire wood also represents an irreversible physical change since the pieces cannot be put back together to form the tree.

FIGURE 2.7
Melting ice in the Beaufort Sea.

FIGURE 2.8
Firewood.

Summary

- A physical change is a change to a sample of matter in which some properties of the material change, but the identity of the matter does not.
- In a reversible physical change, the original form of the matter can be restored.
- In an irreversible physical change, the original form cannot be restored.
- Melting ice and grinding wood into sawdust are examples of physical changes.

Practice

Use the link below to answer the following questions:

http://sites.jmu.edu/chemdemo/2012/07/27/metamorphic-magic-plastic/

1. Is punching a hole in the plastic a physical change?
2. Why is the heating and cooling of the plastic a physical change?

Review

1. Define physical change.
2. Why is melting an ice cube a reversible physical change?
3. Give an example of an irreversible physical change.

- **condensation:** When gas turns to a liquid.
- **freezing:** When a liquid turns to a solid.
- **melting:** When a solid turns to a liquid.
- **physical change:** A change to a sample of matter in which some properties of the material change, but the identity of the matter does not.
- **vaporization:** When liquid turns into gas.

2.6 Homogeneous Mixture

- Define mixture.
- Define homogeneous mixture.
- Give examples of homogeneous mixtures.

Many people enjoy a cup of coffee at some point during the day. Some may drink it black, while others may put cream (or some dairy substitute) and sugar in their coffee. You can buy high-end coffee drinks at espresso stands (either sit-down or drive-through). Whatever your preference, you want the coffee to be the same at the beginning and the end of your drink. You don't want the components to separate out, but you want your drink to be uniform from top to bottom.

Mixtures

Ordinary table salt is called sodium chloride. It is considered a **substance** because it has a uniform and definite composition. All samples of sodium chloride are chemically identical. Water is also a pure substance. Salt easily dissolves in water, but salt water cannot be classified as a substance because its composition can vary. You may dissolve a small amount of salt or a large amount into a given amount of water. A mixture is a physical blend of two or more components, each of which retains its own identity and properties in the **mixture**. Only the form of the salt is changed when it is dissolved into water. It retains its composition and properties.

Homogeneous Mixtures

A **homogeneous** mixture is a mixture in which the composition is uniform throughout the mixture. The salt water described above is homogeneous because the dissolved salt is evenly distributed throughout the entire salt water sample. Often it is easy to confuse a homogeneous mixture with a pure substance because they are both uniform. The difference is that the composition of the substance is always the same. The amount of salt in the salt water can vary from one sample to another. All solutions would be considered homogeneous because the dissolved material is present in the same amount throughout the solution.

One characteristic of mixtures is that they can be separated into their components. Since each part of the mixture has not reacted with another part of the mixture, the identities of the different materials is unchanged.

Summary

- A homogeneous mixture is a mixture in which the composition is uniform throughout the mixture.
- All solutions would be considered homogeneous.

Practice

Use the link below to answer the following questions:

http://www.buzzle.com/articles/homogeneous-mixture-examples.html

1. What is the composition of gunpowder?
2. Why would vinegar be considered a homogeneous mixture?
3. Name three alloys and list what they are composed of.

Review

1. What is a mixture?
2. What is a homogeneous mixture?
3. Are all solutions homogeneous mixtures?
4. Can homogeneous mixtures be separated into their components?

- **homogeneous:** A mixture in which the composition is uniform throughout the mixture.
- **mixture:** consists of multiple substances put together.
- **substance:** It has a uniform and definite composition.

2.7 Heterogeneous Mixtures

- Define heterogeneous mixture.
- Define phase.
- Give examples of heterogeneous mixtures.

How do you eat a bag of jelly beans?

Many people open the bag and eat all the candy, no matter what flavor each piece is. Others pick through the collection. They might say "I don't like the orange ones." Or maybe they just care for the lemon ones. There are different kinds of jelly beans in the mixture and people will eat what they want and get rid of the rest.

Heterogeneous Mixtures

A **heterogeneous mixture** is a mixture in which the composition is not uniform throughout the mixture. Vegetable soup is a heterogeneous mixture. Any given spoonful of soup will contain varying amounts of the different vegetables and other components of the soup.

A **phase** is any part of a sample that has a uniform composition and properties. By definition, a pure substance or a homogeneous mixture consists of a single phase. A heterogeneous mixture consists of two or more phases. When oil and water are combined, they do not mix evenly, but instead form two separate layers. Each of the layers is called a phase.

In the vegetable soup example, one phase would be the liquid soup itself. This phase has vitamins, minerals, and other components dissolved in the water. This phase would be homogeneous. The carrots, peas, corn, or other vegetables represent other phases of the soup. The various vegetables are not mixed evenly mixed in the soup, but are spread around at random.

FIGURE 2.9

Oil and water do not mix, instead forming two distinct layers called phases. The oil phase is less dense than the water phase and so the oil floats on top of the water.

There are a large number of heterogeneous mixtures around us. Soil is composed of a variety of substances and is often of different composition depending on the sample taken. One shovel may come up with dirt and grass while the next shovel could contain an earthworm.

Smog is another example of a heterogeneous mixture. This murky collection of pollutants can be a mixture of water and contaminants from burning gasoline or plastics mixed with nitric oxide derivatives and ozone. You can see that the smog distribution in the air illustrate below is not evenly spread out, but varies from one part of the atmosphere to another.

FIGURE 2.10

Smog in New York City.

Summary

- A heterogeneous mixture is a mixture in which the composition is not uniform throughout the mixture.
- A phase is a separate layer in a heterogeneous mixture.

Practice

Use the link below to answer the following questions:

http://antoine.frostburg.edu/chem/senese/101/matter/faq/what-is-heterogeneous.shtml

1. Why is a mixture of sand and sugar a heterogeneous mixture?
2. What are the phases in a glass of iced tea?
3. How is blood a heterogeneous mixture?

Review

1. Define a heterogeneous mixture.
2. Why is vegetable soup a heterogeneous mixture?
3. How many phases are in a heterogeneous mixture?

- **heterogeneous mixture:** A mixture in which the composition is not uniform throughout the mixture.
- **phase:** A separate layer in a heterogeneous mixture.

2.8 Methods for Separating Mixtures

- Describe techniques for separation of mixtures.

Beginning in the late 1840s, thousands of prospectors rushed to California to search for gold. One of the approaches taken to isolate the gold from the soil was called "panning." Dirt would be placed in the pan and covered with water. After thorough mixing, the pan is gently swirled to remove dissolved material while the heavier gold settles to the bottom of the pan. The gold is then separated from the mixture of soil and water.

Separation of Mixtures

Not everyone is out searching for gold (and not many of those searchers is going to get much gold, either). In a chemical reaction, it is important to isolate the component(s) of interest from all the other materials so they can be further characterized. Studies of biochemical systems, environmental analysis, pharmaceutical research – these and many other areas of research require reliable separation methods.

Here are a number of common separation techniques:

Chromatography

Chromatography is the separation of a mixture by passing it in solution or suspension or as a vapor (as in gas chromatography) through a medium in which the components move at different rates. Thin-layer chromatography is a special type of chromatography used for separating and identifying mixtures that are or can be colored, especially pigments.

Distillation

Distillation is an effective method to separate mixtures comprised of two or more pure liquids. Distillation is a purification process where the components of a liquid mixture are vaporized and then condensed and isolated. In simple distillation, a mixture is heated and the most volatile component vaporizes at the lowest temperature. The vapor passes through a cooled tube (a condenser), where it condenses back into its liquid state. The condensate that is collected is called distillate.

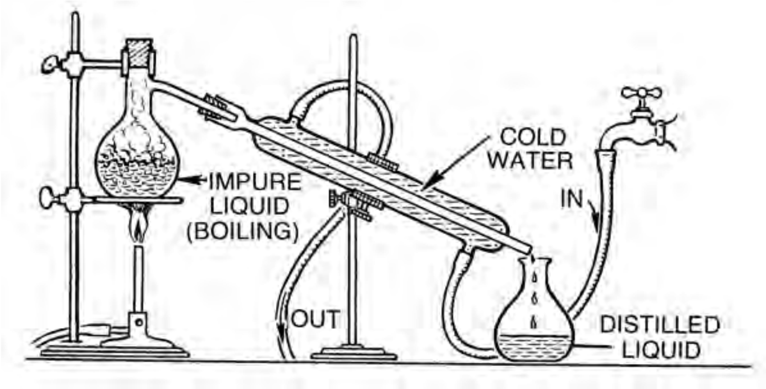


FIGURE 2.11

Distillation apparatus.

In the **Figure** above, we see several important pieces of equipment. There is a heat source, a test tube with a one-hole stopper attached to a glass elbow and rubber tubing. The rubber tubing is placed into a collection tube which is submerged in cold water. There are other more complicated assemblies for distillation that can also be used, especially to separate mixtures, which are comprised of pure liquids with boiling points that are close to one another.

Evaporation

Evaporation is a technique used to separate out homogenous mixtures where there is one or more dissolved solids. This method drives off the liquid components from the solid components. The process typically involves heating the mixture until no more liquid remains, Prior to using this method, the mixture should only contain one liquid component, unless it is not important to isolate the liquid components. This is because all liquid components will evaporate over time. This method is suitable to separate a soluble solid from a liquid.

In many parts of the world, table salt is obtained from the evaporation of sea water. The heat for the process comes from the sun.

Filtration

Filtration is a separation method used to separate out pure substances in mixtures comprised of particles some of which are large enough in size to be captured with a porous material. Particle size can vary considerably, given the type of mixture. For instance, stream water is a mixture that contains naturally occurring biological organisms like bacteria, viruses, and protozoans. Some water filters can filter out bacteria, the length of which is on the order of 1 micron. Other mixtures, like soil, have relatively large particle sizes, which can be filtered through something like a coffee filter.

FIGURE 2.12
Once the sea water in these evaporation ponds has evaporated, the salt can be harvested.

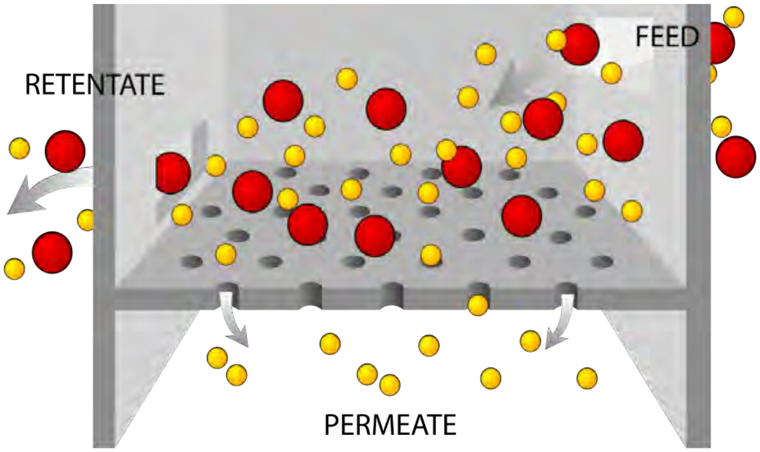


FIGURE 2.13
Filtration.

Summary

- Mixtures can be separated using a variety of techniques.
- Chromatography involves solvent separation on a solid medium.
- Distillation takes advantage of differences in boiling points.
- Evaporation removes a liquid from a solution to leave a solid material.
- Filtration separates solids of different sizes.

Practice

Use this resource to answer the following questions:

http://www.gourmetsleuth.com/Articles/Exotic-Herbs-Spices-and-Salts-639/hawaiian-salt.aspx

1. Where is salt produced in the Hawaiian Islands?
2. What does "paakai" mean?
3. How long does it take for salt to form by evaporation?

Review

1. Why is it important to separate material from a mixture?
2. What is chromatography?
3. What is distillation
4. What is filtration?
5. What is evaporation?
6. What technique would you use to separate sand from water? There are two possibilities.
7. What technique would you use to separate alcohol from water?

- **chromatography:** Involves solvent separation on a solid medium.
- **distillation:** Takes advantage of differences in boiling points.
- **evaporation:** Removes a liquid from a solution to leave a solid material.
- **filtration:** Separates solids of different sizes.

2.9 Elements

- Define element.
- State basic properties of an element.
- Give examples of elements and their uses.

The famous fictional British detective Sherlock Holmes was often said to make the statement "elementary, my dear Watson." In reality, the closest he ever came to that line was an exchange with Watson in the short story "The Crooked Man." Holmes shows shrewd insight into Watson's activities of the day. When asked how he knew what Watson was doing, Holmes simply replies "Elementary." Regardless of exactly how he put it, Sherlock was simply referring to what the Free Dictionary defines as "relating to, or constituting the basic, essential, or fundamental part."

Elements

An **element** is the simplest form of matter that has a unique set of properties. Examples of well-known elements include oxygen, iron, and gold (see the figure below). Elements cannot be broken down into a simpler substance. Likewise, one element cannot be chemically converted into a different element.

Some elements have been known for centuries (gold, silver, iron, copper, among others) while others have been created in the lab only within the last several years. Most elements do not exist as such in nature. They are so reactive that they can be found only in combination with other materials.

Several of the elements are very valuable while others are quite inexpensive. Gold is currently worth almost $1700 per ounce. Aluminum, on the other hand, only sells for about 90 cents per pound, considerably lower than gold.

FIGURE 2.14
Chemical elements are the simplest of substances. (A) An oxygen tank like this is used by people with a need for breathing assistance. (B) A simple skillet can be made from cast iron. (C) Gold bars are formed and used for monetary purposes.

Copper is worth somewhat more, selling for approximately $3.50 pound. Platinum is very valuable at about $1650 an ounce, not quite as expensive as gold.

Enjoy an old song about the elements sung by Harvard lecturer Tom Lehrer. There were only 102 known elements at the time he wrote this song.

MEDIA
Click image to the left for more content.

http://www.youtube.com/watch?v=K8eT-k4f7_8

Summary

- An element is the simplest form of matter that has a unique set of properties.
- One element cannot be chemically converted to another element.

Practice

Select an element from this list:

http://www.lenntech.com/periodic/name/alphabetic.htm

Answer the following questions:

1. What is the name of the element?
2. When was it discovered?
3. Who discovered it?
4. What is one use for this element?

Review

1. What is an element?
2. How much is gold worth today?
3. How many elements did we know about when Tom Lehrer wrote his song?

- **element:** The simplest form of matter that has a unique set of properties.

2.10 Compounds

- Define compound distinguish between element and compound.
- Give examples of compounds.
- Define chemical change.

What do you need to start building a house?

When building a house, you start with a blueprint of what the house will look like. The plan states how many windows and what kind, how many doors and what style, how many rooms and what type (bedroom, kitchen, other). The blueprint shows how the different pieces will go together to make the house. As long as the blueprint is followed and exactly the same items are used, the houses will be identical.

Compounds

A **compound** is a substance that contains two or more elements chemically combined in a fixed proportion. The elements carbon and hydrogen combine to form many different compounds. One of the simplest is called methane, in which there are always four times as many hydrogen particles as carbon particles. Methane is a pure substance because it always has the same composition. However, it is not an element because it can be broken down into simpler substances – carbon and hydrogen.

Recall that the components of a mixture can be separated from one another by physical means. This is not true for a compound. Table salt is a compound consisting of equal parts of the elements sodium and chlorine. Salt cannot be separated into its two elements by filtering, distillation, or any other physical process. Salt and other compounds can only be decomposed into their elements by a chemical process. A **chemical change** is a change that produces matter with a different composition. Many compounds can be decomposed into their elements by heating. When sugar is heated, it decomposes to carbon and water. Water is still a compound, but one which cannot be broken down into hydrogen and oxygen by heating. Instead, the passage of an electrical current through water will produce hydrogen and oxygen gases.

The properties of compounds are generally very different than the properties of the elements from which the compound is formed. Sodium is an extremely reactive soft metal that cannot be exposed to air or water. Chlorine is a deadly gas. The compound sodium chloride is a white solid which is essential for all living things (**Figure** 2.15).

FIGURE 2.15

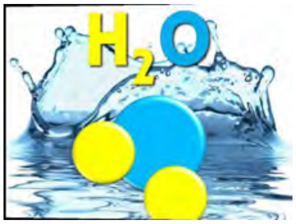
(A) Sodium is so reactive that it must be stored under oil. (B) Chlorine is a poisonous yellow-green gas. (C) Salt crystals, a compound of sodium and chlorine

Summary

1. A compound is a substance that contains two or more elements chemically combined in a fixed proportion.
2. A chemical change is a change that produces matter with a different composition.

Practice

Watch the video at the link below to answer the following questions:



MEDIA

Click image to the left for more content.

http://www.youtube.com/watch?v=9YPvwsDeLUo

1. What lists all the elements we know about?
2. What is the compound made out of two hydrogen atoms and one oxygen atom?
3. What is the compound made out of one carbon atom and two oxygen atoms?

Review

1. What is a compound?
2. How is a compound different from an element?
3. What is a chemical change?

- **chemical change:** A change that produces matter with a different composition.

- **compound:** A substance that contains two or more elements chemically combined in a fixed proportion.

2.11 Chemical Change

- Define chemical change.
- Give examples of chemical changes.

Do you like to cook?

Cooking is a valuable skill that everyone should have. Whether it is fixing a simple grilled cheese sandwich to preparing an elaborate meal, cooking demonstrates some basic ideas in chemistry. When you bake bread, you mix some flour, sugar, yeast, and water together. After baking, this mixture has been changed to form another substance (bread) that has different characteristics and qualities from the original materials. The process of baking has produced chemical changes in the ingredients that result in bread being made.

Chemical Change

Most of the elements we know about do not exist free in nature. Sodium cannot be found by itself (unless we prepare it in the laboratory) because it interacts easily with other materials. On the other hand, the element helium does not interact with other elements to any extent. So we can isolate helium from natural gas during the process of drilling for oil.

A chemical change produces a different materials than the ones we started with. One aspect of the science of chemistry is interest in the changes that matter undergoes. If all we had were the elements and they did nothing, life would be very boring (in fact, life would not exist since we need all those compounds to put our bodies together and sustain us). But the processes of change that take place when different chemicals are combined produce all the materials that we use daily.

One type of chemical change (already mentioned) is when two elements combine to form a compound. Another type involves the breakdown of a compound to produce the elements that make it up. If we pass an electric current through bauxite (aluminum oxide, the raw material for aluminum metal), we get metallic aluminum as a product.

FIGURE 2.16

Electrolytic production of aluminum.

However, the vast majority of chemical changes involve one compound being transformed into another compound. There are literally millions of possibilities when we take this approach to chemical change. New compounds can be made that produce better fabrics that are easier to clean and maintain, they can help preserve food so it doesn't spoil as quickly, and we can make new medicines to treat diseases – all made possible by studying chemical change.

Summary

1. A chemical change produces a different materials than the ones we started with.

Practice

Use the link below to answer the following questions:

http://chemistry.about.com/od/lecturenotesl3/a/chemphyschanges.htm

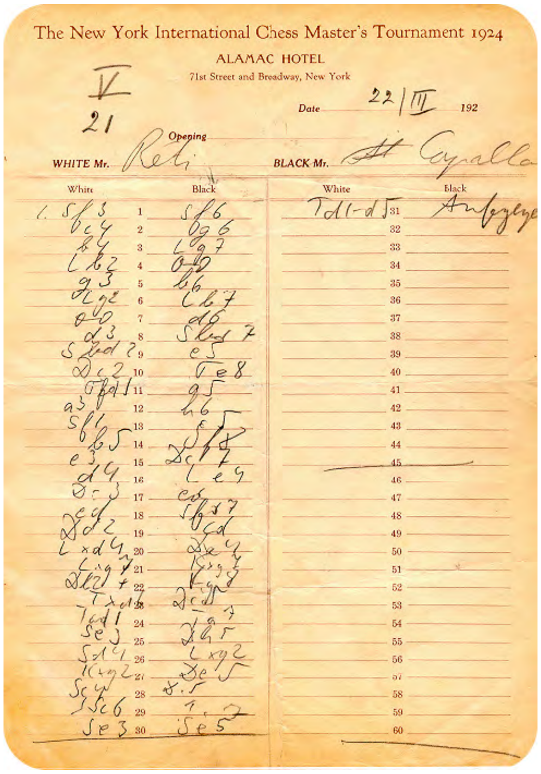
1. Where do chemical changes take place?
2. What does a chemical change produce?
3. What are physical changes concerned with?

Review

1. What is a chemical change?
2. List three types of chemical changes.

2.12 Chemical Symbols and Formulas

- Define chemical symbol.
- Define chemical formula.
- Give the Latin name for elements that use the Latin name for their symbol.



The New York International Chess Master's Tournament 1924

ALAMAC HOTEL

71st Street and Broadway, New York

V

21

Date 22/III 192

Opening

WHITE Mr. Reti

BLACK Mr. Capablanca

Suppose you were walking along and noticed a piece of paper on the ground with markings on it. You pick it up and see the paper in the picture above.

To most people, these notes are meaningless (maybe they're a secret spy code). But to a chess player, these symbols tell the story of a chess game. Each abbreviation describes a chess piece or a move during the game. The use of special symbols allows us to "see" the game without having to read a wordy and possibly incomplete description of what happened.

Chemical Symbols and Formulas

In order to illustrate chemical reactions and the elements and **compounds** involved in them, chemists use symbols and formulas. A **chemical symbol** is a one-or two-letter designation of an element. Some examples of chemical symbols are O for oxygen, Zn for zinc, and Fe for iron. The first letter of a symbol is always capitalized. If the symbol contains two letters, the second letter is lower case. The majority of elements have symbols that are based on their English names. However, some of the elements that have been known since ancient times have maintained symbols that are based on their Latin names.

FIGURE 2.17
Chess game.

TABLE 2.1: **Symbols and Latin Names for Elements**

Chemical Symbol	Name	Latin Name
Na	sodium	natrium
K	potassium	kalium
Fe	iron	ferrum
Cu	copper	cuprum
Ag	silver	argentum
Sn	tin	stannum
Sb	antimony	stibium
Au	gold	aurum
Pb	lead	plumbum

Compounds are combinations of two or more elements. A **chemical formula** is an expression that shows the elements in a compound and the relative proportions of those elements. Water is composed of hydrogen and oxygen in a two to one ratio. The chemical formula for water is H_2O. Sulfuric acid is one of the most widely produced chemicals in the Unites States and is composed of the elements hydrogen, sulfur, and oxygen. The chemical formula for sulfuric acid is H_2SO_4.

Summary

- A chemical symbolis a one- or two-letter designation of an element.
- Compounds are combinations of two or more elements.
- A chemical formula is an expression that shows the elements in a compound and the relative proportions of those elements.
- Many elements have symbols that derive from the Latin name for the element.

Practice

Use the link below to answer the following questions:

http://suite101.com/article/chemical-symbols-and-formulae-a206723

1. Why do elements and compounds need to be represented in a short and accurate way?
2. Do we have different symbols in different countries?
3. What do the numbed in a formula stand for?

2.13 Chemical Property and Chemical Reaction

- Define chemical property.
- Give examples of chemical properties.
- Define chemical reaction.
- Give examples of chemical reactions.

Have you ever left your bicycle out in the rain?

It's not a good idea because the bicycle can soon begin to rust. You start to get a reddish-orange build-up of a rough deposit on the metal. It may start with the chain, but can spread to other parts of the bicycle, especially if there are scratches that create a bare metal surface. The formation of rust is a chemical process that takes place when iron is exposed to water and oxygen. It is estimated that damage due to rust costs U.S. businesses, military, and government over 276 billion dollars a year - a very expensive chemical process.

Chemical Properties

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. The more general term for rusting and other similar processes is corrosion. Other terms that are commonly used in descriptions of chemical changes are burn, rot, explode, decompose, and ferment. Chemical properties are very useful in identifying substances. However, unlike physical properties, chemical properties can only be observed as the substance is in the process of being changed into a different substance.

Chemical Change

A **chemical change** is also called a chemical reaction. A chemical reaction is a process that occurs when one or more substances are changed into one or more new substances. Zinc (Zn) is a silver gray element that can be ground into a powder. If zinc is mixed at room temperature with powdered sulfur (S), a bright yellow element, the result will simply be a mixture of zinc and sulfur. No chemical reaction occurs. However, if energy is provided to the mixture in the form of heat, the zinc will chemically react with the sulfur to form the compound zinc sulfide (ZnS). The figure below shows the substances involved in this reaction.

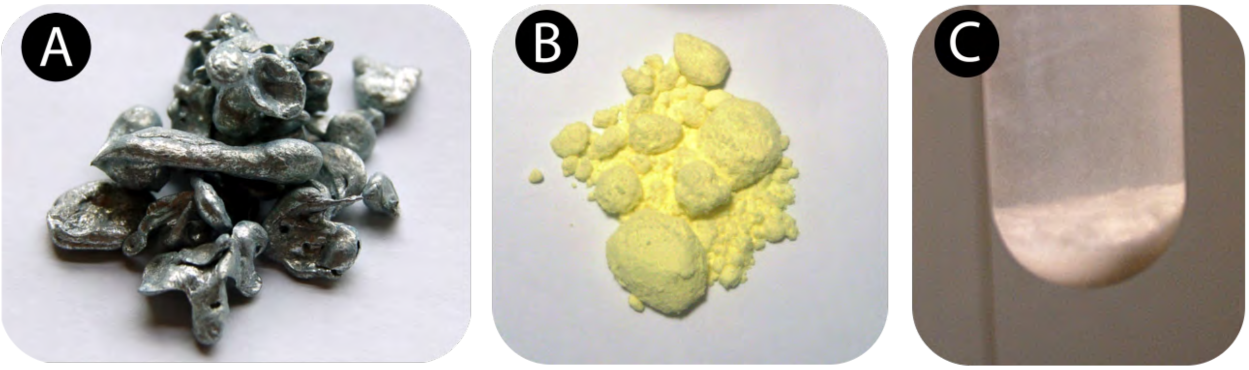


FIGURE 2.18

Zinc and sulfur are two elements that undergo a chemical reaction when heated to from the compound zinc sulfide.

Summary

- A chemical property describes the ability of a substance to undergo a specific chemical change.
- A chemical reaction is a process that occurs when one or more substances are changed into one or more new substances.

Practice

Use the link below to answer the following questions:

http://chemistry.about.com/od/matter/a/Chemical-Properties.htm

1. How do we determine a chemical property of a material?
2. What must be changed for a chemical property to become apparent?
3. How do scientists use chemical properties?
4. Which of these is not a chemical property?
    a. toxicity
    b. flammability
    c. melting point
    d. heat of combustion

Review

1. What is a chemical property?
2. What is a chemical reaction?

3. When can we observe a chemical property?
4. Is freezing water a chemical property?

- **chemical property:** Describes the ability of a substance to undergo a specific chemical change.
- **chemical reaction:** A process that occurs when one or more substances are changed into one or more new substances.

2.14 Reactants and Products

- Define chemical equation.
- Define reactant.
- Define product.

Over the last few decades, computers have proven to be extremely useful tools for organizing and processing information. You put data into the computer (such as the structural parameters of a compound) and your output can be a detailed diagram of how that molecule looks in three dimensions. The computer and its programs transform input data into a useful final product.

Chemical Equation

The reaction between zinc and sulfur can be shown in what is called a **chemical equation**. In words, we could write the reaction as:

zinc + sulfur → zinc sulfide

The more convenient way to express a chemical reaction is to use the symbols and formulas of the substances involved:

$\text{Zn} + \text{S} \rightarrow \text{ZnS}$

The substance(s) to the left of the arrow in a chemical equation are called reactants. A **reactant** is a substance that is present at the start of a chemical reaction. The substance(s) to the right of the arrow are called **products**. A product is a substance that is present at the end of a chemical reaction. In the equation above, the zinc and sulfur are the reactants that chemically combine to form the zinc sulfide product.

There is a standard way of writing chemical equations. The reactants are all written on the left-hand side of the equation, with the products on the right-hand side. An arrow points from the reactants to the products to indicate the direction of the reaction:

reactants $\rightarrow$ products

When appropriate, a symbol may be written above or below the arrow to indicate some special circumstance. The symbol Δ is often used to indicate that the reaction is to be heated.

The presence of the arrow also indicates that the reaction goes in one direction under the conditions indicated. There are reactions which can be easily reversed, but we will not take those up right now.

There are a wide variety of reactions possible: elements may form compounds (as seen in the reaction above), compounds may form elements (water will break down in the presence of an electric current to form hydrogen gas and oxygen gas) or compounds may combine, break apart, or rearrange to form new materials.

Summary

- A chemical equation describes a chemical reaction.
- Reactants are starting materials and are written on the left-hand side of the equation.
- Products are the end-result of the reaction and are written on the right-hand side of the equation.

Practice

Use the link below to answer the following questions:

http://www.chemprofessor.com/outline7b.htm

1. Where are reactants written in a chemical equation?
2. Where are products written in a chemical equation?
3. What chemical information is found in a chemical equation?

Review

1. What is a reactant?
2. What is a product?
3. What does a chemical equation do?
4. In the reaction sodium + water $\rightarrow$ sodium hydroxide + hydrogen,
    (a) what are the reactants?
    (b) what are the products?

- **chemical equation:** Describes a chemical reaction.
- **product:** Are the end-result of the reaction and are written on the right-hand side of the equation.
- **reactant:** Starting materials and are written on the left-hand side of the equation.

2.15 Recognizing Chemical Reactions

- Describe ways a chemical reaction can be recognized.

Have you ever cooked a pizza?

Making a pizza can be as easy as buying a "take and bake" from a store and putting it in the oven to mixing up the dough and loading it up with your favorite toppings before baking it. How do you know when it is done? The most obvious sign is that the crust turns light brown. The dough is no longer flexible, but much more solid. Maybe the cheese has melted. You want the pizza to be cooked, not half-raw.

Recognizing Chemical Reactions

How can you tell if a **chemical reaction** is taking place? There are four visual clues that indicate that a chemical reaction is likely occurring.

1. A change of color occurs during the reaction.
2. A **gas** is produced during the reaction.
3. A solid product called a **precipitate** is produced in the reaction.
4. A transfer of energy occurs as a result of the reaction.

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 mercury oxide reactant becomes the silver color of mercury. The color change is the sign that the reaction is occurring.

When zinc reacts with hydrochloric acid, the reaction bubbles vigorously as hydrogen gas is produced. The production of a gas is also an indication that a chemical reaction is occurring.

FIGURE 2.19

Mercuric oxide.

FIGURE 2.20

Mercury metal.

FIGURE 2.21

Zinc reacting with hydrochloric acid produces 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. A precipitate is a solid product that forms from a reaction and settles out of a liquid mixture. The formation of a precipitate is an indication 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 also involve a transfer of energy. Melting of a solid absorbs energy, while the condensation of a gas releases energy. The only way to be certain that a chemical reaction has taken place is to test the composition of the substances after the change has taken place to see if they are different from the starting substances.

Summary

- There are four visual clues that indicate that a chemical reaction is likely occurring.
  - A change of color occurs during the reaction.
  - A gas is produced during the reaction.
  - A solid product called a precipitate is produced in the reaction.

FIGURE 2.22

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

  - A transfer of energy occurs as a result of the reaction.

Practice

Use the link below to answer the following questions:

http://www.harpercollege.edu/tm-ps/chm/100/dgodambe/thedisk/chemrxn/signs.htm

1. What happened when the yellow solution and the clear solution were mixed?
2. What happened when the chalk was added to the clear liquid?
3. How much did the temperature change when two liquids were mixed together?

Review

1. What was the color change when mercury (II) oxide was heated?
2. What happened when zinc metal was mixed with hydrochloric acid?
3. What happens when lead nitrate and potassium iodide are mixed?

- **chemical reaction:** Involves a transfer of energy. There are four visual clues to indicate a chemical reaction.
- **gas:** A state of matter that is air-like, with a low density and viscosity.
- **precipitate:** A substance that is created from a precipitation reaction.

2.16 References

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CHAPTER 3 Measurements

Chapter Outline

3.1 SI Base Units

- Define the SI system of units.
- List the seven base units of measurement.

How long is a yard?

It depends on whom you ask and when you asked the question. Today we have a standard definition of the yard, which you can see marked on every football field. If you move the ball ten yards, you get a first down and it doesn't matter whether you are playing in Los Angeles, Dallas, or Green Bay. But at one time that yard was arbitrarily defined as the distance from the tip of the king's nose to the end of his outstretched hand. Of course, the problem there is simple: new king, new distance (and then you have to remark all those football fields).

SI Base Units

All measurements depend on the use of units that are well known and understood. The **English system** of measurement units (inches, feet, ounces, etc.) are not used in science because of the difficulty in converting from one unit to another. The **metric system** is used because all metric units are based on multiples of 10, making conversions very simple. The metric system was originally established in France in 1795. **The International System of Units** is a system of measurement based on the metric system. The acronym **SI** is commonly used to refer to this system and stands for the French term, *Le Système International d'Unités*. The SI was adopted by international agreement in 1960 and is composed of seven base units.

TABLE 3.1: SI Base Units of Measurement

Quantity	SI Base Unit	Symbol
Length	meter	m
Mass	kilogram	kg
Temperature	kelvin	K
Time	second	s
Amount of a Substance	mole	mol
Electric Current	ampere	A
Luminous Intensity	candela	cd

The first five units are frequently encountered in chemistry. All other measurement quantities, such as volume, force, and energy, can be derived from these seven base units.

The map in **Figure** 3.3 shows the adoption of the SI units in countries around the world. The United States has legally adopted the metric system for measurements, but does not use it in everyday practice. Great Britain and much of Canada use a combination of metric and imperial units.

Summary

- The SI system is based on multiples of ten.
- There are seven basic units in the SI system.
- Five of these units are commonly used in chemistry.

FIGURE 3.1
Meter standard.

FIGURE 3.2
Kilogram standard

FIGURE 3.3
Areas of world using metric system.

Practice

Use the link below to answer the following questions:

http://physics.nist.gov/cuu/Units/history.html

1. When was the metric system created?
2. What was deposited in the Archives de la République in Paris?
3. What was the CGS system based on?
4. When was the name *International System of Units* (*SI*) assigned?

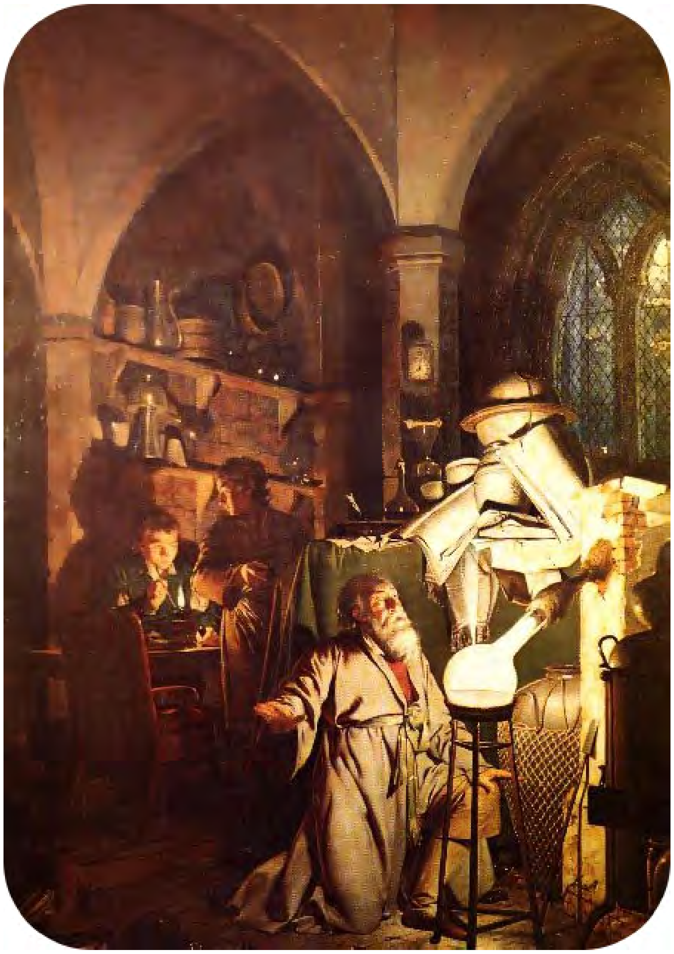
Review

1. What does SI stand for?
2. When was this system adopted by the international community?
3. Which of the units are commonly used in chemistry?

- **English system:** A system of measurements based on feet inches, and other somewhat arbitrary units.
- **The International System of Units:** Based on the metric system of measurements.
- **Metric system**: Based on units of 10.
- **SI:** The metric system and stands for the French term, *Le Système International d'Unités.*

3.2 Metric Prefixes

- List common metric prefixes and their exponential values.
- Convert from one exponential factor to another for a given unit.



What do Latin and Greek have to do with modern science?

Isn't it hard enough to learn English terms? For hundreds of years, the languages of the educated class were Latin and Greek. In part, because the literature of philosophy was Latin and Greek. Even the medieval Bibles were written in those two languages – the first English translation was in the late 1380s. Using Latin and Greek allowed scholars from different countries to communicate more easily with one another. Today we still see many Latin phrases in legal communications ("pro bono" meaning to do something "for the good" and not charge legal fees), scientific naming of biological species, and Latin is used for the annual student speech at Harvard University graduations. Not bad for a "dead" language.

Metric Prefixes

Conversions between metric system units are straightforward because the system is based on powers of ten. For example, meters, centimeters, and millimeters are all metric units of length. There are 10 millimeters in 1 centimeter and 100 centimeters in 1 meter. **Metric prefixes** are used to distinguish between units of different size. These prefixes all derive from either Latin or Greek terms. For example, *mega* comes from the Greek word μέγας, meaning "great"

The table below lists the most common metric prefixes and their relationship to the central unit that has no prefix. Length is used as an example to demonstrate the relative size of each prefixed unit.

TABLE 3.2: SI Prefixes

Prefix	Unit Abbrev.	Meaning	Example
giga	G	1,000,000,000	1 gigameter (Gm) = 10^9 m
mega	M	1,000,000	1 megameter (Mm) = 10^6 m
kilo	k	1000	1 kilometer (km) = 1000 m
hecto	h	100	1 hectometer (hm) = 100 m
deka	da	10	1 dekameter (dam) = 10 m
		1	**1 meter (m)**
deci	d	1/10	1 decimeter (dm) = 0.1 m
centi	c	1/100	1 centimeter (cm) = 0.01 m
milli	m	1/1000	1 millimeter (mm) = 0.001 m
micro	μ	1/1,000,000	1 micrometer (μm) = 10^{-6} m
nano	n	1/1,000,000,000	1 nanometer (nm) = 10^{-9} m
pico	p	1/1,000,000,000,000	1 picometer (pm) = 10^{-12} m

There are more prefixes - some of them rarely used. Have you ever heard of a zeptometer? You can learn more about prefixes at http://www.essex1.com/people/speer/large.html.

There are a couple of odd little practices with the use of metric abbreviations. Most abbreviations are lower-case. We use "m" for meter and not "M". However, when it comes to volume, the base unit "liter" is abbreviated as "L" and not "l". So we would write 3.5 milliliters as 3.5 mL.

As a practical matter, whenever possible you should express the units in a small and manageable number. If you are measuring the weight of a material that weighs 6.5 kg, this is easier that saying it weighs 6500 g or 0.65 dag. All three are correct, but the kg units in this case make for a small and easily managed number. However, if a specific problem needs grams instead of kilograms, go with the grams for consistency.

Summary

- Metric prefixes derive from Latin or Greek terms.
- The prefixes are used to make the units manageable.

Practice

Do the online metric system crossword puzzle at http://education.jlab.org/sciencecrossword/index.html

Click on “metric system” to get to the puzzle

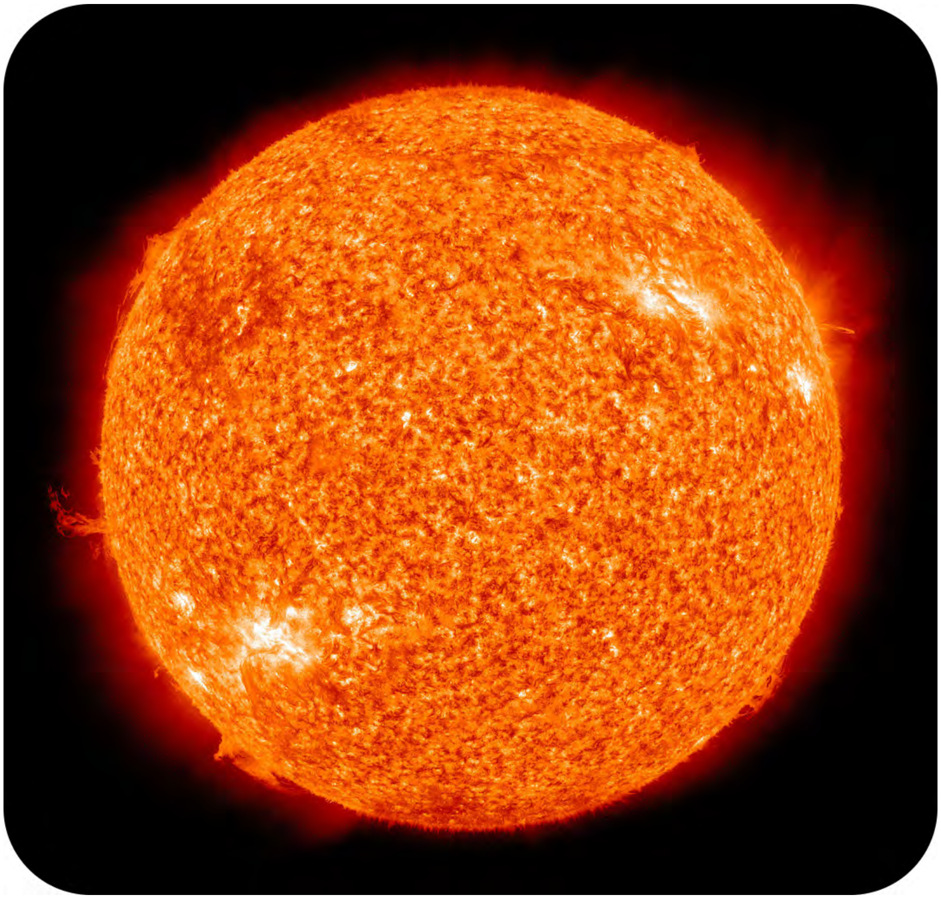
Review

1. What is the prefix for “thousand”?
2. What is the prefix for 0.01?
3. How would you write 500 milliliters?
4. How many decimeters in one meter?
5. You have a mass that weighs 1.2 hectograms. How many grams does it weigh?

- **metric prefixes:** Prefixes used to distinguish between metric units of different sizes.

3.3 Scientific Notation in Chemistry

- Define scientific (exponential) notation.
- Use this notation to simplify very large or very small numbers.



How far is the Sun from Earth?

Astronomers are used to really big numbers. While the moon is only 406,697 km from earth at its maximum distance, the sun is much further away (150 million km). Proxima Centauri, the star nearest the earth, is 39, 900, 000, 000, 000 km away and we have just started on long distances. On the other end of the scale, some biologists deal with very small numbers: a typical fungus could be as small as 30 μmeters (0.000030 meters) in length and a virus might only be 0.03 μmeters (0.00000003 meters) long.

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. It is a very useful tool for working with numbers that are either very large or very small. 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 the 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 because you would have to multiply 1.5 by 10^{11} to get the correct number. Scientific notation is sometimes referred to as exponential notation.

TABLE 3.3: SI Prefixes

Prefix	**Unit Abbrev.**	**Exponential Factor**	**Meaning**	**Example**
giga	G	10^9	1,000,000,000	1 gigameter (Gm) = 10^9 m
mega	M	10^6	1,000,000	1 megameter (Mm) = 10^6 m
kilo	k	10^3	1000	1 kilometer (km) = 1000 m
hecto	h	10^2	100	1 hectometer (hm) = 100 m
deka	da	10^1	10	1 dekameter (dam) = 10 m
		$\mathbf{10^0}$	**1**	**1 meter (m)**
deci	d	10^{-1}	1/10	1 decimeter (dm) = 0.1 m
centi	c	10^{-2}	1/100	1 centimeter (cm) = 0.01 m
milli	m	10^{-3}	1/1000	1 millimeter (mm) = 0.001 m
micro	μ	10^{-6}	1/1,000,000	1 micrometer (μm) = 10^{-6} m
nano	n	10^{-9}	1/1,000,000,000	1 nanometer (nm) = 10^{-9} m
pico	p	10^{-12}	1/1,000,000,000,000	1 picometer (pm) = 10^{-12} m

When working with small numbers, we use a negative exponent. So 0.1 meters is 1×10^{-1} meters, 0.01 is 1×10^{-2} and so forth. The table above gives examples of smaller units. Note the use of the **leading zero** (the zero to the left of the decimal point). That digit is there to help you see the decimal point more clearly. The figure 0.01 is less likely to be misunderstood than .01 where you may not see the decimal.

Summary

- Scientific notation allows us to express very large or very small numbers in a convenient way.
- This notation uses a coefficient (a number between 1 and 10) and a power of ten sufficient for the actual number.

Practice

Practice scientific notation using the link below:

http://www.mathsisfun.com/numbers/scientific-notation.html

Review

1. What is scientific notation?
2. What do we use scientific notation for?
3. What is a leading zero?

4. Express 150,000,000 in scientific notation.
5. Express 0.000043 in scientific notation.

- **exponent:** A number placed to the right and above another number, symbol, or expression to indicate the power to which the expression is raised.
- **leading zero:** The zero to the left of the decimal point which is there to help you see the decimal point more clearly.

3.4 SI Length and Volume Units

- Define length.
- Define volume.
- Describe standard measure of length and volume.

Back in the days before all the electronic gadgets sailors now have for measuring depth and locating undersea objects, the fathom was the unit of measurement for depth. A rope was knotted every six feet and the end was dropped over the side of the ship. You could tell how deep the water was by how many knots went under the water before the rope hit bottom. Today we just turn on an instrument and read the depth to a high level of accuracy.

Length and Volume

Length is the measurement of the extent of something along its greatest dimension. The SI basic unit of length, or linear measure, is the **meter** (m). All measurements of length may be made in meters, though the prefixes listed in various tables will often be more convenient. The width of a room may be expressed as about 5 meters (m), whereas a large distance such as the distance between New York City and Chicago is better expressed as 1150 kilometers (km). Very small distances can be expressed in units such as the millimeter or the micrometer. The width of a typical human hair is about 20 micrometers (μm).

Volume is the amount of space occupied by a sample of matter. The volume of a regular object can be calculated by multiplying its length by its width by its height. Since each of those is a linear measurement, we say that units of volume are derived from units of length. The SI unit of volume is the cubic meter (m^3), which is the volume occupied by a cube that measures 1 m on each side. This very large volume is not very convenient for typical use in a chemistry laboratory. A liter (L) is the volume of a cube that measures 10 cm (1 dm) on each side. A liter is thus equal to both 1000 cm^3 (10 cm $\times$ 10 cm $\times$ 10 cm) and to 1 dm^3. A smaller unit of volume that is commonly used is the milliliter (mL – note the capital L which is a standard practice). A milliliter is the volume of a cube that measures 1 cm on each side. Therefore, a milliliter is equal to a cubic centimeter (cm^3). There are 1000 mL in 1 L, which is the same as saying that there are 1000 cm^3 in 1 dm^3.

FIGURE 3.4

A typical water bottle is 1 liter in volume

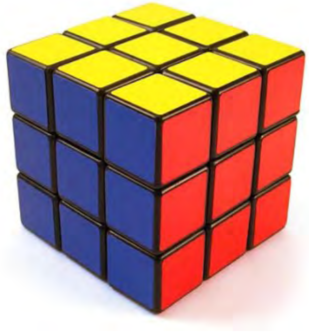


FIGURE 3.5

Rubik's cube. This Rubik's cube is 5.7 cm on each side and has a volume of 185.2 cm^3 or 185.2 mL.

Summary

- Length is the measurement of the extent of something along its greatest dimension.
- Volume is the amount of space occupied by a sample of matter.
- Volume can be determined by knowing the length of each side of the item.

Practice

Read the section of length and volume in the link below and answer the following questions:

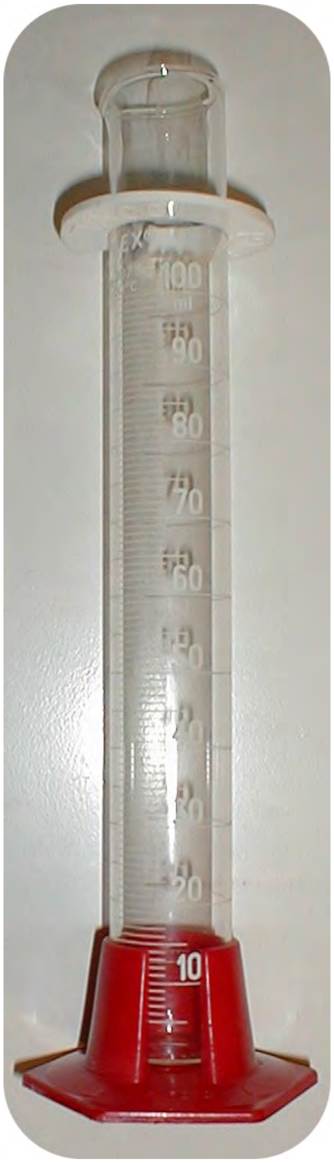


FIGURE 3.6

Graduated cylinder. Volume in the laboratory is often measured with a graduated cylinder, which come in a variety of sizes.

http://www.montgomerycollege.edu/Departments/biotp/Metric.html

1. What are some units of length in the metric system?
2. Do the first three length conversions.
3. Where on the meniscus do you measure volume in a graduated cylinder?
4. Do the first two conversion examples for volume.

Review

1. Define length.
2. Define volume.
3. An object measures 6.2 cm × 13.7 cm × 26.9 cm. Which value is the length of the object?
4. How big is a mL?

- **length:** The measurement of the extent of something along its greatest dimension

- **meter:** The SI basic unit of length, or linear measure
- **volume:** The amount of space occupied by a sample of matter. The volume of a regular object can be calculated by multiplying its length by its width by its height. Since each of those is a linear measurement, we say that units of volume are derived from units of length

3.5 SI Mass and Weight Units

- Define mass.
- Define weight.
- Explain the difference between mass and weight.

How is he floating?

One of the many interesting things about travel in outer space is the idea of weightlessness. If something is not fastened down, it will float in mid-air. Early astronauts learned that weightlessness had bad effects on bone structure. If there was no pressure on the legs, those bones would begin to lose mass. Weight provided by gravity is needed to maintain healthy bones. Specially designed equipment is now a part of every space mission so the astronauts can maintain good body fitness.

Mass and Weight

Mass is a measure of the amount of matter that an object contains. The mass of an object is made in comparison to the standard mass of 1 kilogram. The kilogram was originally defined as the mass of 1 L of liquid water at 4°C (volume of a liquid changes slightly with temperature). In the laboratory, mass is measured with a balance (**Figure** 3.7), which must be calibrated with a standard mass so that its measurements are accurate.

Other common units of mass are the gram and the milligram. A gram is 1/1000th of a kilogram, meaning that there are 1000 g in 1 kg. A milligram is 1/1000th of a gram, so there are 1000 mg in 1 g.

Mass is often confused with the term weight. **Weight** is a measure of force that is equal to the gravitational pull on an object. The weight of an object is dependent on its location. On the moon, the force due to **gravity** is about one sixth that of the gravitational force on Earth. Therefore, a given object will weigh six times more on Earth than it does on the moon. Since mass is dependent only on the amount of matter present in an object, mass does not change with location. Weight measurements are often made with a spring scale by reading the distance that a certain object pulls down and stretches a spring.

FIGURE 3.7

An analytical balance makes very sensitive mass measurements in a laboratory, usually in grams.

Summary

- Mass is a measure of the amount of matter that an object contains.
- Weight is a measure of force that is equal to the gravitational pull on an object.
- Mass is independent of location, while weight depends on location.

Practice

Use the link below to answer the following questions:

http://hyperphysics.phy-astr.gsu.edu/hbase/mass.html

1. The mass of an object is a __________ measure of its inertia.
2. What is the SI unit for mass?
3. How is weight different from mass?
4. What is the unit of weight in the United States?

Review

1. Define mass.
2. Define weight.
3. If I weigh 180 pounds on Earth, what will I weigh on the moon?

- **gravity:** The force that causes two particles to pull towards each other
- **mass:** A measure of the amount of matter that an object contains. The mass of an object is made in comparison to the standard mass of 1 kilogram.
- **weight:** A measure of force that is equal to the gravitational pull on an object. The weight of an object is dependent on its location.

3.6 SI Kinetic Energy Units

- Define kinetic energy.
- Define potential energy.
- Write the expression for calculating energy in joules.

Have you ever watched a cat in action?

When they are chasing something, they move very fast. We may comment, “That cat has a lot of energy”. In saying that, we are more correct than we realize. One form of energy is seen when an object is moving and this type of energy is the basis for many chemical processes.

SI Kinetic Energy Units

An object’s **kinetic energy** is the energy due to motion. Kinetic energy can be defined mathematically as

$$\text{KE} = \frac{1}{2}\,\text{mv}^2$$

where KE = kinetic energy

m = mass

v = velocity

Energy is defined as the capacity to do work or to produce heat. As discussed previously, kinetic energy is one type of energy and is associated with motion. Another frequently encountered energy is **potential energy**, a type of energy that is stored in matter and released during a chemical reaction. The **joule** (J) is the SI unit of energy and is named after English physicist James Prescott Joule (1818-1889). If we go back to the equation for kinetic energy written above, we can put units in (kg for mass and m^2/s^2 for velocity squared). Then, in terms of SI base units a joule is equal to a kilogram times meter squared divided by a second squared ($kg \bullet m^2/s^2$). Another common unit of energy that is often used is the **calorie** (cal), which is equal to 4.184 J.

FIGURE 3.8

James Prescott Joule.

Summary

- Energy is the capacity to do work or to produce heat.
- Kinetic energy is the energy due to motion.
- Potential energy is energy stored in matter.
- The joule (J) is the SI unit of energy and equals $kg \bullet m^2/s^2$.

Practice

Use the link below to answer the following questions:

http://chemwiki.ucdavis.edu/Physical_Chemistry/Thermodynamics/State_Functions/Kinetic_Energy

1. What is kinetic energy dependent upon?
2. Do molecules at a higher temperature move faster or slower than molecules at a lower temperature?
3. What happens when a chemical reaction releases energy?
4. What happens when a chemical reaction absorbs energy?

Review

1. What is kinetic energy?
2. What is the mathematical equation for kinetic energy?
3. What is potential energy?
4. What is the SI unit for energy?

- **calorie:** common unit of energy, which is equal to 4.184 J.
- **energy:** As the capacity to do work or to produce heat.
- **joule:** The SI unit of energy and is named after English physicist James Prescott Joule (1818-1889).
- **kinetic energy:** The energy due to motion.
- **potential energy:** A type of energy that is stored in matter and released during a chemical reaction.

3.7 Temperature and Temperature Scales

- Define temperature.
- Describe the Fahrenheit temperature scale.
- Describe the Celsius temperature scale.
- Describe the Kelvin temperature scale.

Touch the top of the stove after it has been on and it feels hot. Hold an ice cube in your hand and it feels cold. Why? The particles of matter in a hot object are moving much faster than the particles of matter in a cold object. An object's **kinetic energy** is the energy due to motion. The particles of matter that make up the hot stove have a greater amount of kinetic energy than those in the ice cube.

Temperature and Temperature Scales

Temperature is a measure of the average kinetic energy of the particles in matter. In everyday usage, temperature is how hot or cold an object is. Temperature is an important parameter in chemistry. When a substance changes from solid to liquid, it is because there was an increase in the temperature of the material. Chemical reactions usually proceed faster if the temperature is increased. Many unstable materials (such as enzymes) will be viable longer at lower temperatures.

FIGURE 3.9

The glowing charcoal on the left represents high kinetic energy, while the snow and ice on the right are of much lower kinetic energy.

Temperature Scales

The first thermometers were glass and contained alcohol, which expanded and contracted as the temperature changed. The German scientist, Daniel Gabriel Fahrenheit used mercury in the tube, an idea put forth by Ismael Boulliau. The Fahrenheit scale was first developed in 1724 and tinkered with for some time after that. The main problem with this scale is the arbitrary definitions of temperature. The freezing point of water was defined as 32°F and the boiling point as 212°F. The Fahrenheit scale is typically not used for scientific purposes.

The Celsius scale of the metric system is named after Swedish astronomer Anders Celsius (1701-1744). The Celsius scale sets the freezing point and boiling point of water at 0°C and 100°C respectively. The distance between those two points is divided into 100 equal intervals, each of which is one degree. Another term sometimes used for the Celsius scale is "centigrade" because there are 100 degrees between the freezing and boiling points of water on this scale. However, the preferred term is "Celsius."

FIGURE 3.10

Daniel Gabriel Fahrenheit.

FIGURE 3.11

Anders Celsius.

The Kelvin temperature scale is named after Scottish physicist and mathematician Lord Kelvin (1824-1907). It is based on molecular motion, with the temperature of 0 K, also known as absolute zero, being the point where all molecular motion ceases. The freezing point of water on the Kelvin scale is 273.15 K, while the boiling point is 373.15 K. Notice that here is no "degree" used in the temperature designation. Unlike the Fahrenheit and Celsius scales where temperatures are referred to as "degrees F" or "degrees C," we simply designated temperatures in the Kelvin scale as kelvins.

As can be seen by the 100 kelvin difference between the two, a change of one degree on the Celsius scale is equivalent to the change of one kelvin on the Kelvin scale. Converting from one scale to another is easy, as you simply add or subtract 273.

Summary

- Temperature is a measure of the average kinetic energy of the particles in matter.
- The Fahrenheit scale defines the freezing point of water as 32°F and the boiling point as 212°F.
- The Celsius scale sets the freezing point and boiling point of water at 0°C and 100°C respectively.
- The Kelvin scale is based on molecular motion, with the temperature of 0 K, also known as absolute zero, being the point where all molecular motion ceases.

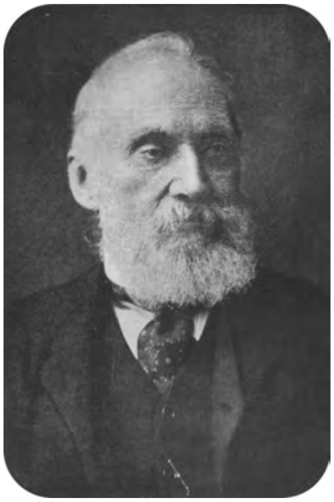


FIGURE 3.12

Lord Kelvin.

Practice

Use the link below to answer the following questions:

http://www.visionlearning.com/library/module_viewer.php?mid=48

1. What mixture did Fahrenheit use to set his thermometer at zero degrees?
2. Why is the Celsius scale preferred in scientific work over the Fahrenheit scale?
3. What was the idea behind the establishment of the Kelvin temperature scale?
4. What is the advantage of using the Kelvin scale at low temperatures?

Review

1. What is absolute zero on the Celsius temperature scale?
2. What are the freezing and boiling points of water in the Celsius scale?
3. Convert the following Kelvin temperatures to degrees Celsius.
    (a) 188 K
    (b) 631 K
4. Temperature in degrees Fahrenheit can be converted to Celsius by first subtracting 32, then dividing by 1.8. What is the Celsius temperature outside on a warm day (88°F)?
5. Why is the Celsius scale sometimes called "centigrade"?

- **kinetic energy:** The energy due to motion
- **temperature:** A measure of the average kinetic energy of the particles in matter. In everyday usage, temperature is how hot or cold an object is
- **temperature scale:** A way of measuring temperature quantitatively. There are three major scales used today.

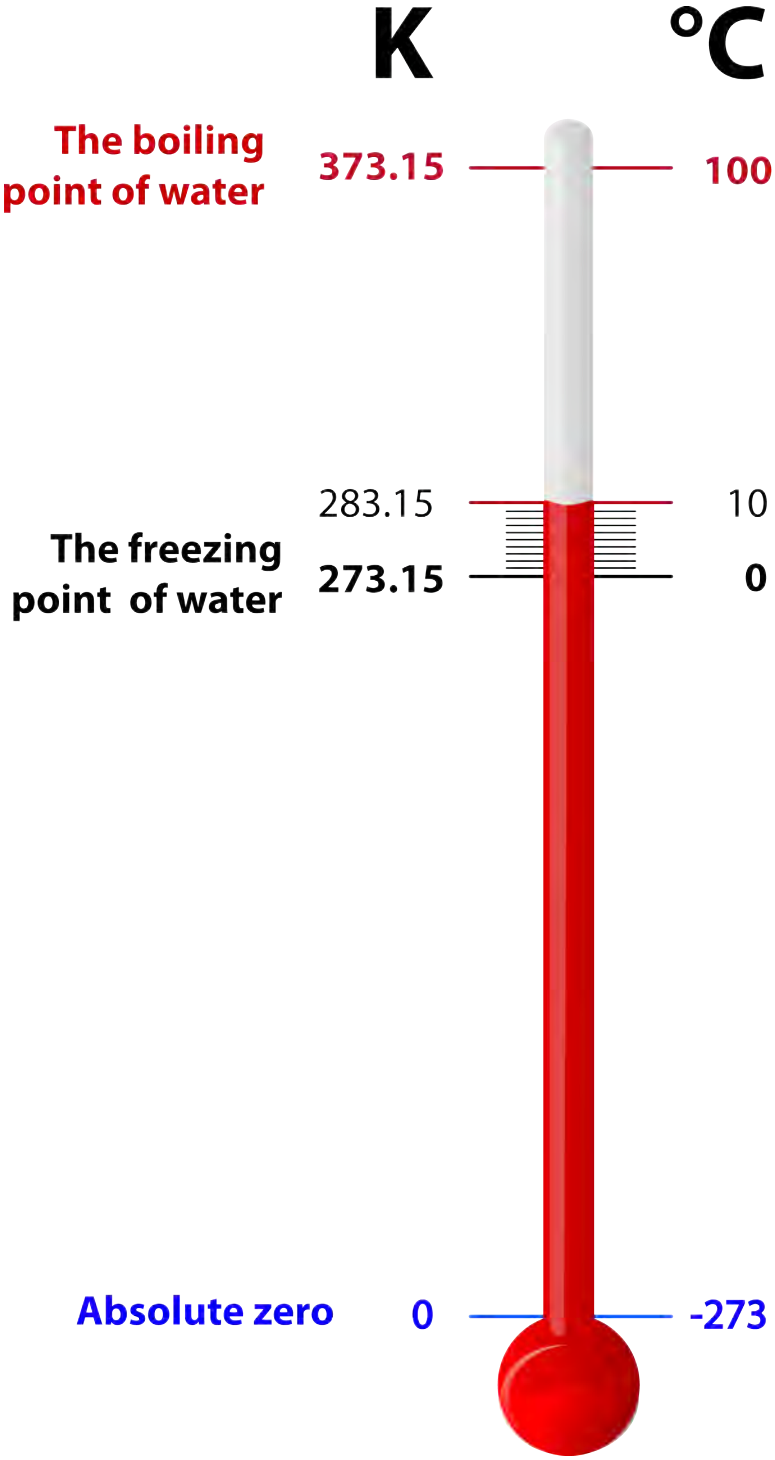


FIGURE 3.13

Comparison between Kelvin and Celsius temperature scales.

3.8 Scientific Dimensional Analysis

- Define dimensional analysis.
- Use dimensional analysis in solving problems.

Conversion Factors

Many quantities can be expressed in several different ways. The English system measurement of 4 cups is also equal to 2 pints, 1 quart, and $\frac{1}{4}$ of a gallon.

4 cups = 2 pints = 1 quart = 0.25 gallon

Notice that the numerical component of each quantity is different, while the actual amount of material that it represents is the same. That is because the units are different. We can establish the same set of equalities for the metric system:

1 meter = 10 decimeters = 100 centimeters = 100 millimeters

The metric system's use of powers of 10 for all conversions makes this quite simple.

Whenever two quantities are equal, a ratio can be written that is numerically equal to 1. Using the metric examples above:

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

The $\frac{1\text{ m}}{100\text{ cm}}$ is called a **conversion factor**. A conversion factor is a ratio of equivalent measurements. Because both 1 m and 100 cm represent the exact same length, the value of the conversion factor is 1. The conversion factor is read as "1 meter per 100 centimeters". Other conversion factors from the cup measurement example can be:

$$\frac{4\text{ cups}}{2\text{ pints}} = \frac{2\text{ pints}}{1\text{ quart}} = \frac{1\text{ quart}}{0.25\text{ gallon}} = 1$$

Since the numerator and denominator represent equal quantities in each case, all are valid conversion factors.

Scientific Dimensional Analysis

Conversion factors are used in solving problems in which a certain measurement must be expressed with 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 solve problems. Dimensional analysis is best illustrated with an example.

Sample Problem: Dimensional Analysis

How many seconds are in a day?

Step 1: List the known quantities and plan the problem.

Known

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

Unknown

- 1 day = ? seconds

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.

Step 2: Calculate

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

Applying the first conversion factor, the "d" unit cancels and 1 × 24 = 24. Applying the second conversion factor, the "h" unit cancels and 24 × 60 = 1440. Applying the third conversion factor, the "min" unit cancels and 1440 × 60 = 86,400. The unit that remains is "s" for seconds.

Step 3: Think about your result.

Seconds is a much smaller unit of time than a day, so it makes sense that there are a very large number of seconds in one day.

Summary

- A conversion factor is a ratio of equivalent measurements.
- Dimensional analysis is a technique that uses the units (dimensions) of the measurement in order to correctly solve problems.

Practice

Use the link below to answer the following questions:

http://www4.ncsu.edu/unity/lockers/users/f/felder/public/kenny/papers/units.html

1. What do we always need to express measurements correctly?
2. What does dimensional analysis tell you?
3. How do you know that you have set the problem up incorrectly?
4. How do you know that you have set the problem up correctly?

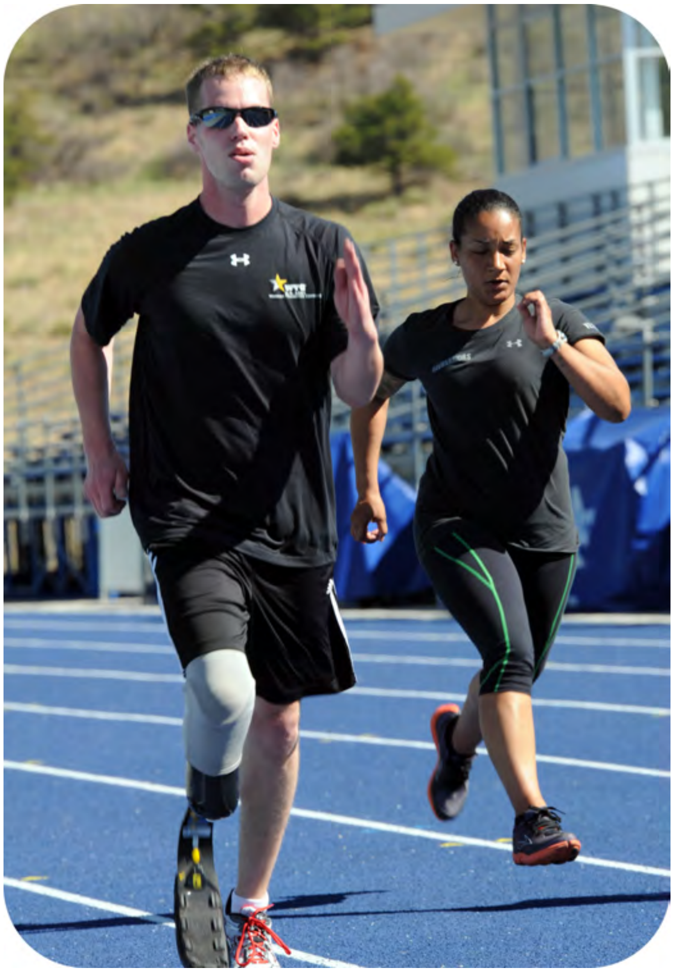
Review

1. What is a conversion factor?
2. What is dimensional analysis?
3. How many meters are in 3.7 km?
4. How many kg in 12980 g?

- **conversion factor:** A ratio of equivalent measurements.
- **dimensional analysis:** A technique that uses the units (dimensions) of the measurement in order to correctly solve problems.

3.9 Metric Unit Conversions

- Use dimensional analysis to carry out metric unit conversions.



You are training for a 10-kilometer run by doing laps on a 400-meter track. You ask yourself "How many times do I need to run around this track in order to cover ten kilometers?" (more than you realize). By using dimensional analysis, you can easily determine the number of laps needed to cover the 10 k distance.

Metric Unit Conversions

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.

Sample Problem: Metric Unit Conversions

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: List the known quantities and plan the problem.

Known

- 1 exp requires 120 mL
- 1 L = 1000 mL

Unknown

- L of solution for 40 exp

Since each experiment requires 120 ml of solution and the teacher needs to prepare enough for 40 experiments, multiply 120 by 40 to get 4800 mL of solution needed. Now you must convert ml to L by using a conversion factor.

Step 2: Calculate

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

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

Step 3: Think about your result.

A liter is much larger than a milliliter, so it makes sense that the number of liters required is less than the number of milliliters.

Two-Step Metric Unit Conversions

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.

Sample Problem 3.3: Two-Step Metric Conversion

Convert 4.3 cm to μm.

Step 1: List the known quantities and plan the problem.

Known

- 1 m = 100 cm
- 1 m = 10^6 μm

Unknown

- 4.3 cm = ? μm

You may need to consult a table for the multiplication factor represented by each metric prefix. First convert cm to m, followed by a conversion of m to μm.

Step 2: Calculate

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

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

Step 3: Think about your result.

A micrometer is a smaller unit of length than a centimeter, so the answer in micrometers is larger than the number of centimeters given.

Summary

- Dimensional analysis can be used to carry out metric unit conversions.

Practice

Use the link below to answer the following questions:

http://www.purplemath.com/modules/metric.htm

1. Why are metric units nice to work with?
2. What are the basic metric units?
3. To move to a smaller unit, which direction do you move the decimal?

Review

1. Perform the following conversions.
   (a) 0.074 km to m
   (b) 24,600 μg to g
   (c) 4.9×10^7 μg to kg
   (d) 84 dm to mm

- **unit conversion:** Conversion factors between different units of measurement for the same quantity.

3.10 Derived Units

- Define derived unit.
- Carry out unit conversions using derived units.

As farming becomes more expensive and less profitable (at least for small farms), many families will sell the land to builders who want to erect either commercial or residential properties. In order to sell, an accurate property tile is needed. The dimensions of the farm must be determined and the acreage calculated from those dimensions.

Dimensional Analysis and Derived Units

Some units are combinations of SI base units. A **derived unit** is a unit that results from a mathematical combination of SI base units. We have already discussed volume and energy as two examples of derived units. Some others are listed in the **Table** 3.4:

TABLE 3.4: **Derived SI Units**

Quantity	Symbol	Unit	Unit Abbreviation	Derivation
Area	A	square meter	m^2	length × width
Volume	V	cubic meter	m^3	length × width × height
Density	D	kilograms/cubic meter	kg/m^3	$\frac{\text{mass}}{\text{volume}}$
Concentration	c	moles/liter	mol/L	$\frac{\text{amount}}{\text{volume}}$
Speed (velocity)	v	meters/second	m/s	$\frac{\text{length}}{\text{time}}$
Acceleration	a	meters/second/second	m/s^2	$\frac{\text{speed}}{\text{time}}$

TABLE 3.4: (continued)

Force	F	newton	N	mass × acceleration
Energy	E	joule	J	force × length

Using dimensional analysis with derived units requires special care. When units are squared or cubed as with area or volume, the conversion factors themselves must also be squared. Shown below is the conversion factor for cubic centimeters and cubic meters.

$$\left(\frac{1\text{ m}}{100\text{ cm}}\right)^3 = \frac{1\text{ m}^3}{10^6\text{ cm}^3} = 1$$

Because a cube has 3 sides, each side is subject to the conversion of 1 m to 100 cm. Since 100 cubed is equal to 1 million (10^6), there are 10^6 cm^3 in 1 m^3. Two convenient volume units are the liter, which is equal to a cubic decimeter, and the milliliter, which is equal to a cubic centimeter. The conversion factor would be:

$$\left(\frac{1\text{ dm}}{10\text{ cm}}\right)^3 = \frac{1\text{ dm}^3}{1000\text{ cm}^3} = 1$$

There are thus 1000 cm^3 in 1 dm^3, which is the same thing as saying there are 1000 mL in 1 L

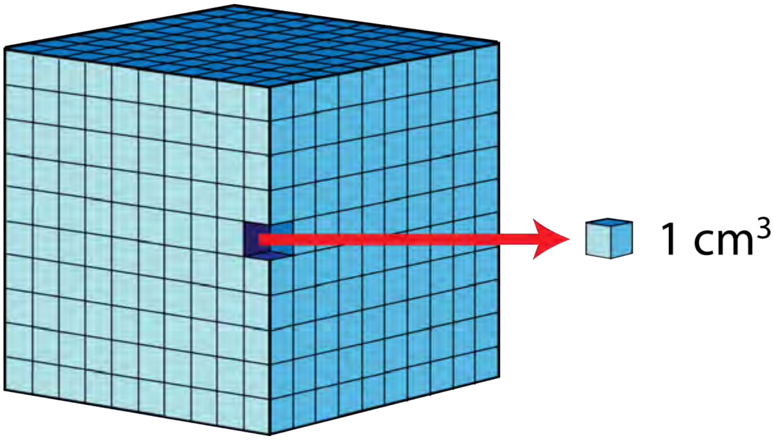


FIGURE 3.14

There are 1000 cm^3 in 1 dm^3. Since a cm^3 is equal to a mL and a dm^3 is equal to a L, we can say that there are 1000 mL in 1 L.

Sample Problem: Derived Unit Conversion

Convert 3.6×10^8 mm^3 to mL.

Step 1: List the known quantities and plan the problem.

Known

- 1 m = 1000 mm
- 1 ml = 1 cm^3
- 1 m = 100 cm

Unknown

- 3.6 mm^3 = ? mL

This problem requires multiple steps and the technique for converting with derived units. Simply proceed one step at a time: mm^3 to m^3 to cm^3 = mL.

Step 2: Calculate

$$3.6\ mm^3 \times \left(\frac{1\ m}{1000\ mm}\right)^3 \times \left(\frac{100\ cm}{1\ m}\right)^3 \times \frac{1\ mL}{1\ cm^3} = 0.0036\ mL$$

Numerically, the steps are to divide 3.6 by 10^9, followed by multiplying by 10^6. You may find that you can shorten the problem by a step by first determining the conversion factor from mm to cm and using that instead of first converting to m. There are 10 mm in 1 cm.

$$3.6\ \text{mm}^3 \times \left(\tfrac{1\ \text{cm}}{10\ \text{mm}}\right)^3 \times \tfrac{1\ \text{mL}}{1\ \text{cm}^3} = 0.0036\ \text{mL}$$

In this case 3.6 / 1000 gives the same result of 0.0036.

Step 3: Think about your result.

Cubic millimeters are much smaller than cubic centimeters, so the final answer is much less than the original number of mm^3.

Summary

- A derived unit is a unit that results from a mathematical combination of SI base units.
- Calculations involving derived units follow the same principles as other unit conversion calculations.

Practice

Use the link below to answer the following questions:

http://www.unc.edu/ rowlett/units/siderive.html

1. How many derived units are there?
2. Who established these units?
3. What derived unit gives rise to the definition of the watt?
4. What derived units are defined by the newton?

Review

1. What is a derived unit?
2. Convert 0.00722 km^2 to m^2
3. Convert 129 cm^3 to L
4. Convert 4.9×10^5 μm^3 to mm^3.

- **derived unit:** A unit that results from a mathematical combination of SI base units.

3.11 Density

- Define density.
- Use physical measurements to calculate density.
- Use density values to calculate mass or volume.

After trees are cut, logging companies often move these materials down a river to a sawmill where they can be shaped into building materials or other products. The logs float on the water because they are less dense than the water they are in. Knowledge of density is important in the characterization and separation of materials. Information about density allows us to make predictions about the behavior of matter.

Density

A golf ball and a table tennis ball are about the same size. However, the golf ball is much heavier than the table tennis ball. Now imagine a similar size ball made out of lead. That would be very heavy indeed! What are we comparing? By comparing the mass of an object relative to its size, we are studying a property called **density.** Density is the ratio of the mass of an object to its volume.

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

Density is an intensive property, meaning that it does not depend on the amount of material present in the sample. Water has a density of 1.0 g/mL. That density is the same whether you have a small glass of water or a swimming pool full of water. Density is a property that is constant for the particular identity of the matter being studied.

The SI units of density are kilograms per cubic meter (kg/m^3), since the kg and the m are the SI units for mass and length respectively. In everyday usage in a laboratory, this unit is awkwardly large. Most solids and liquids have densities that are conveniently expressed in grams per cubic centimeter (g/cm^3). Since a cubic centimeter is equal to a milliliter, density units can also be expressed as g/mL. Gases are much less dense than solids and liquids, so their densities are often reported in g/L. Densities of some common substances at 20°C are listed in the **Table** 3.5 .

TABLE 3.5: **Densities of Some Common Substances**

Liquids and Solids	**Density at 20°C (g/ml)**	**Gases**	**Density at 20°C (g/L)**
Ethanol	0.79	Hydrogen	0.084
Ice (0°C)	0.917	Helium	0.166
Corn oil	0.922	Air	1.20
Water	0.998	Oxygen	1.33
Water (4°C)	1.000	Carbon dioxide	1.83
Corn syrup	1.36	Radon	9.23
Aluminum	2.70		
Copper	8.92		
Lead	11.35		
Mercury	13.6		
Gold	19.3		

Since most materials expand as temperature increases, the density of a substance is temperature dependent and usually decreases as temperature increases.

You know that ice floats in water and it can be seen from the table that ice is less dense. Alternatively, corn syrup, being denser, would sink if placed into water.

Sample Problem: Density Calculations

An 18.2 g sample of zinc metal has a volume of 2.55 cm^3. Calculate the density of zinc.

Step 1: List the known quantities and plan the problem.

Known

- mass = 18.2 g
- volume = 2.55 cm^3

Unknown

- density = ? g/cm^3

Use the equation for density, $D = \frac{m}{V}$, to solve the problem.

Step 2: Calculate

$$D = \frac{m}{V} = \frac{18.2\ \text{g}}{2.55\ \text{cm}^3} = 7.14\ \text{g/cm}^3$$

Step 3: Think about your result.

If 1 cm^3 of zinc has a mass of about 7 grams, then 2 and a half cm^3 will have a mass about 2 and a half times as great. Metals are expected to have a density greater than that of water and zinc's density falls within the range of the other metals listed above

Since density values are known for many substances, density can be used to determine an unknown mass or an unknown volume. Dimensional analysis will be used to ensure that units cancel appropriately.

Sample Problem: Using Density to Determine Mass and Volume

1. What is the mass of 2.49 cm^3 of aluminum?
2. What is the volume of 50.0 g of aluminum?

Step 1: List the known quantities and plan the problem.

Known

- density = 2.70 g/cm^3
- 1. volume = 2.49 cm^3
- 2. mass = 50.0 g

Unknown

- 1. mass = ? g
- 2. volume = ? cm^3

Use the equation for density, $D = \frac{m}{V}$, and dimensional analysis to solve each problem.

Step 2: Calculate

1. $2.49 \text{ cm}^3 \times \frac{2.70 \text{ g}}{1 \text{ cm}^3} = 6.72 \text{ g}$
2. $50.0 \text{ g} \times \frac{1 \text{ cm}^3}{2.70 \text{ g}} = 18.5 \text{ cm}^3$

In problem 1, the mass is equal to the density multiplied by the volume. In problem 2, the volume is equal to the mass divided by the density.

Step 3: Think about your results.

Because a mass of 1 cm^3 of aluminum is 2.70 g, the mass of about 2.5 cm^3 should be about 2.5 times larger. The 50 g of aluminum is substantially more than its density, so that amount should occupy a relatively large volume.

Summary

- Density is the ratio of the mass of an object to its volume.
- Gases are less dense that either solids or liquids
- Both liquid and solid materials can have a variety of densities
- For liquids and gases, the temperature will affect the density to some extent.

Practice

You can perform a density experiment to identify a mystery object online. Find this simulation at http://phet.colorado.edu/en/simulation/density

Review

1. Define "density."

2. Are gases more or less dense that liquids or solids at room temperature?
3. How does temperature affect the density of a material?
4. A certain liquid sample has a volume of 14.7 mL and a mass of 22.8 grams. Calculate the density.
5. A material with a density of 2.7 grams/mL occupies 35.6 mL. How many grams of the material are there?
6. A certain material has a density of 19.3 g/mL. What is the material?

- **density:** The ratio of the mass of an object to its volume. Density $= \frac{\text{mass}}{\text{volume}}$. Density is an intensive property, meaning that it does not depend on the amount of material present in the sample.

3.12 Accuracy and Precision

- Define accuracy.
- Define precision.
- Describe situations with varying levels of accuracy and precision.

Basketball is one of those sports where you need to hit the target. A football field goal kicker might have room for some deviation from a straight line – for college and pro football there is an 18 foot 6 inch space for the ball to go through. In basketball, the basket is only 18 inches across and the ball is a little less than 10 inches across – not much room for error. The ball has to be on target in order to go into the basket and score.

Accuracy and Precision

In everyday speech, the terms **accuracy** and **precision** are frequently used interchangeably. However, their scientific meanings are quite different. Accuracy is a measure of how close a measurement is to the correct or accepted value of the quantity being measured. Precision is a measure of how close a series of measurements are to one another. Precise measurements are highly reproducible, even if the measurements are not near the correct value.

Darts thrown at a dartboard are helpful in illustrating accuracy and precision

Assume that three darts are thrown at the dartboard, with the bulls-eye representing the true, or accepted, value of what is being measured. A dart that hits the bulls-eye is highly accurate, whereas a dart that lands far away from the bulls-eye displays poor accuracy. The **Figure** 3.15 demonstrates four possible outcomes.

a. The darts have landed far from each other and far from the bulls-eye. This grouping demonstrates measurements that are neither accurate, nor precise.

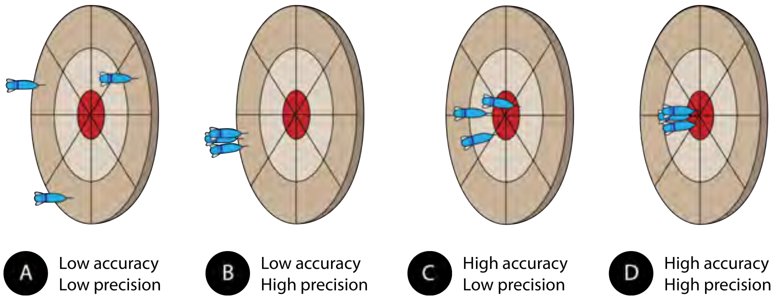


FIGURE 3.15
The distribution of darts on a dartboard shows the difference between accuracy and precision.

b. The darts are close to one another, but far from the bulls-eye. This grouping demonstrates measurements that are precise, but not accurate. In a laboratory situation, high precision with low accuracy often results from a systematic error. Either the measurer makes the same mistake repeatedly or the measuring tool is somehow flawed. A poorly calibrated balance may give the same mass reading every time, but it will be far from the true mass of the object.
c. The darts are not grouped very near to each other, but are generally centered around the bulls-eye. This demonstrates poor precision, but fairly high accuracy. This situation is not desirable in a lab situation because the "high" accuracy may simply be random chance and not a true indicator of good measuring skill.
d. The darts are grouped together and have hit the bulls-eye. This demonstrates high precision and high accuracy. Scientists always strive to maximize both in their measurements.

FIGURE 3.16
Students in a chemistry lab are making careful measurements with a series of volumetric flasks. Accuracy and precision are critical in every experiment.

Summary

- Accuracy is a measure of how close a measurement is to the correct or accepted value of the quantity being measured.
- Precision is a measure of how close a series of measurements are to one another.

Practice

Take the quiz at the link below:

http://www.quia.com/quiz/1863743.html?AP_rand=980502951

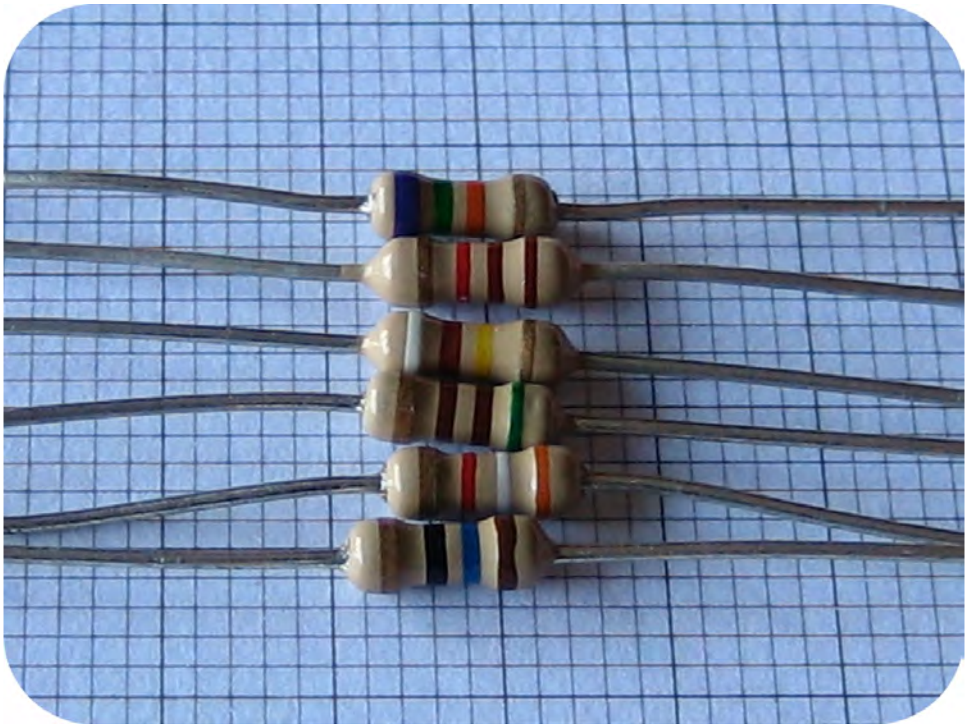
Review

1. Define accuracy.
2. Define precision.
3. What can be said about the reproducibility of precise values?

- **accuracy:** A measure of how close a measurement is to the correct or accepted value of the quantity being measured
- **precision:** A measure of how close a series of measurements are to one another. Precise measurements are highly reproducible, even if the measurements are not near the correct value.

3.13 Percent Error

- Define accepted value.
- Define experimental value.
- Define error and calculate the error given appropriate data.
- Define percent error and calculate the error given appropriate data.



A complicated piece of electronics equipment may contain several resistors whose role is to control the voltage and current in the electrical circuit. Too much current and the apparatus malfunctions. Too little current and the system simply does not perform. The resistors values are always given with an error range. A resistor may have a stated value of 200 ohms, but a 10% error range, meaning the resistance could be anywhere between 195-205 ohms. By knowing these values, an electronics person can design and service the equipment to make sure it functions properly.

Percent Error

An individual measurement may be accurate or inaccurate, depending on how close it is to the true value. Suppose that you are doing an experiment to determine the density of a sample of aluminum metal. The **accepted value** of a measurement is the true or correct value based on general agreement with a reliable reference. For aluminum the accepted density is 2.70 g/cm^3. The **experimental value** of a measurement is the value that is measured during the experiment. Suppose that in your experiment you determine an experimental value for the aluminum density to be 2.42 g/cm^3. The **error** of an experiment is the difference between the experimental and accepted values.

$$\text{Error} = \text{experimental value} - \text{accepted value}$$

If the experimental value is less than the accepted value, the error is negative. If the experimental value is larger than the accepted value, the error is positive. Often, error is reported as the absolute value of the difference in order to avoid the confusion of a negative error. The **percent error** is the absolute value of the error divided by the accepted value and multiplied by 100%.

$$\% \text{ Error} = \frac{|\text{experimental value} - \text{accepted value}|}{\text{accepted value}} \times 100\%$$

To calculate the percent error for the aluminum density measurement, we can substitute the given values of 2.45 g/cm^3 for the experimental value and 2.70 g/cm^3 for the accepted value.

$$\% \text{ Error} = \frac{|2.45 \text{ g/cm}^3 - 2.70 \text{ g/cm}^3|}{2.70 \text{ g/cm}^3} \times 100\% = 9.26\%$$

If the experimental value is equal to the accepted value, the percent error is equal to 0. As the accuracy of a measurement decreases, the percent error of that measurement rises.

Summary

- Definitions of accepted value and experimental value are given.
- Calculations of error and percent error are demonstrated.

Practice

Read the material at the link below and then do "Your Turn" questions to see how well you did.

http://www.mathsisfun.com/numbers/percentage-error.html

Review

1. Define accepted value.
2. Define experimental value
3. What happens as the accuracy of the measurement decreases?

- **accepted value:** The true or correct value based on general agreement with a reliable reference.
- **error:** The difference between the experimental and accepted values.
- **experimental value:** The value that is measured during the experiment.
- **percent error:** The absolute value of the error divided by the accepted value and multiplied by 100%.

3.14 Measurement Uncertainty

- Describe uncertainty in measurements.

After a bank robbery has been committed, police will ask witnesses to describe the robbers. They will usually get some answer such as "medium height." Others may say "between 5 foot 8 inches and 5 foot 10 inches." In both cases, there is a significant amount of uncertainty about the height of the criminals.

Measurement Uncertainty

Some error or **uncertainty** always exists in any measurement. The amount of uncertainty depends both upon the skill of the measurer and upon the quality of the measuring tool. While some balances are capable of measuring masses only to the nearest 0.1 g, other highly sensitive balances are capable of measuring to the nearest 0.001 g or even better. Many measuring tools such as rulers and graduated cylinders have small lines which need to be carefully read in order to make a measurement. The figure below shows two rulers making the same measurement of an object (indicated by the blue arrow).

With either ruler, it is clear that the length of the object is between 2 and 3 cm. The bottom ruler contains no millimeter markings. With that ruler, the tenths digit can be estimated and the length may be reported as 2.5 cm. However, another person may judge that the measurement is 2.4 cm or perhaps 2.6 cm. While the 2 is known for certain, the value of the tenths digit is uncertain.

The top ruler contains marks for tenths of a centimeter (millimeters). Now the same object may be measured as 2.55 cm. The measurer is capable of estimating the hundredths digit because he can be certain that the tenths digit is a 5. Again, another measurer may report the length to be 2.54 cm or 2.56 cm. In this case, there are two certain digits (the 2 and the 5), with the hundredths digit being uncertain. Clearly, the top ruler is a superior ruler for measuring lengths as precisely as possible.

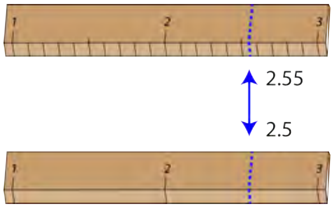


FIGURE 3.17

Uncertainty in measurement.

Summary

- Uncertainty exists in all measurements.
- The degree of uncertainty is affected in part by the quality of the measuring tool.

Practice

Read the material at the link below and answer the questions on the web site:

http://www2.southeastern.edu/Academics/Faculty/rallain/plab194/error.html

Review

1. What is uncertainty in measurements?
2. Why is the top ruler more reliable in measuring length than the bottom ruler?
3. How could the top ruler be made more accurate?

- **uncertainty:** lack of sureness about something.

3.15 Significant Figures

- Define significant figures.
- Use significant figure rules to express numerical values correctly.

As you enter the town of Jacinto City, Texas, the sign below tells you that the speed limit is 30 miles per hour. But what if you happen to be driving 31 miles an hour? Are you in trouble? Probably not, because there is a certain amount of leeway built into enforcing the regulation. Most speedometers do not measure the vehicle speed very accurately and could easily be off by a mile or so (on the other hand, radar measurements are much more accurate). So, a couple of miles/hour difference won't matter that much. Just don't try to stretch the limits any further unless you want a traffic ticket.

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 ruler illustration below, the bottom ruler gave a length with 2 significant figures, while the top ruler gave a length with 3 significant figures. In a correctly reported measurement, the final digit is significant but not certain. Insignificant digits are not reported. With either ruler, it would not be possible to report the length as 2.553 cm as there is no possible way that the thousandths digit could be estimated. The 3 is not significant and would not be reported.

When you look at a reported measurement, it is necessary to be able to count the number of significant figures. The table below 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.

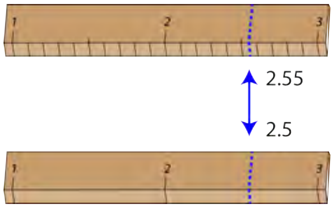


FIGURE 3.18

Measurement with two different rulers.

TABLE 3.6: 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 to say a certain digit is not significant does not mean that it is not important or 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. For a number with left-end zeros, such as 0.000416, it can be written as 4.16×10^{-4} with 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.

Summary

- Significant figures give an indication of the certainty of a measurement.
- Rules allow decisions to be made about how many digits to use in any given situation.

Practice

Take a quiz at the link below:

http://www.sciencegeek.net/APchemistry/APtaters/sigfigs.htm

Review

1. What does a significant figure tell us?
2. What is a left-end zero?
3. What is a right-end zero?
4. What does an insignificant zero do?

3.16 Rounding

- Learn and apply rules for rounding numbers.

People who fish often are a little unreliable when it comes to what they caught and how much it weighed. It's easier to say your fish weighed ten pounds than it is to describe accurately the weight of 8 pounds 11 ounces. Ten pounds is "close enough" when you are talking about fishing.

Rounding

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

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

TABLE 3.7:

Number of Significant Figures	Rounded Value	Reasoning
6	207.518	All digits are significant
5	207.52	8 rounds the 1 up to 2

TABLE 3.7: (continued)

4	207.5	2 is dropped
3	208	5 rounds the 7 up to 8
2	210	8 is replaced by a 0 and rounds the 0 upto 1
1	200	1 is replaced by a 0

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

Summary

- Rounding involves the adjustment of a value to account for the proper number of significant digits.
- Rules exist for rounding of numbers.

Practice

Practice rounding numbers using the following link:

http://www.mathscore.com/math/practice/Rounding%20Numbers/

Review

1. Why do we round numbers?
2. What do we need to know before we round a number?
3. What is "rounding up"?
4. What is "rounding down"?

- **round:** Adjust a value to reflect the actual number of significant figures.
- **rounding down:** Adjusting a value to less than the original value.
- **rounding up:** Adjusting a value to more than the original value.

3.17 Uncertainty in Multiplication and Division

- State the rule for rounding values obtained by multiplication or division.
- Apply the rule to appropriate problems.

Calculators do just what you ask of them, no more and no less. However, they sometimes can get a little out of hand. If I multiply 2.48 times 6.3, I get an answer of 15.687, a value that ignores the number of significant figures in either number. Division with a calculator is even worse. When I divide 12.2 by 1.7, the answer I obtain is 7.176470588. Neither piece of data is accurate to nine decimal places, but the calculator doesn't know that. The human being operating the instrument has to make the decision about how many places to report.

Uncertainty in Multiplication and Division

The density of a certain object is calculated by dividing the mass by the volume. Suppose that a mass of 37.46 g is divided by a volume of 12.7 cm^3. The result on a calculator would be:

$$D = \frac{m}{V} = \frac{37.46\text{ g}}{12.7\text{ cm}^3} = 2.949606299\text{ g/cm}^3$$

The value of the mass measurement has four significant figures, while the value of the volume measurement has only three significant figures. For multiplication and division problems, the answer should be rounded to the same number of significant figures as the measurement with the least number of significant figures. Applying this rule results in a density of 2.95 g/cm^3, for three significant figures – the same as the volume measurement.

Sample Problem: Significant Figures in Calculations

Perform the following calculations, rounding the answers to the appropriate number of significant figures.

A. $0.048 \text{ m} \times 32.97 \text{ m}$
B. $14,570 \text{ kg} \div 5.81 \text{ L}$

Step 1: Plan the problem.

Analyze each of the measured values to determine how many significant figures should be in the result. Perform the calculation and round appropriately. Apply the correct units to the answer. When multiplying or dividing, the units are also multiplied or divided.

Step 2: Calculate

A. $0.048 \text{ m} \times 32.97 \text{ m} = 1.6 \text{ m}^2$ Round to two significant figures because 0.048 has two.
B. $14,570 \text{ kg} \div 5.81 \text{ L} = 2510 \text{ kg/L}$ Round to three significant figures because 5.81 has three.

Summary

- For multiplication and division problems, the answer should be rounded to the same number of significant figures as the measurement with the least number of significant figures.

Practice

Read the information and work the problems on the following web site:

http://sigfigscalculator.appspot.com/tutorial/multiply_and_divide

Review

1. What is the basic principle involved in working with multiplication and division?
2. What happens to units in multiplication and division problems?

3.18 Uncertainty in Addition and Subtraction

- State the rule for rounding values obtained by addition or subtraction.
- Apply the rule to appropriate problems.

Calculators are great devices. They allow quick computation at work, school, or other places where manipulation of numbers needs to be done rapidly and accurately. But they are only as good as the numbers put into them. The calculator cannot determine how accurate each of a set of numbers is and the answer given on the screen must be assessed by the user for reliability.

Uncertainty in Addition and Subtraction

Consider two separate mass measurements: 16.7 g and 5.24 g. The first mass measurement (16.7 g) is known only to the tenths place or to one digit after the decimal point. There is no information about its hundredths place and so that digit cannot be assumed to be zero. The second measurement (5.24 g) is known to the hundredths place or to two digits after the decimal point.

When these masses are added together, the result on a calculator is 16.7 + 5.24 = 21.94 g. Reporting the answer as 21.94 g suggests that the sum is known all the way to the hundredths place. However that cannot be true because the hundredths place of the first mass was completely unknown. The calculated answer needs to be rounded in such a way as to reflect the certainty of each of the measured values that contributed to it. For addition and subtraction problems, the answer should be rounded to the same number of decimal places as the measurement with the least number of decimal places. The sum of the above masses would be properly rounded to a result of 21.9 g.

When working with whole numbers, pay attention to the last significant digit that is to the left of the decimal point and round your answer to that same point. For example, consider the subtraction: 78,500 m – 362 m. The calculated result is 78,138 m. However, the first measurement is known only to the hundreds place, as the 5 is the last significant digit. Rounding the result to that same point means that the correct result is 78,100 m.

Summary

- For addition and subtraction problems, the answer should be rounded to the same number of decimal places as the measurement with the least number of decimal places.

Practice

Read the information and work the problems on the following web site:

http://sigfigscalculator.appspot.com/tutorial/add_and_subtract

Review

1. What is the basic principle to use in working with addition and subtraction?
2. What do you pay attention to when working with whole numbers?

3.19 References

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CHAPTER 4 Atomic Structure

Chapter Outline

4.1 Democritus' Idea of the Atom

- Describe how the Greek philosophers approached nature.
- Describe the discussion about matter.
- Describe the contribution Democritus made to our understanding of matter.

People enjoy getting together to discuss things, whether it is how your favorite sports team is doing, what the best movie out is, politics, or any number of other topics. Often the question is raised about who is right and who is wrong. If the football game is to be played this coming weekend, all we can do is offer opinions. The game has not been played yet, so we don't know who will actually win.

The ancient Greek **philosophers** did a lot of discussing, with part of their conversations concerning the physical world and its composition. There were different opinions about what made up matter. Some felt one thing while others believed another set of ideas. Since these scholars did not have laboratories and had not developed the idea of the experiment, they were left with debate. Whoever could offer the best argument as considered right and often the best argument had little to do with reality.

One of the on-going debates had to do with sand. The question was: how small can you divide a grain of sand? The prevailing thought at the time, pushed by Aristotle, was that the grain of sand could be divided indefinitely, that you could always get a smaller particle by dividing a larger one and there was no limit to how small the resulting particle could be.

FIGURE 4.1

Since Aristotle was such an influential philosopher, very few people disagreed with him.

However, there were some philosophers who believed that there was a limit to how small a grain of sand could be divided. One of these philosophers was Democritus (460- 370 B.C.), often referred to as the "laughing philosopher" because of his emphasis on cheerfulness. He taught that there were substances called **atoms** and that these atoms made up all material things. The atoms were unchangeable, indestructible, and always existed.

The word "**atom**" comes from the Greek *atomos* and means "indivisible." The atomists of the time (and Democritus appeared to be one of the leading atomists) believed there were two realities that made up the physical world: atoms and void. There was an infinite number of atoms, but different types of atoms had different sizes and shapes. The void was the empty space in which the atoms moved and collided with one another. When these atoms collided with one another, they might repel each other or they might connect in clusters, held together by tiny hooks and barbs on the surface of the atoms.

Aristotle disagreed with Democritus and offered his own idea of the composition of matter. According to Aristotle, everything was composed of four elements: earth, air, fire, and water. The theory of Democritus explained things better, but Aristotle was more influential, so his ideas prevailed. We had to wait almost two thousand years before scientists came around to seeing the atom as Democritus did.

How Right was Democritus?

It is very interesting that Democritus had the basic idea of atoms, even though he had no experimental evidence to support his thinking. We know more now about how atoms hold together in "clusters" (compounds), but the basic concept was there over two thousand years ago. We also know that atoms can be further subdivided, but there is still a lower limit to how far we can break up that grain of sand.

Summary

- Greek philosophers debated about many things.
- Aristotle and others believed that a grain of sand could be divided indefinitely.
- Democritus believed there was a lower limit to the dividing of a grain of sand.

Practice

Use the link below to answer the following questions:

http://plato.stanford.edu/entries/democritus/

1. Who influenced the thinking of Democritus?
2. Who were the atomists?
3. How did Democritus explain how we saw objects?
4. What type of atom did Democritus believe the soul was composed of?

Review

1. How did the ancient Greek philosophers spend their time?
2. What approach did they not have for studying nature?
3. Who was the most influential philosopher of that time?
4. What was the major contribution Democritus made to the thinking of his day?
5. List characteristics of atoms according to Democritus.

- **philosopher:** People who do a lot of discussing and debate, with part of their conversations concerning the physical world and its composition.
- **atom:** The philosopher Democritus (460- 370 B.C.), taught that there were substances called atoms and that these atoms made up all material things. The atoms were unchangeable, indestructible, and always existed.

4.2 Conservation of Mass

- Define the law of conservation of mass.

The following situation happens all too often. You have taken apart a piece of equipment to clean it up. When you put the equipment back together, somehow you have an extra screw or two. Or you find out that a piece is missing that was a part of the original equipment. In either case, you know something is wrong. You expect to end up with the same amount of material that you started with, not with more or less than what you had originally.

Law of Conservation of Mass

By the late 1700s, chemists accepted the definition of an element as a substance that cannot be broken down into a simpler substance by ordinary chemical means. It was also clear that elements combine with one another to form more complex substances called compounds. The chemical and physical properties of these compounds are different than the properties of the elements from which they were formed. There were questions about the details of these processes.

In the 1790s, a greater emphasis began to be placed on the quantitative analysis of chemical reactions. Accurate and reproducible measurements of the masses of reacting elements and the compounds they form led to the formulation of several basic **laws**. One of these is called the law of **conservation of mass**, which states that during a chemical reaction, the total mass of the **products** must be equal to the total mass of the **reactants**. In other words, mass cannot be created or destroyed during a chemical reaction, but must always be conserved.

As an example, consider the reaction between silver nitrate and sodium chloride. These two compounds will dissolve in water to form silver chloride and sodium nitrate. The silver chloride does not dissolve in water, so it forms a solid that we can filter off. When we evaporate the water, we can recover the sodium nitrate formed. If we react 58.5 grams of sodium chloride with 169.9 grams of silver nitrate, we start with 228.4 grams of materials. After the reaction is complete and the materials separated, we find that we have formed 143.4 grams of silver chloride and 85.0 grams of sodium nitrate, giving us a total mass of 228.4 grams for the products. So, the total mass of reactants equals the total mass of products, a proof of the law of conservation of mass.

Watch a video demonstrating this idea at http://www.youtube.com/watch?v=J5hM1DxaPLw

MEDIA

Click image to the left for more content.

Summary

- The law of conservation of mass states that, during a chemical reaction, the total mass of the products must be equal to the total mass of the reactants.

Practice

Use the link below to answer the following questions:

https://www.etap.org/demo/grade8_science/lesson5/instruction1tutor.html

1. If you want to say something about chemical reactions, what would you use?
2. What does the Law of Conservation of Mass mean?
3. How much oxygen gas would I need if I react six molecules of hydrogen?
4. How many molecules of water would be formed?

Review

1. State the Law of Conservation of Mass.
2. What does this law mean?

- **law:** Accurate and reproducible measurements of the masses of reacting elements and the compounds they form led to the formulation of several basic laws.
- **conservation of mass:** States that during a chemical reaction, the total mass of the products must be equal to the total mass of the reactants.
- **reactant:** A substance that undergoes change in a chemical reaction.
- **product:** The result of a chemical reaction.

4.3 Law of Definite Proportions

- State the law of definite proportions.

We use electricity for many purposes, from cooking to powering our televisions to charging our cell phones. Wherever we travel in the United States, we want electricity to be available. What we also want (although we usually don't think about it) is for the electricity supply to be the same wherever we go. We want the same voltage (110 volts for the U.S.) to come from the outlet to whatever we plug in. If the voltage is less, the system will not work. If it is more, the equipment will be damaged. We want a definite amount of voltage – no more and no less.

Law of Definite Proportions

The discovery that mass was always conserved in chemical reactions was soon followed by the **law of definite proportions**, which states that a given chemical compound always contains the same elements in the exact same proportions by mass. As an example, any sample of pure water contains 11.19% hydrogen and 88.81% oxygen by mass. It does not matter where the sample of water came from or how it was prepared. Its composition, like that of every other compound, is fixed.

Another example is carbon dioxide. This gas is produced from a variety of reactions, often by the burning of materials. The structure of the gas consists of one atom of carbon and two atoms of oxygen. Carbon dioxide production is of interest in many areas, from the amount we breather out to the amount of the gas produced by burning wood or fossil fuels. By knowing the exact composition of carbon dioxide, we can make predictions as to the effects of different chemical processes.

Summary

- The law of definite proportions states that a given chemical compound always contains the same elements in the exact same proportions by mass.

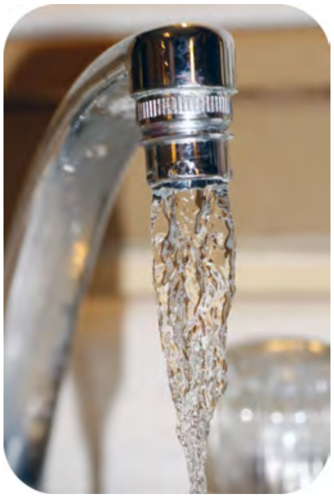


FIGURE 4.2

Water.

FIGURE 4.3

Carbon dioxide is produced during the burning process.

Practice

Watch the video (link below) and answer the questions:

http://www.youtube.com/watch?v=nvTB2cMbWU8

5.8a Law of Definite Proportions

MEDIA

Click image to the left for more content.

1. When was the law of definite proportions developed?
2. Who proposed this law?
3. How many hydrogen atoms are there in a molecule of water?

4. How many oxygen atoms are there in a molecule of water?

Review

1. State the law of definite proportions.
2. Will the composition of water vary depending on its source?
3. Why is this law important?

- **law of definite proportions:** States that a given chemical compound always contains the same elements in the exact same proportions by mass.

4.4 Law of Multiple Proportions

- Define the law of multiple proportions.

What are the similarities and differences between a unicycle and a bicycle?

Just from the words themselves, the astute Latin-speaking scholar can tell that, whatever it is made of, the unicycle has one of them (*uni* = "one") and the bicycle has two (*bi* = "two"). From the picture above, we get additional information that helps us tell the two apart. The unicycle has one wheel and the bicycle has two. Practically speaking they are made up of the same materials and the only significant difference is the number of wheels on the two vehicles. Now- how many wheels on a tricycle?

Law of Multiple Proportions

Once the idea that elements combined in definite proportions to form compounds was established, experiments also began to demonstrate that the same pairs of certain elements could combine to form more than one compound. Consider the elements carbon and oxygen. Combined in one way, they form the familiar compound called carbon dioxide. In every sample of carbon dioxide, there is 32.0 g of oxygen present for every 12.0 g of carbon. By dividing 32.0 by 12.0, this simplifies to a mass ratio of oxygen to carbon of 2.66 to 1. There is another compound that forms from the combination of carbon and oxygen called carbon monoxide. Every sample of carbon monoxide contains 16.0 g of oxygen for every 12.0 g of carbon. This is a mass ratio of oxygen to carbon of 1.33 to 1. In the carbon dioxide, there is exactly twice as much oxygen present as there is in the carbon monoxide. This example illustrates the **law of multiple proportions**: Whenever the same two elements form more than one compound, the different masses of one element that combine with the same mass of the other element are in the ratio of small whole numbers.

In carbon monoxide, on the left, there is 1.333 g of oxygen for every 1 g of carbon. In carbon dioxide, on the right, there is 2.666 g of oxygen for every gram of carbon. So the ratio of oxygen in the two compounds is 1:2, a small whole number ratio.

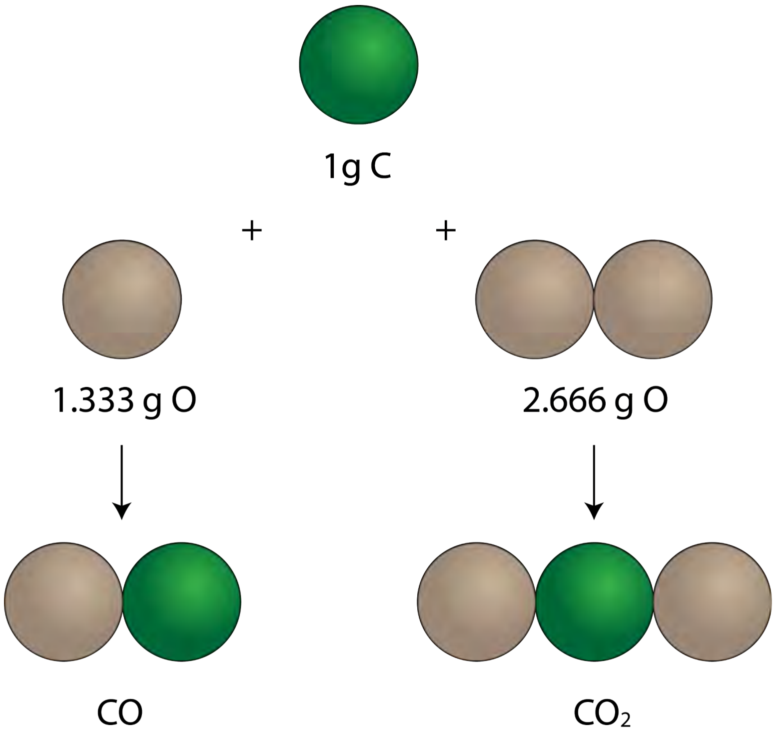


FIGURE 4.4

Carbon can form two different compounds with oxygen.

The difference between carbon monoxide and carbon dioxide is significant. Carbon monoxide is a deadly gas, formed from the incomplete combustion of some carbon-containing materials (such as wood and gasoline). This compound will attach to hemoglobin in the red blood cell and block the binding of oxygen to those cells. If oxygen does not bind, it cannot be carried to the cells of the body where it is needed and death can occur. Carbon dioxide, on the other hand, is not toxic like carbon monoxide is. However, it can displace oxygen in systems since it is heavier. Carbon dioxide fire extinguishers cut off the flow of oxygen in a fire, putting out the fire.

Summary

- The law of multiple proportions states that whenever the same two elements form more than one compound, the different masses of one element that combine with the same mass of the other element are in the ratio of small whole numbers.

Practice

Watch the video at the link below or read the transcript and answer the following questions:

http://www.brightstorm.com/science/chemistry/matter/law-of-definite-proportions-law-of-multiple-proportions/

1. What is the carbon:oxygen ratio in carbon monoxide?
2. What is the carbon:oxygen ratio in carbon dioxide?
3. What is the hydrogen:oxygen ratio in water?
4. What is the hydrogen:oxygen ratio in hydrogen peroxide?

Review

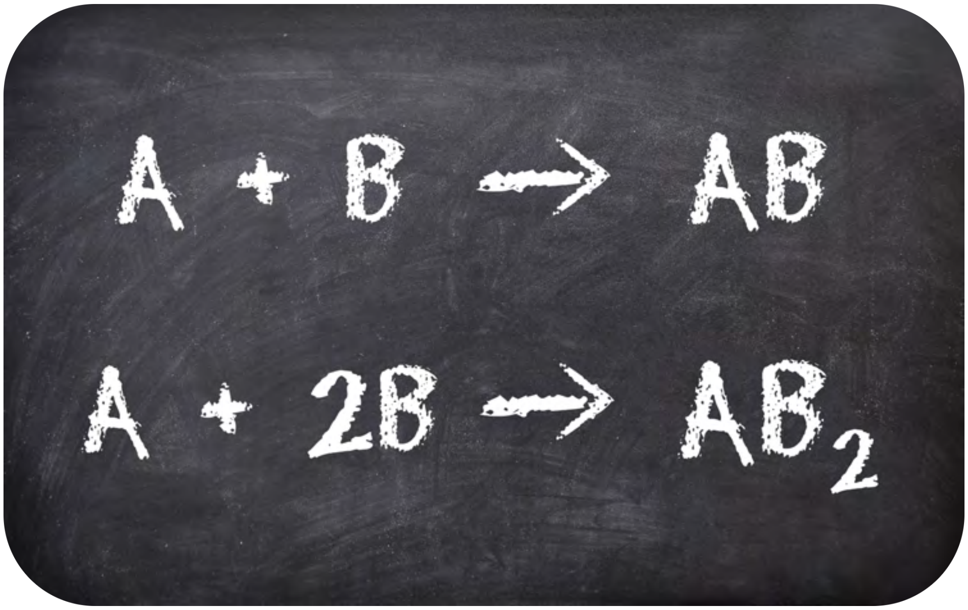
1. State the law of multiple proportions.

2. In carbon dioxide, how many grams of oxygen would there be if there are 24 grams of carbon?
3. How many grams of carbon would be present in carbon monoxide that contains 2.66 grams of oxygen?

- **law of multiple proportions:** Whenever the same two elements form more than one compound, the different masses of one element that combine with the same mass of the other element are in the ratio of small whole numbers.

4.5 Mass Ratio Calculation

- Define mass ratio.
- Calculate the mass ratio of an element in two different compounds.



One of the fundamental laws of chemistry deals with the fact that we cannot (using chemical means) create or destroy matter. When a reaction is run, the number of atoms of each specific kind must be the same on both sides of the equation. For some materials, it turns out that one element can combine with a second element in more than one ratio. Carrying out mass ratio calculations helped establish the law of multiple proportions.

Mass Ratio Calculations

Copper reacts with chlorine to form two compounds. Compound A consists of 4.08 g of copper for every 2.28 g of chlorine. Compound B consists of 7.53 g of copper for every 8.40 g of chlorine. What is the lowest whole number mass ratio of copper that combines with a given mass of chlorine?

Step 1: List the known quantities and plan the problem.

Known

Compound A = 4.08 g Cu and 2.28 g Cl

Compound B = 7.53 g Cu and 8.40 g Cl

Apply the law of multiple proportions to the two compounds. For each compound, find the grams of copper that combine with 1.00 g of chlorine by dividing the mass of copper by the mass of chlorine. Then find the ratio of the masses of copper in the two compounds by dividing the larger value by the smaller value.

Step 2: Calculate

Compound A $\frac{4.08 \text{ g Cu}}{2.28 \text{ g Cl}} = \frac{1.79 \text{ g Cu}}{1.00 \text{ g Cl}}$

Compound B $\frac{7.53 \text{ g Cu}}{8.40 \text{ g Cl}} = \frac{0.896 \text{ g Cu}}{1.00 \text{ g Cl}}$

Compare the masses of copper per gram of chlorine in the two samples.

$$\frac{1.79 \text{ g Cu (in compound A)}}{0.896 \text{ g Cu (in compound B)}} = \frac{2.00}{1} = 2:1$$

The mass ratio of copper per gram of chlorine in the two compounds is 2:1.

Step 3: Think about your result.

The ratio is a small whole-number ratio. For a given mass of chlorine, compound A contains twice the mass of copper as does compound B.

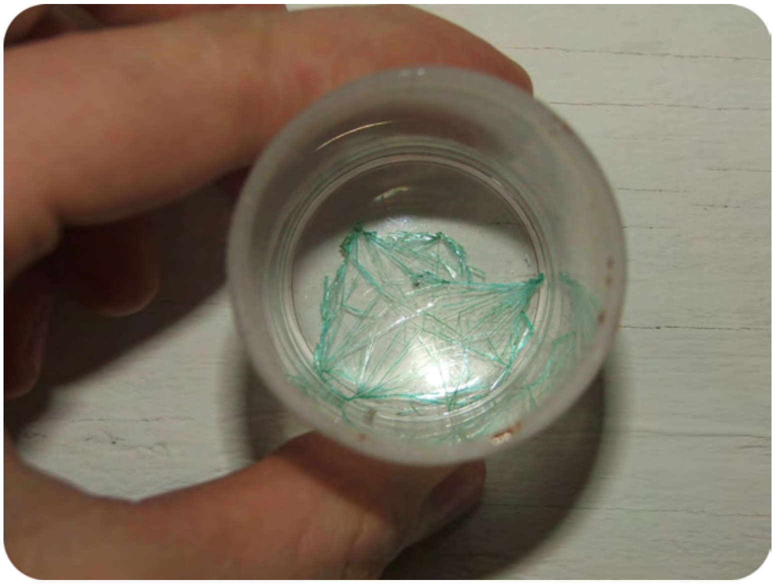


FIGURE 4.5

$CuCl_2$.

Summary

- The mass ratio gives the mass of an element that is found in combination with another element.

Practice

Use the link below to answer the following questions:

http://www.ehow.com/how_8326233_calculate-mass-ratio.html

1. What is the mass ratio?
2. What is the hydrogen:water mass ratio?
3. How many molecules of water per molecule of oxygen?

Review

1. What does the mass ratio tell us?
2. In the compound CH_4, what is the carbon:hydrogen mass ratio?
3. Methane is CH_4 and ethane is C_2H_6. What is the mass ratio of carbon per gram of hydrogen in the two compounds?

4.6 Dalton's Atomic Theory

- List the components of Dalton's atomic theory.

Pick a little, talk a little, pick a little, talk a little,

Cheep cheep cheep, talk a lot, pick a little more

These lyrics from the musical "Music Man" summed up the way science was done for centuries. OK, the lyrics referred to a group of gossiping ladies, but the outcome was the same. The Greek and Roman philosophers debated, discussed, and sometimes even attacked one another. But the mode of discovery was talk. There was no experimentation – the idea had not been thought of yet. So science did not develop very far and there was no reliable way to establish what was true and what was false.

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 the British scientist John Dalton. He started teaching school at age twelve, and was primarily known as a teacher. In his twenties, he moved to the growing city of Manchester, where he was able to pursue some scientific studies. His work in several areas of science brought him a number of honors. When he died, over 40,000 people in Manchester marched at his funeral.

Dalton studied the weights of various elements and compounds. He noticed that matter always combined in fixed ratios based on weight, or 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 could be more than one combination of two elements.

FIGURE 4.6

Dalton's Atomic Theory (1804)

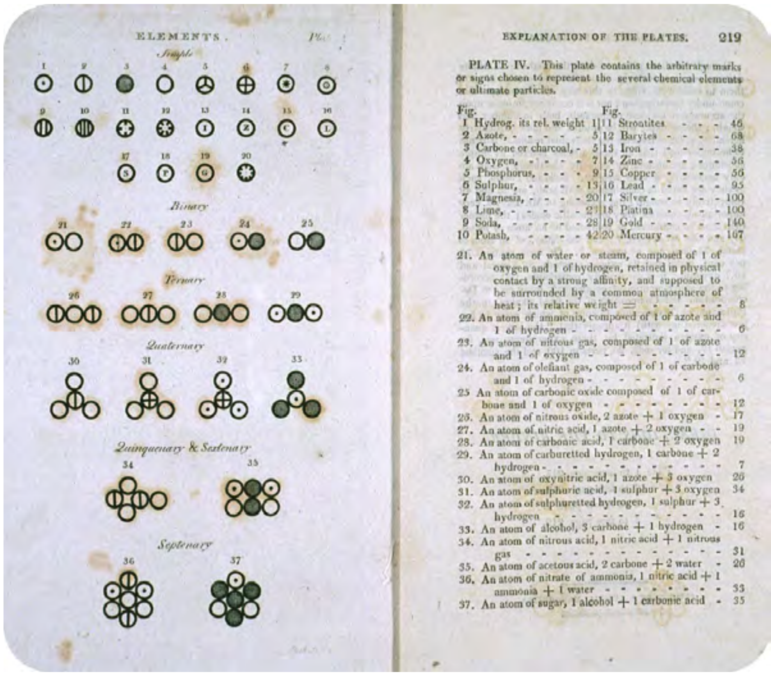
From his experiments and observations, as well as the work from peers of his time, Dalton proposed a new theory of the **atom**. This later became known as Dalton's **atomic theory**. The general tenets of this theory were as follows:

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

Dalton's atomic theory has been largely accepted by the scientific community, with the exception of three changes. We know now that (1) an atom can be further sub-divided, (2) all atoms of an element are not identical in mass, and (3) using nuclear fission and fusion techniques, we can create or destroy atoms by changing them into other atoms.

Summary

- Dalton proposed his atomic theory in 1804.
- The general tenets of this theory were as follows:
  - All matter is composed of extremely small particles called atoms.
  - Atoms of a given element are identical in size, mass, and other properties. Atoms of different elements differ in size, mass, and other properties.
  - Atoms cannot be subdivided, created, or destroyed.
  - Atoms of different elements can combine in simple whole number ratios to form chemical compounds.
  - In chemical reactions, atoms are combined, separated, or rearranged



EXPLANATION OF THE PLATES. 219

PLATE IV. This plate contains the arbitrary marks or signs chosen to represent the several chemical elements or ultimate particles.

Fig.			Fig.		
1	Hydrog. its rel. weight	1	11	Strontites	46
2	Azote,	5	12	Barytes	68
3	Carbone or charcoal,	5	13	Iron	38
4	Oxygen,	7	14	Zinc	56
5	Phosphorus,	9	15	Copper	56
6	Sulphur,	13	16	Lead	95
7	Magnesia,	20	17	Silver	100
8	Lime,	23	18	Platina	100
9	Soda,	28	19	Gold	140
10	Potash,	42	20	Mercury	167

21. An atom of water or steam, composed of 1 of oxygen and 1 of hydrogen, retained in physical contact by a strong affinity, and supposed to be surrounded by a common atmosphere of heat; its relative weight = - - - - - - 8
22. An atom of ammonia, composed of 1 of azote and 1 of hydrogen - - - - - - - - - - - - - 6
23. An atom of nitrous gas, composed of 1 of azote and 1 of oxygen - - - - - - - - - - - - 12
24. An atom of olefiant gas, composed of 1 of carbone and 1 of hydrogen - - - - - - - - - - - 6
25 An atom of carbonic oxide composed of 1 of carbone and 1 of oxygen - - - - - - - - - 12
26. An atom of nitrous oxide, 2 azote + 1 oxygen - 17
27. An atom of nitric acid, 1 azote + 2 oxygen - - 19
28. An atom of carbonic acid, 1 carbone + 2 oxygen 19
29. An atom of carburetted hydrogen, 1 carbone + 2 hydrogen - - - - - - - - - - - - - 7
30. An atom of oxynitric acid, 1 azote + 3 oxygen 26
31. An atom of sulphuric acid, 1 sulphur + 3 oxygen 34
32. An atom of sulphuretted hydrogen, 1 sulphur + 3 hydrogen - - - - - - - - - - - - - 16
33. An atom of alcohol, 3 carbone + 1 hydrogen - 16
34. An atom of nitrous acid, 1 nitric acid + 1 nitrous gas - - - - - - - - - - - - - - 31
35. An atom of acetous acid, 2 carbone + 2 water - 26
36. An atom of nitrate of ammonia, 1 nitric acid + 1 ammonia + 1 water - - - - - - - - 33
37. An atom of sugar, 1 alcohol + 1 carbonic acid - 35

FIGURE 4.7

Practice

Use the link below to do the exercise. Read the sections and take the quiz at the end.

http://antoine.frostburg.edu/chem/senese/101/atoms/dalton.shtml

Review

1. How did the Greek and Roman philosophers study nature?
2. When did John Dalton start teaching school?
3. Did Dalton believe that atoms could be created or destroyed?
4. List the basic components of Dalton's atomic theory.
5. What parts of the theory are not considered valid any more?

- **atom:** The smallest unit of an element.
- **atomic theory:** The general tenets of Dalton's atomic theory were as follows:
  - All matter is composed of extremely small particles called atoms.
  - Atoms of a given element are identical in size, mass, and other properties.
  - Atoms of different elements differ in size, mass, and other properties.
  - Atoms cannot be subdivided, created, or destroyed.
  - Atoms of different elements can combine in simple whole number ratios to form chemical compounds.
  - In chemical reactions, atoms are combined, separated, or rearranged

4.7 Cathode Ray Tube

- Describe how the Crooke's tube functioned.
- Describe experiments that showed that cathode rays had mass.

The TV set seen above is becoming harder and harder to find these days. The main reason is because they are older and based on outdated technology. The new TV sets are flat screen technology that take up less space and give better picture quality, especially with the advent of high-definition broadcasting. The technology used in the older TV sets used cathode ray tubes. A beam of electrons was sprayed to a picture tube which was treated to react with the electrons to produce an image. Similar CRT devices were used in computer monitors, now also replaced by flat screen monitors.

Discovery of the Electron

The first discovery of a subatomic particle was a result of experiments into the nature of the relationship between electricity and matter.

Cathode Rays

The first **cathode ray tube** prototype was developed by Heinrich Geissler, a German glassblower and physicist. He used a mercury pump to create a vacuum in a tube. Geissler explored a number of techniques to remove air from the tube and to prevent leaks, as well as ways to get good connections of the wires in the tubes.

In 1878, Sir William **Crookes**, a British scientist, displayed the first cathode rays using a modification of the Geissler apparatus. His major contribution to construction of the tube was to develop ways to evacuate almost all the air from the tube. Crookes also carried out many experiments using more reliable equipment to confirm earlier finding about the properties of cathode rays. He discovered two things which supported the hypothesis that the cathode ray consisted of a stream of particles:

- When an object was placed between the cathode and the opposite end of the tube, it cast a shadow on the glass. The shadow caused by the object indicates that particles were being blocked on their way from the cathode to the anode.

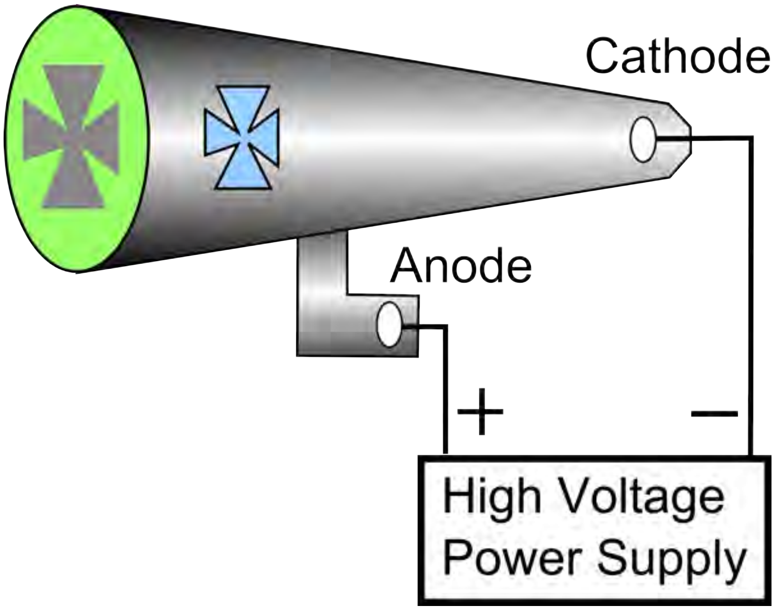


FIGURE 4.8

- A cathode ray tube was constructed with a small metal rail between the two electrodes. Attached to the rail was a paddle wheel capable of rotating along the rail. Upon starting up the cathode ray tube, the wheel rotated from the cathode towards the anode. Notice that the cathode and anode are positioned so that the rays will strike the top of the paddle wheel. Crookes concluded that the cathode ray was made of particles which must have mass.

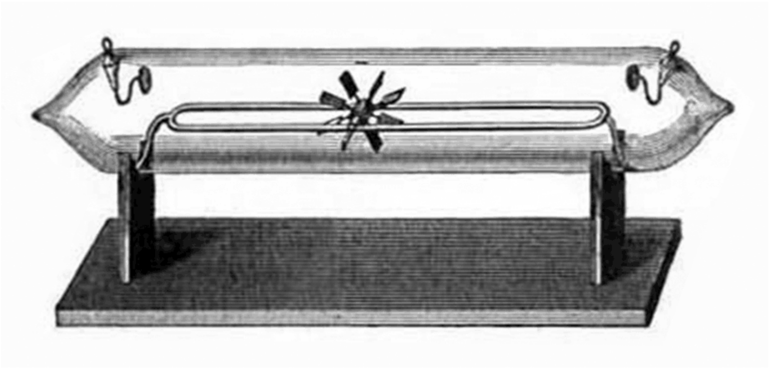


FIGURE 4.9

Further Research with the Crookes Tube

Crookes' work opened the door to a number of important discoveries. Other scientists were able to demonstrate that the "cathode ray" was actually a stream of **electrons**. In 1897, Karl Ferdinand Braun developed the first oscilloscope, using a cathode ray tube to see an electrical pulse as it passed through the instrument. The invention of television would not have been possible without the cathode ray tube. Work with a modified system led to the discovery of X-rays in 1895 by the German physicist Wilhelm Roentgen. This simple device has led to major advances in science and technology.

Summary

- The cathode ray tube was first invented by Sir William Crookes.
- Experiments showed that the rays had mass.

Practice

Use the link below to answer the following questions:

http://www.madehow.com/inventorbios/92/William-Crookes.html

1. What did Crookes start to study in college?
2. Who changed his mind and what did he then focus on?
3. What element did Crookes discover?
4. What did Crookes think was happening in the tube?

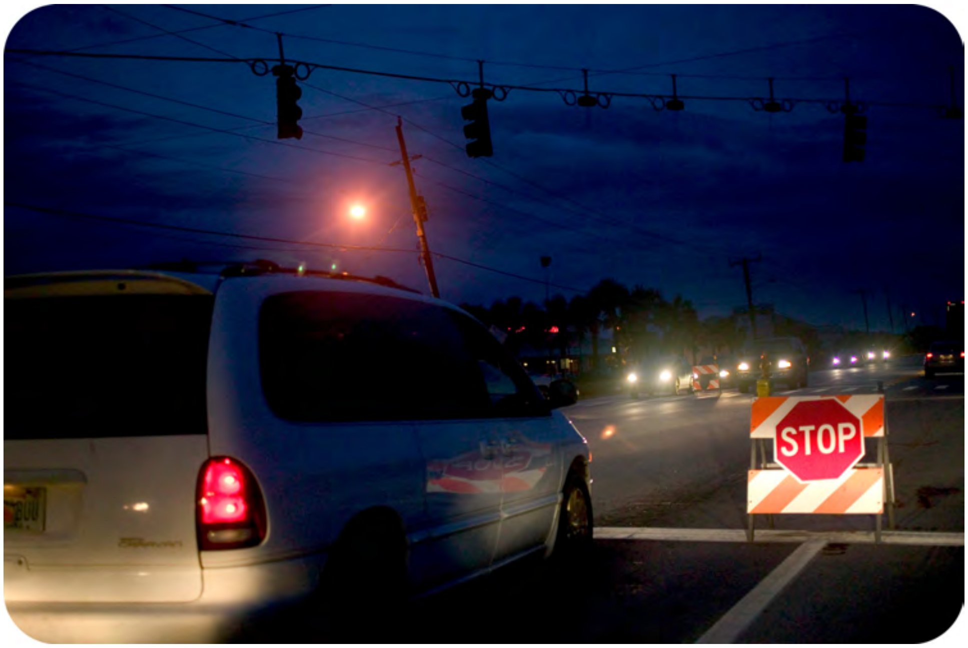
Review

1. Who developed the first cathode ray tube?
2. What improvement did Crookes make to the cathode ray tube?
3. How did Crookes show there were particles being emitted?
4. What did Karl Ferdinand Braun invent?
5. What did Wilhelm Roentgen invent?

- **Crookes:** In 1878, Sir William Crookes, a British scientist, displayed the first cathode rays using a modification of the Geissler apparatus. His major contribution to construction of the tube was to develop ways to evacuate almost all the air from the tube.
- **cathode ray:** A stream of electrons.
- **electron:** A subatomic particle with a negative charge.

4.8 Electrons

- Describe evidence from cathode ray tube experiments that demonstrate properties of the electron.



In a power outage all your electrical equipment suddenly stops working. The radio was on just a minute ago and now it is silent. What happened? Somewhere between a power generator and your electrical device was an interruption. Power stopped flowing through the wires and into your radio. That "power" turns out to be electrons that move through the wires and cause an electrical current to flow.

Is There Anything Inside an Atom?

As the nineteenth century began to draw to a close, the concept of atoms was well-established. We could determine the mass of different atoms and had some good ideas about the atomic composition of many compounds. Dalton's atomic theory held that atoms were indivisible, so scientists did not ask questions about what was inside the atom – it was solid and could not be broken down further. But then things began to change.

The Electron

In 1897, English physicist J.J. Thomson (1856-1940) experimented with a device called a cathode ray tube, in which an electric current was passed through gases at low pressure. A cathode ray tube consists of a sealed glass tube fitted at both ends with metal disks called electrodes. The electrodes were then connected to a source of electricity. One electrode, called the **anode**, becomes positively charged while the other electrode, called the **cathode**, becomes negatively charged. A glowing beam (the cathode ray) traveled from the cathode to the anode.

Earlier investigations by Sir William Crookes and others had been carried out to determine the nature of the cathode ray. Thomson modified and extended these experiments in an effort to learn about these mysterious rays. He discovered two things, which supported the hypothesis that the cathode ray consisted of a stream of particles.

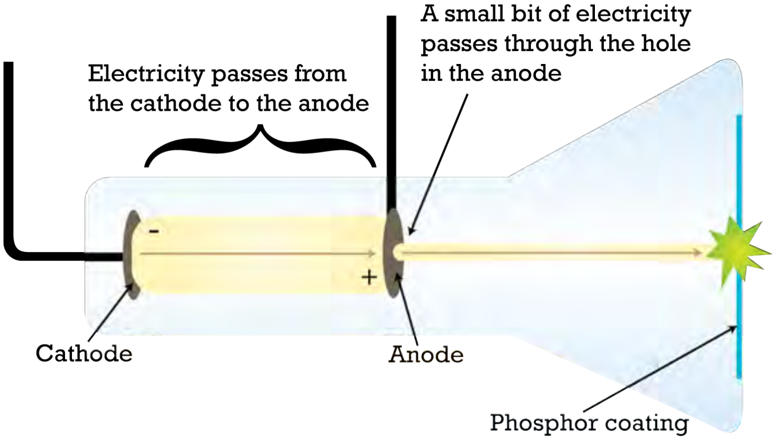
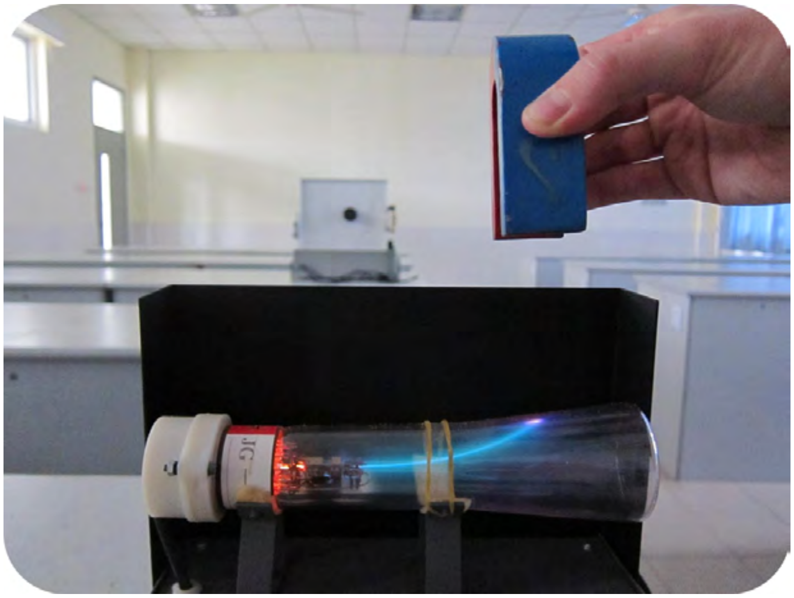


FIGURE 4.10

- When an object was placed between the cathode and the opposite end of the tube, it cast a shadow on the glass.
- A cathode ray tube was constructed with a small metal rail between the two electrodes. Attached to the rail was a paddle wheel capable of rotating along the rail. Upon starting up the cathode ray tube, the wheel rotated from the cathode towards the anode. This proved that the cathode ray was made of particles which must have mass. Crooke had first observed this phenomenon and attributed it to pressure by these particles on the wheel. Thomson correctly surmised that these particles were producing heat, which caused the wheel to turn.

In order to determine if the cathode ray consisted of charged particles, Thomson used magnets and charged plates to deflect the cathode ray. He observed that cathode rays were deflected by a **magnetic field** in the same manner as a wire carrying an electric current, which was known to be negatively charged. In addition, the cathode ray was deflected away from a negatively charged metal plate and towards a positively charged plate.



Thomson knew that opposite charges attract one another, while like charges repel one another. Together, the results of the cathode ray tube experiments showed that cathode rays are actually streams of tiny negatively charged particles moving at very high speeds. While Thomson originally called these particles corpuscles, they were later named electrons.

Thomson conducted further experiments, which allowed him to calculate the charge-to-mass ratio $\left(\frac{e}{m_e}\right)$ of the electron. In units of coulombs to grams, this value is 1.8×10^8 Coulombs/gram. He found that this value was a constant and did not depend on the gas used in the cathode ray tube or on the metal used as the electrodes. He concluded that electrons were negatively charged subatomic particles present in atoms of all elements.

Watch a video of a cathode ray tube experiment:

www.dlt.ncssm.edu/core/Chapter3-Atomic_Str_Part1/cathode-rm-lg.htm.

Summary

- Cathode rays are deflected by a magnetic field.
- The rays are deflected away from a negatively charged electrical field and toward a positively charge field.
- The charge/mass ratio for the electron is 1.8×10^8 Coulombs/gram.

Practice

Use the link below to answer the following questions:

http://www.nobelprize.org/nobel_prizes/physics/laureates/1906/thomson-bio.html

1. How old was Thomson when he enrolled in college?
2. What was his academic position at Cambridge?
3. Where and when did he announce his discovery of the electron?
4. What was he awarded in 1906?

Review

1. What is electric power made up of?
2. Whose work did Thomson repeat and revise?
3. What experiment did Thomson perform that showed cathode rays to be particles?
4. How did he show that these particles had a charge on them?
5. Was the charge positive or negative?

- **anode:** Positively charged electrode, when electric current runs through a cathode ray tube.
- **cathode:** Negatively charged electrode, when electric current runs through a cathode ray tube.
- **magnetic field:** An area where magnetism acts. It deflects cathode rays.

4.9 Oil Drop Experiment

- Describe the oil drop experiment.

How tall are you? How much do you weigh? Questions like these are easy to answer because we have the tools to make the measurements. A yard stick or tape measure will suffice to measure height. You can stand on a bathroom scale and determine your weight.

But it is a very different matter to measure things we cannot see with the naked eye. If we want to measure the size of a germ, we have to use a microscope. To learn the size of a single molecule, we have to use even more sophisticated instruments. So how would we measure something even smaller than a molecule, even smaller than an atom?

Charge and Mass of the Electron

The man who measured properties of the **electron** was Robert Millikan (1868-1953). He taught physics to himself while a student at Oberlin College since there was nobody on the faculty to instruct him in this field. Postgraduate research training was both in the U.S. and in Germany. His studies on the properties of the electron proved to be of great value in many areas of physics and chemistry.

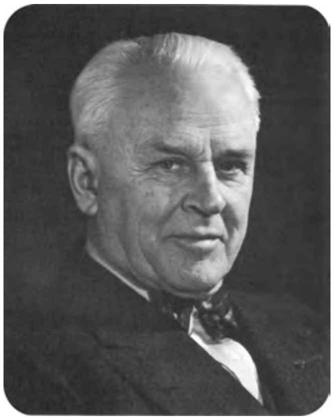


FIGURE 4.11

Oil Drop Experiment

Millikan carried out a series of experiments between 1908 and 1917 that allowed him to determine the charge of a single electron. Millikan's experiment was called the oil drop

He sprayed tiny drops of oil into a chamber. In his first experiment, he simply measured how fast the drops fell under the force of gravity. He could then calculate the mass of the individual drops. The he sprayed oil drops and applied an electrical charge to then by shining X-rays up through the bottom of the apparatus. The X-rays ionized the air, causing electrons to attach to the oil drops. The oil drops picked up static charge and were suspended between two charged plates. Millikan was able to observe the motion of the oil drops with a microscope and found that the drops lined up in a specific way between the plates, based on the number of electric charges they had acquired.

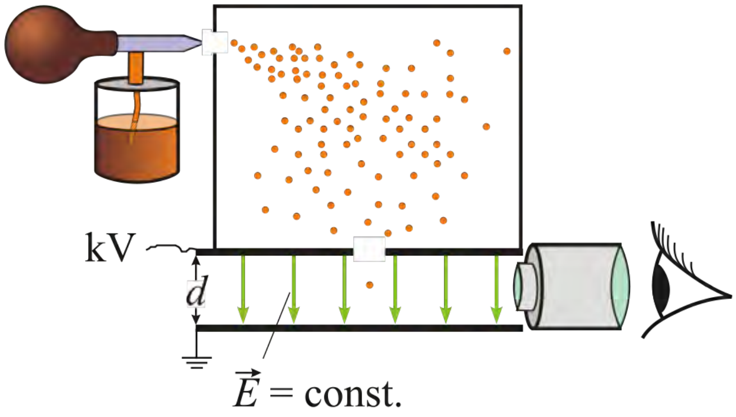


FIGURE 4.12

Millikan used the information to calculate the charge of an electron. He determined the charge to be 1.5924×10^{-19} C, where C stands for **coulomb**, which is one ampere/second. Today the accepted value of the charge of an electron is $1.602176487 \times 10^{-19}$ C. Millikan's value was within 1% of the currently accepted value. Millikan later used the information from his oil drop experiment to calculate the mass of an electron. The accepted value today is $9.10938215 \times 10^{-31}$ kg. The incredibly small mass of the electron was found to be approximately 1/1840 the mass of a hydrogen atom. Therefore, scientists realized that atoms must contain another particle that carries a positive charge and is far more massive than the electron.

Participate in a simulation of Millikan's oil drop experiment at this site: http://www.dlt.ncssm.edu/core/Chapter3-Atomic_Str_Part1/Chapter3-Animations/OilDrop.htm

Summary

- The oil drop experiment allowed Millikan to determine the charge on the electron.
- He later used this data to determine the mass of the electron.

Practice

Use the link below to answer the following questions:

http://www.aip.org/history/gap/Millikan/Millikan.html

1. Why did he take a position at Chicago?
2. How did he first make his mark at Chicago?
3. Was he happy with his situation? Explain your answer.
4. Why did Millikan use oil drops instead of water?
5. What other contributions did Millikan make to science?

Review

1. How did Millikan learn physics in college?
2. What did Millikan use to pick up static charge?
3. Where did the oil drops go to be measured?

- **coulomb:** C is short for coulomb, which is one ampere/second.

- **electron:** A subatomic particle with a negative charge.

4.10 Protons

- Describe Goldstein's research that led to the discovery of the proton.

Describing what we can see is a fairly easy matter. If we are asked to describe the sports car illustrated below, we could all quickly come up with a fairly accurate description. A person knowledgeable about cars would include more details, but everyone would have the basic information in their description.

What makes the description easy to come up with? We can see it, we have a common language to describe it (size, color, construction), and we have a basic idea of what it is (a car, not a house or a tree). Scientists have far more difficulty in describing things they cannot see. There is no way to look directly at an atom to see its detailed structure. When we first make a discovery, there is often no language to use to tell others exactly what it is. This was the problem in talking about the atom and its make-up.

Putting the Puzzle Pieces Together

Research builds upon itself – one piece connects to another. Sometimes the puzzle doesn't seem to make sense because some of the pieces are missing at the moment. Each finding gives a clearer picture of the whole and also raises new questions. The detective work that led to the discovery of the proton was built upon finding pieces to the puzzle and putting them together in the right way.

The electron was discovered using a cathode ray tube. An electric current was passed from the **cathode** (the negative pole) to the anode (positive pole). Several experiments showed that particles were emitted at the cathode and that these particles had a negative charge. These experiments demonstrated the presence of electrons.

If cathode rays are electrons that are given off by the metal atoms of the cathode, then what remains of the atoms that have lost those electrons? We know several basic things about electrical charges. They are carried by particles of matter. Millikan's experiment showed that they exist as whole-number multiples of a single basic unit. Atoms

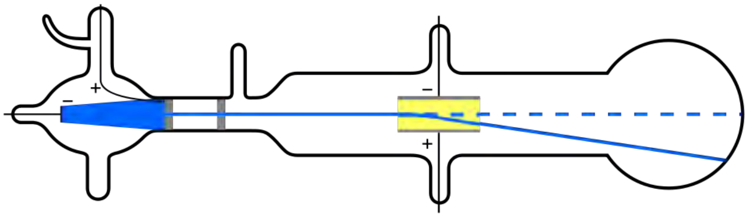


FIGURE 4.13

have no overall electrical charge, meaning that each and every atom contains an exactly equal number of positively and negatively charged particles. A hydrogen atom is the simplest kind of atom with only one electron. When that electron is removed, a positively charged particle should remain.

Discovery of the Proton

In 1886 Eugene Goldstein (1850-1930) discovered evidence for the existence of this positively charged particle. Using a cathode ray tube with holes in the cathode, he noticed that there were rays traveling in the opposite direction from the cathode rays. He called these **canal rays** and showed that they were composed of positively charged particles. The **proton** is the positively charged subatomic particle present in all atoms. The mass of the proton is about 1840 times the mass of the electron.

Summary

- When an electron is removed from a hydrogen atom, a proton remains.
- Goldstein observed rays travelling in the opposite direction of the cathode rays in a cathode ray tube.
- He demonstrated that these rays were positive particles and called the canal rays.

Practice

Use the link below to answer the following questions:

www.crtsite.com/page7-2.html

1. What color is produced by electrons in the cathode ray tube?
2. What color is produced by protons in the cathode ray tube?
3. Could the "canal rays" be deflected by a magnetic field?

Review

1. Why is it easy to describe things we can see?
2. What are some problems in describing new ideas in science?
3. Why did researchers believe that the particle left after electrons were emitted had to be positive?
4. How do we know the proton has a positive charge?
5. How many electrons does it take to weight the same as one proton?

- **canal ray:** Using a cathode ray tube with holes in the cathode, he noticed that there were rays traveling in the opposite direction from the cathode rays. Eugene Goldstein (1850-1930) called these canal rays and showed that they were composed of positively charged particles.
- **cathode:** Negatively charged electrode, when electric current runs through a cathode ray tube.

- **proton:** The positively charged subatomic particle present in all atoms.

4.11 Neutrons

- Describe research findings that led to the discovery of the neutron.
- Describe uses for neutrons.

The most famous detective in history and literature never existed. Sherlock Holmes was the creation of the British author Sir Arthur Conan Doyle. This mythical person had capabilities far beyond those of mere mortals. Holmes was capable of spotting the tiniest clue, the smallest piece of evidence to solve the crime. He could link all sorts of seemingly irrelevant data into a coherent whole to clear up whatever mystery he was dealing with.

The Quest for the Neutron

Clues are generally considered to involve the presence of something – a footprint, a piece of fabric, a bloodstain, something tangible that we can measure directly. The discoveries of the electron and the proton were accomplished by those kinds of clues. Cathode ray tube experiments showed both the electrons emitted by the cathode with their negative charge that could be measured and the proton (also emitted by the cathode) with its positive charge. The **neutron** initially was found not by a direct observation, but by noting what was not found.

Research had shown the properties of the electron and the proton. Scientists learned that approximately 1837 electrons weighted the same as one proton. There was evidence to suggest that electrons went around the heavy nucleus composed of protons. Charge was balanced with equal numbers of electrons and protons making up an electrically neutral atom. But there was a problem with this model – the atomic number (number of protons) did not match the atomic weight. In fact, the atomic number was usually about half the atomic weight. Therefore, something else must be present. That something must weigh about the same as a proton, but could not have a charge – this new particle had to be electrically neutral.

In 1920 Ernest Rutherford tried to explain this phenomenon. He proposed that the "extra" particles were combinations of protons and electrons in the nucleus. These new particles would have a mass very similar to a proton, but would be electrically neutral since the positive charge of the proton and the negative charge of the electron would cancel each other out.

In 1930 German researchers bombarded the element beryllium with alpha particles (helium nuclei containing two protons and two neutrons with a charge of +2). The particles produced in this process had strong penetrating power, which suggested they were fairly large. In addition, they were not affected by a magnetic field, so they were electrically neutral. The French husband-wife research team of Frederic and Irene Joliot-Curie used these new "rays" to bombard paraffin, which was rich in protons. The unknown particles produced a large emission of protons from the paraffin.

The English physicist James Chadwick (1891-1974) repeated these experiments and studied the energy of these particles. By measuring velocities, he was able to show that the new particle has essentially the same mass as a proton. So we now have a third subatomic particle with a mass equal to that of a proton, but with no charge. This particle was called the neutron. Chadwick won the Nobel Prize in Physics in 1935 for his research.

Neutron Applications

Neutrons can be used in a variety of ways. One important use is in nuclear **fission** to produce new isotopes. A neutron will collide with a large atom (such as uranium) and cause it to split into smaller atoms.

Nuclear reactors utilize **chain reactions** involving neutrons to heat water to drive turbines for the generation of electricity. When a neutron collides with a large atom, the atom splits with the release of more neutrons and also a large amount of energy. The energy converts water to steam for the turbine, while the neutrons serve to continue the chain reaction.

Summary

- Rutherford proposed that "extra" particles in nucleus were combinations of protons and electrons.
- Bombardment of beryllium with alpha particles produced large, neutral particles.
- Chadwick determined the mass of the neutron.
- Nuclear fission produces new elements.
- Nuclear reactors use chain reactions to produce heat.

Practice

Use the link below to answer the following questions:

http://www-outreach.phy.cam.ac.uk/camphy/neutron/neutron2_1.htm

1. When did Rutherford first propose the existence of the neutron?
2. Why are protons poorly penetrating?
3. Who did Chadwick do research with?
4. Why did the Curies believe that gamma rays were not responsible for proton release?
5. How did Chadwick detect the production of protons?

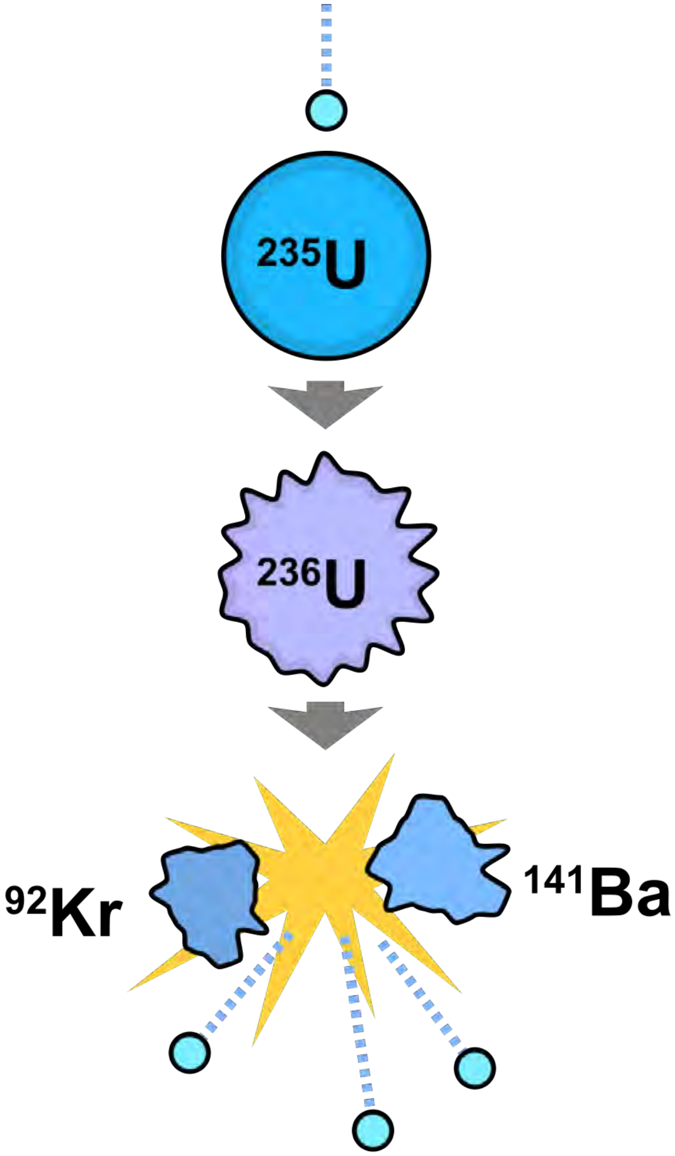


FIGURE 4.14

Review

1. What is a clue?
2. What clues suggested the existence of the neutron?
3. How did Rutherford try to explain the differences between the number of protons in the nucleus and the atomic weight?
4. What did German researchers find when they bombarded beryllium with alpha particles?
5. Describe the research of the Curies.
6. How did Chadwick determine these new particle were about the same size as the proton?

- **neutron:** A subatomic particle with no electric charge.
- **fission:** Neutrons are used to produce new isotopes. A neutron will collide with a large atom and cause it to split into smaller atoms.

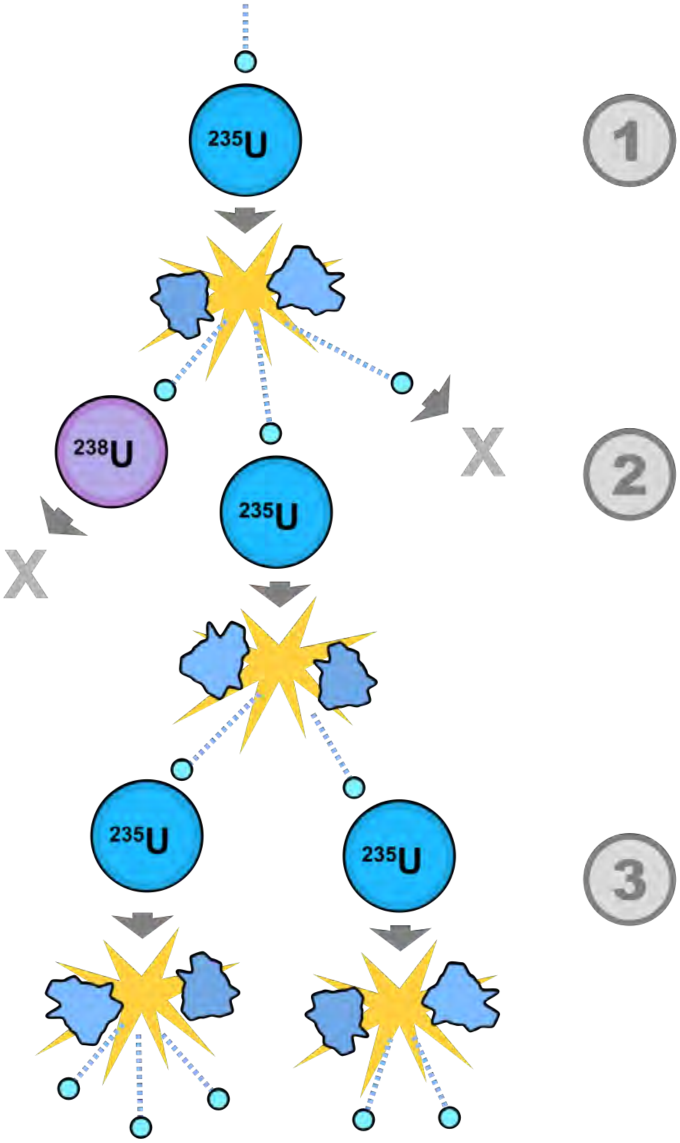
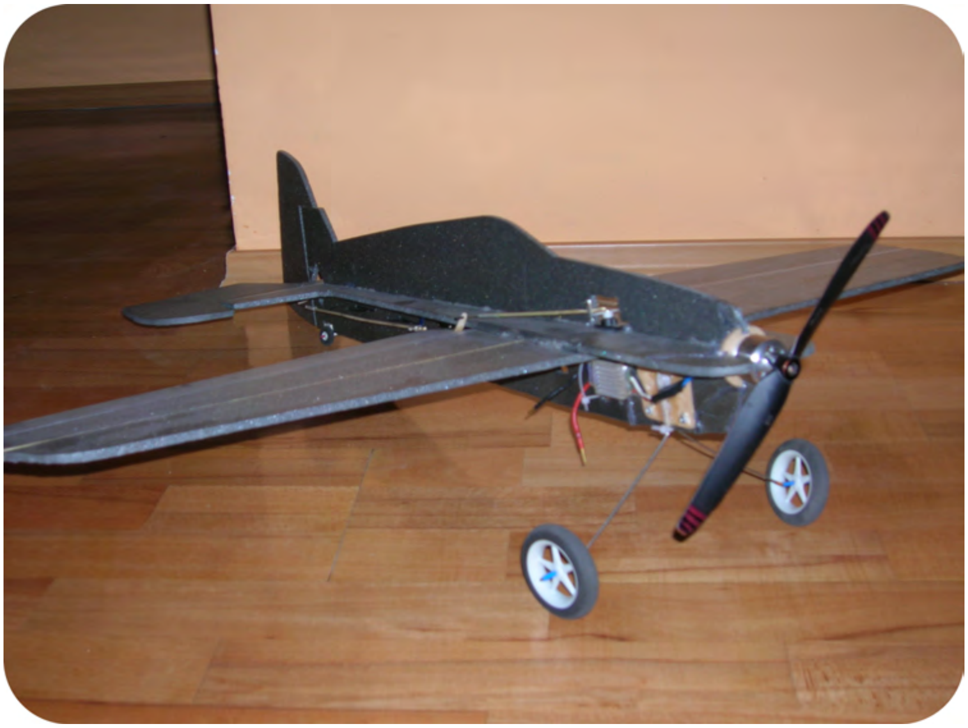


FIGURE 4.15

- **chain reaction:** When a neutron collides with a large atom, the atom splits with the release of more neutrons and also a large amount of energy. The neutrons then continue the chain reaction. Nuclear reactors use chain reactions to produce heat.

4.12 Thomson's Atomic Model

- Explain what a model is.
- Describe the "plum pudding" model of the atom.



Millions of children over the years have enjoyed building models - this model airplane is one example of the types that can be constructed. Perhaps sixty years ago the models were made of balsa wood, a very light material. Parts would be cut by hand, carefully glued together, and then covered with paper or other fabric. The development of plastics made the construction of model aircraft must simpler in many respects and the end-product is more durable and damage-proof.

A model serves a useful purpose – it gives us an idea of what the real thing is like. The model plane seen above has wings, a tail, and an engine just like the real thing. This model also has a propeller, as is the case with most small planes and some smaller passenger planes. However, the model is not the real thing. We certainly cannot fly people or cargo in the model, but we can get some idea of what a real plane looks like and how it works.

Science uses many models to explain ideas. We model the electron as a very small particle with a negative charge. That gives us a picture, but a very incomplete one. This picture works fine for most chemists, but is inadequate for a physicist. Models give us a start toward understanding structures and processes, but certainly are not a complete representation of the entity we are examining.

Atomic Models

The electron was discovered by J.J. Thomson in 1897. Protons were also known, as was the fact that atoms were neutral in charge. Since the intact atom had no net charge and the electron and proton had opposite charges, the next step after the discovery of subatomic particles was to figure out how these particles were arranged in the atom. This is a difficult task because of the incredibly small size of the atom. Therefore, scientists set out to design a model of what they believed the atom could look like. The goal of each **atomic model** was to accurately represent all of the experimental evidence about atoms in the simplest way possible.

Following the discovery of the electron, J.J. Thomson developed what became known as the "**plum pudding**" model in 1904. Plum pudding is an English dessert similar to a blueberry muffin. In this model, the electrons were stuck into a uniform lump of positive charge like blueberries in a muffin. In Thomson's plum pudding model of the atom, the electrons were embedded in a uniform sphere of positive charge. The positive matter was thought to be jelly-like or a thick soup. The electrons could move around somewhat. As they got closer to the outer portion of the atom, the positive charge in the region was greater than the neighboring negative charges and the electron would be pulled back more toward the center region of the atom.

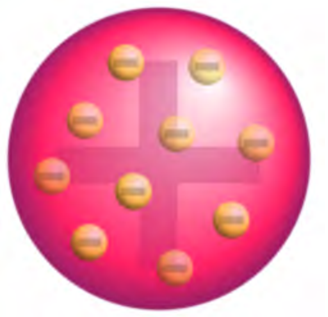


FIGURE 4.16

This model of the atom soon gave way, however, to a new model developed by New Zealander Ernest Rutherford (1871-1937) about five years later. Thomson received many honors during his lifetime, including being awarded the Nobel Prize in Physics in 1906 and a knighthood in 1908

Summary

- A model gives an idea of what something looks like, but is not the real thing.
- The "plum pudding" model of the atom consisted of a uniform sphere of positive charge with negative electrons imbedded in the sphere.

Practice

Use the link below to answer the following questions:

http://www.universetoday.com/38326/plum-pudding-model/

1. In the plum pudding model of the atom, what are the plums?
2. In this model, what is the dough?
3. What was the major purpose of the plum pudding model?
4. How is this model different from modern modes of the atom?

Review

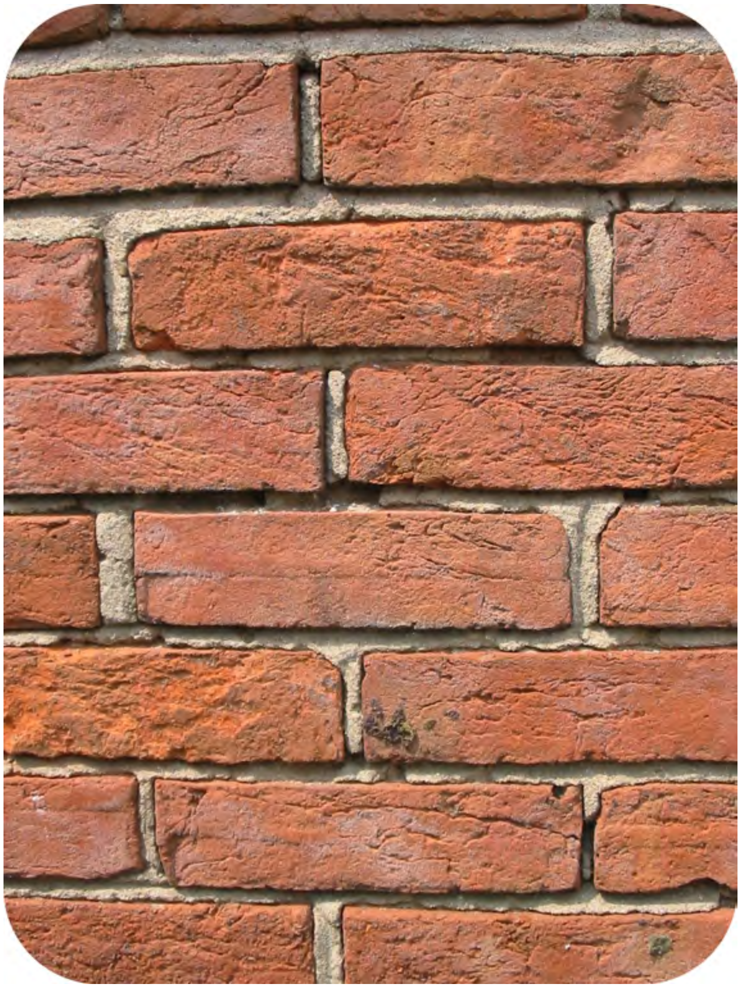
1. What is a model?
2. Why are models useful in science?
3. In Thomson's model of the atom, where were the electrons?
4. What was the positive charge in this model?

5. What kept the electrons in the atom?
6. Whose model replaced Thomson's?
7. What awards did Thomson receive?

- **atomic model:** When scientists set out to design a model of what they believed the atom could look like, the goal of each atomic model was to accurately represent all of the experimental evidence about atoms in the simplest way possible.
- **plum pudding:** In 1904 J.J. Thomson developed this model. The electrons were stuck into a uniform lump of positive charge like blueberries in a muffin. The positive matter was thought to be jelly- like or a thick soup. The electrons could move around somewhat. As they got closer to the outer portion of the atom, the positive charge in the region was greater than the neighboring negative charges and the electron would be pulled back more toward the center region of the atom.

4.13 Rutherford's Atomic Model

- Describe Rutherford's gold foil experiment.
- Describe the nuclear model of the atom.



As we look at the world around us, it looks pretty solid. We hit a wall with our hand and the hand stops – it does not (normally) go through the wall. We think of matter as occupying space. But there is a lot of empty space in matter. In fact, most of the matter *is* empty space.

The Gold Foil Experiment

In 1911, Rutherford and coworkers Hans Geiger and Ernest Marsden initiated a series of groundbreaking experiments that would completely change the accepted model of the atom. They bombarded very thin sheets of gold foil with fast moving **alpha particles**. Alpha particles, a type of natural radioactive particle, are positively charged particles with a mass about four times that of a hydrogen atom.

According to the accepted atomic model, in which an atom's mass and charge are uniformly distributed throughout the atom, the scientists expected that all of the alpha particles would pass through the gold foil with only a slight deflection or none at all. Surprisingly, while most of the alpha particles were indeed undeflected, a very small

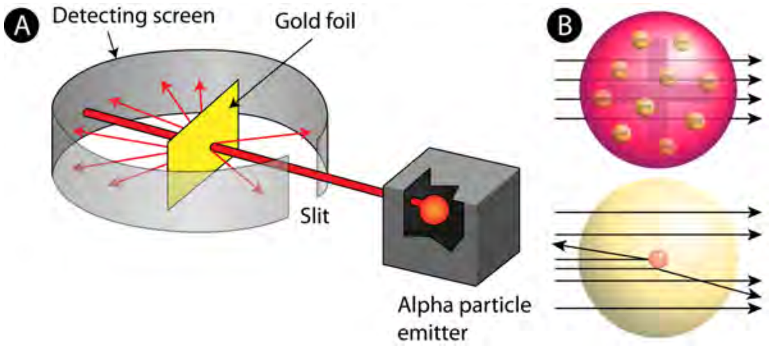


FIGURE 4.17

(A) The experimental setup for Rutherford's gold foil experiment: A radioactive element that emitted alpha particles was directed toward a thin sheet of gold foil that was surrounded by a screen which would allow detection of the deflected particles. (B) According to the plum pudding model (top) all of the alpha particles should have passed through the gold foil with little or no deflection. Rutherford found that a small percentage of alpha particles were deflected at large angles, which could be explained by an atom with a very small, dense, positively-charged nucleus at its center (bottom).

percentage (about 1 in 8000 particles) bounced off the gold foil at very large angles. Some were even redirected back toward the source. Nothing had prepared them for this discovery. In a famous quote, Rutherford exclaimed that it was "as if you had fired a 15-inch [artillery] shell at a piece of tissue paper and it came back and hit you."

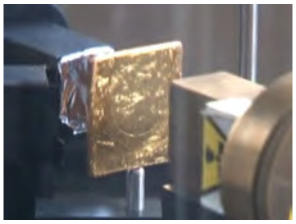
Rutherford needed to come up with an entirely new model of the atom in order to explain his results. Because the vast majority of the alpha particles had passed through the gold, he reasoned that most of the atom was empty space. In contrast, the particles that were highly deflected must have experienced a tremendously powerful force within the atom. He concluded that all of the positive charge and the majority of the mass of the atom must be concentrated in a very small space in the atom's interior, which he called the nucleus. The **nucleus** is the tiny, dense, central core of the atom and is composed of protons and neutrons.

Rutherford's atomic model became known as the **nuclear model**. In the nuclear atom, the protons and neutrons, which comprise nearly all of the mass of the atom, are located in the nucleus at the center of the atom. The electrons are distributed around the nucleus and occupy most of the volume of the atom. It is worth emphasizing just how small the nucleus is compared to the rest of the atom. If we could blow up an atom to be the size of a large professional football stadium, the nucleus would be about the size of a marble.

Rutherford's model proved to be an important step towards a full understanding of the atom. However, it did not completely address the nature of the electrons and the way in which they occupied the vast space around the nucleus. It was not until some years later that a full understanding of the electron was achieved. This proved to be the key to understanding the chemical properties of elements.

Watch a video that explains the gold foil experiment:

http://www.youtube.com/watch?v=XBqHkraf8iE



MEDIA

Click image to the left for more content.

Summary

- Bombardment of gold foil with alpha particles showed that some particles were deflected.
- The nuclear model of the atom consists of a small and dense positively charged interior surrounded by a cloud of electrons.

Practice

Use the link below to answer the following questions:

http://www.icbse.com/topics/rutherfords-model-atom

1. How thick was the gold foil?
2. What alpha source did he use?
3. How many were deflected straight back?
4. What was one drawback of Rutherford's theory?

Review

1. When did Rutherford and coworkers carry out their research?
2. What is an alpha particle?
3. How did Rutherford explain the observation that most alpha particles went straight through the gold foil?
4. What did he say about the particles that were deflected?
5. Describe Rutherford's nuclear model.

- **alpha particle:** A type of natural radioactive particle, are positively charged particles with a mass about four times that of a hydrogen atom.
- **nuclear model**: The nuclear model of the atom consists of a small and dense positively charged interior surrounded by a cloud of electrons.

4.14 Atomic Nucleus

- Describe the current model of the atomic nucleus.

Many people enjoy putting jigsaw puzzles together. As the different pieces go together, the picture begins to become clearer. When the puzzle is completed, you see that what had been a confused collection of individual components that made little or no sense by themselves fit together to give a clear picture.

Science works the same way as a jigsaw puzzle. Different researchers make individual discoveries that answer a specific question or questions. When enough data are gathered, we get a better understanding of a process or a structure. The experiments of Crooke, Millikan, Rutherford, and many others gave us pieces of the puzzle that is the atomic nucleus.

Different Models of the Nucleus

After the electron and proton were discovered, people began to try to build a picture of the atom. The Bohr model had electrons mixed in with a positive core of some sort that provided electrical neutrality. Rutherford showed that this model was incomplete. His picture of the atom involved a small solid core that alpha particles could zoom past with very few collisions. So the picture of the atom became a little clearer – electrons surrounded a very small core nucleus. The discovery of the neutron helped fill out the picture even more. We now have protons and neutrons in a concentrated center of the atom with electrons surrounding the nucleus.

One problem still existed. We have a number of positively charged protons in the nucleus. Why don't they push each other apart? Physicists postulate a strong nuclear force that acts at very short distances. At these distances the attraction between protons is greater than the force causing the positive charges to push each other away. Neutrons are also involved in this process somehow. So the strong force holds protons together, it holds neutrons together, and it causes protons and neutrons to be attracted to one another.

Video on atomic nucleus:

http://www.youtube.com/watch?v=PexDMyB3MwY

Summary

- Rutherford proposed a model of the atomic nucleus which had a solid core.
- There is no good explanation for why the nuclear particles stay together.

Practice

Use the link below to answer the following questions:

http://www.chemistryexplained.com/Ar-Bo/Atomic-Nucleus.html

1. What is the radius of the nucleus as compared to the radius of the atom?
2. What is the density of the nucleus?

Review

1. What was our first model of the atom?
2. How did Rutherford change our thinking about atomic structure?
3. What is our current picture of the atom?
4. Why is the presence of positively charged protons a problem with current models of the atom?
5. How do we explain why the nucleus does not fall apart?

- **electron:** A subatomic particle with a negative charge.
- **neutron:** A subatomic particle with no electric charge.
- **proton:** The positively charged subatomic particle present in all atoms.
- **nucleus:** The positively charged center of an atom, containing most of its mass.

4.15 Atomic Number

- Define the atomic number.
- Relate the number of electrons in an element to the atomic number for that element.

What is unique about each one of us?

For the vast majority of people, it is not their name, because it is quite possible for others in the world to have the same name (check it out by doing an internet search for your name and see how many other of "you" there are). It is not your physical description. Eye-witnesses to crime scenes often pick the wrong person when trying to identify the criminal.

There may be some unique identifiers for us. If you have a cell phone in your name, nobody else in the world has that number. Email addresses are different for each of us, which is a good thing since we can email almost anywhere in the world. Our DNA is unique, but getting a DNA analysis is expensive and time-consuming, so we really don't want to have to explore that.

Organizing the Elements

One of the goals of science is to discover the order in the universe and to organize information that reflects that order. As information about the different elements was made known, efforts were made to see if there were patterns in all that data. An early attempt to organize data was made by Mendeleev, who developed the first period table. His data set was based on **atomic weights** and was instrumental in providing clues as to the possible identity of new elements. Once we learned the details of the atomic nucleus, the table was based on the number of protons in the nucleus, called the **atomic number** of the element.

Atomic Number

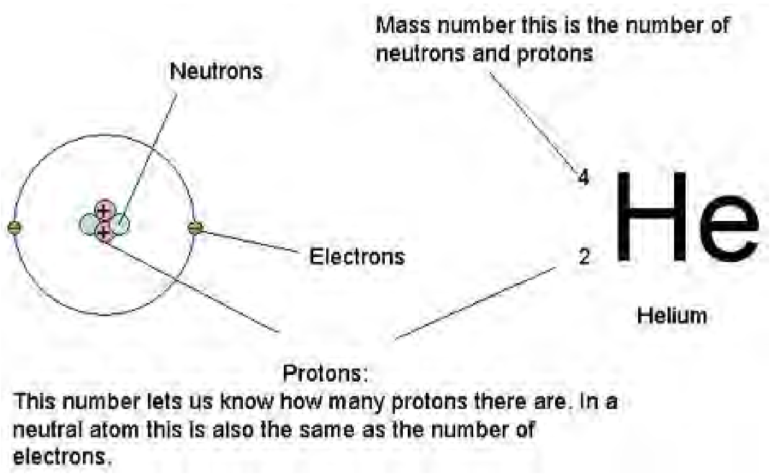


FIGURE 4.18

The atomic number (Z) of an element is the number of protons in the nucleus of each atom of that element. This means that it is the number of protons that is the characteristic which makes each element unique compared to other elements. Elements are different because of their atomic number. The **periodic table** 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. Following on the table is helium, whose atoms have two protons in the nucleus. Lithium atoms have three protons and so forth.

Since atoms are neutral, the number of electrons is equal to the number of protons. Hydrogen atoms all have one electron occupying the space outside of the nucleus. Manganese (atomic number 25) would have twenty-five protons and twenty-five electrons.

The classification of elements by atomic number allows us to understand many properties of the atom and makes it possible to predict behaviors instead of just having to memorize everything.

Summary

- The atomic number (Z) of an element is the number of protons in the nucleus of each atom of that element
- The number of electrons is equal to the number of protons in an element.

Practice

Use the link below to answer the following questions:

http://en.citizendium.org/wiki/atomic_number

1. What letter is used by convention to designate the atomic number?
2. What determines the chemical properties of an element?
3. What are the atomic numbers of the elements that appear in nature?
4. How many elements were known in John Dalton's day?

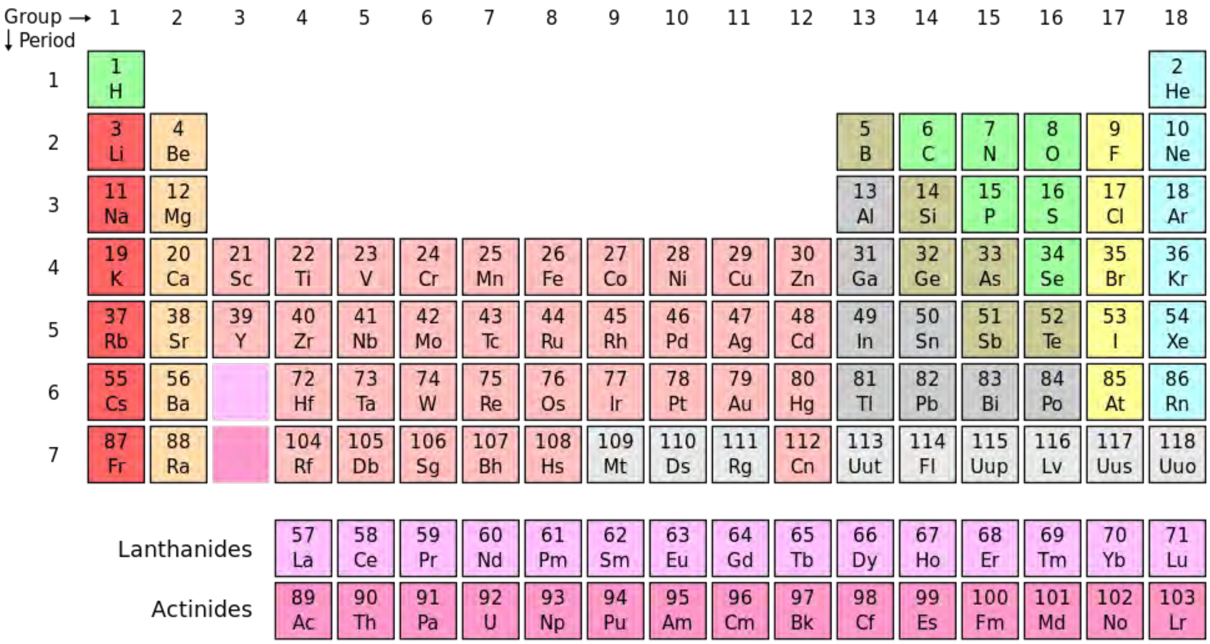


FIGURE 4.19

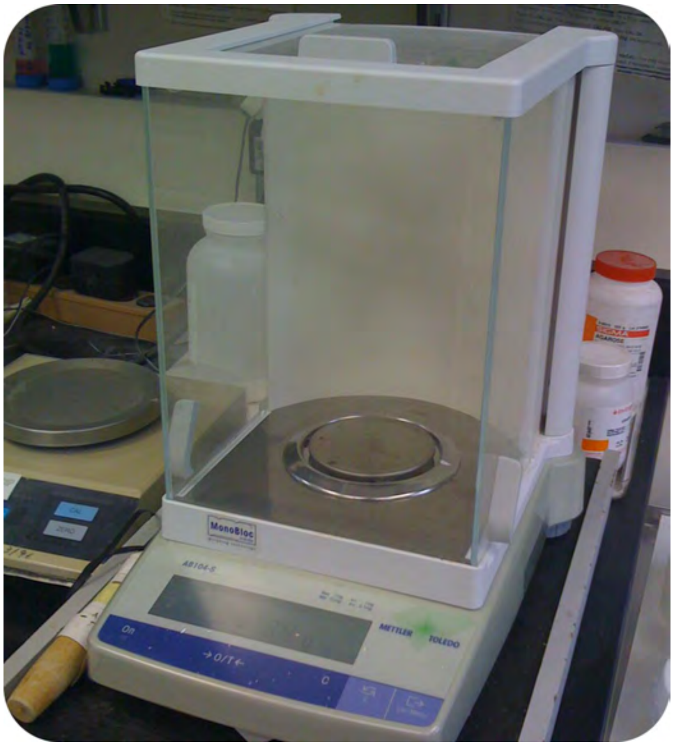
Review

1. Name two unique identifiers of people.
2. Who developed the first periodic table?
3. What was this table based upon?
4. What is the current periodic table based upon?
5. What does the atomic number represent?
6. How many protons are in the following elements:?
   (a) Ne
   (b) Ca
   (c) Pt
7. Write the symbol for the element with the following atomic number:
   (a) 18
   (b) 41
   (c) 82
   (d) 12

- **periodic table:** This table displays all of the known elements and is arranged in order of increasing atomic number.
- **atomic weight:** Each chemical element has an atom with a given mass.
- **atomic number:** The number of protons in the nucleus of each atom of that element.

4.16 Mass Number

- Define mass number.
- Calculate the mass number when given number of protons and neutrons.
- Calculate number of neutrons when given atomic number.



Often a student will need to weigh out a chemical for an experiment. If he or she uses a watch glass (a small round piece that will hold the solid chemical), the weight of the watch glass must be determined first. Then the solid is added to the glass and the weight of the glass plus the solid is measured. The balance reading will be the total of the glass plus the chemical.

History of Atomic Weight Determinations

As a part of his research on atoms, John Dalton determined a number of atomic weights of elements in the early 1800s. Atomic weights were the basis for the periodic table that Mendeleev developed. Originally all atomic weights were based on a comparison to hydrogen, which had an atomic weight of one. After the discovery of the proton, scientists assumed that the weight of an atomic was essentially that of the proton – electrons were known to contribute almost nothing to the atomic weight of the element.

This approach worked until we learned how to determine the number of protons in an element. We then saw that the atomic weight for an element was often twice the number of protons (or more). The discovery of the neutron provided the missing part of the picture. The atomic mass is the sum of the protons and neutrons in the nucleus.

FIGURE 4.20

Mass Number

Rutherford 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 number** is defined as the total number of protons and neutrons in an atom. Consider the table below which shows data from the first six elements of the periodic table.

TABLE 4.1: Atoms of the First Six Elements

Name	Symbol	Atomic Number	Protons	Neutrons	Electrons	Mass Number
Hydrogen	H	1	1	0	1	1
Helium	He	2	2	2	2	4
Lithium	Li	3	3	4	3	7
Beryllium	Be	4	4	5	4	9
Boron	B	5	5	6	5	11
Carbon	C	6	6	6	6	12

Consider the element helium. Its atomic number is 2, so it has two protons in its nucleus. Its nucleus also contains two neutrons. Since 2 + 2 = 4, we know that the mass number of the helium atom is 4. Finally, the helium atom also contains two electrons since the number of electrons must equal the number of protons. This example may lead you to believe that atoms have the same number of protons and neutrons, but further examination of the table above will show that this is not the case. Lithium, for example has three protons and four neutrons, leaving it with a mass number of 7.

Knowing the mass number and the atomic number of an atom allows you to determine the number of neutrons present in that atom by subtraction.

Number of neutrons = mass number - atomic number

Atoms of the element chromium (Cr) have an atomic number of 24 and a mass number of 52. How many neutrons are in the nucleus of a chromium atom? To determine this, you would subtract as shown:

52 - 24 = 28 neutrons in a chromium atom

The composition of any atom can be illustrated with a shorthand notation using the atomic number and the mass number. Both are written before the chemical symbol, with the mass number written as a superscript and the atomic number written as a subscript. The chromium atom discussed above would be written as:

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

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.

3. What is the mass number for an atom?

Review

1. Who first determined atomic weights for elements?
2. What were the original atomic weights based on?
3. Why were calculations based on numbers of protons not valid for determining atomic weights?
4. A tin atom has an atomic number of 50 and a mass number of 118. How many neutrons are present in this atom?
5. What is the mass number of a cobalt atom that has 27 protons and 30 neutrons?

- **mass number:** The total number of protons and neutrons in an atom.

4.17 Isotopes

- Define isotope.
- Calculate the number of neutrons in an isotope when given atomic number and atomic mass.

Are all the members of the football team shown above identical?

They are on the same team and are all known by the same team name, but there are individual differences among the players. We do not expect the kicker to be as big as the quarterback. The tight end is very likely to weigh less than the defensive tackle on the other side of the ball. They play as a unit, but they have different weights and heights.

Isotopes

The history of the atom is full of some of these differences. Although John Dalton stated in his atomic theory of 1804 that all atoms of an element are identical, the discovery of the neutron began to show that this assumption was not correct. The study of radioactive materials (elements that spontaneously give off particles to form new elements) by Frederick Soddy (1877-1956) gave important clues about the internal structure of atoms. His work showed that some substances with different radioactive properties and different atomic weights were in fact the same element. He coined the term **isotope** from the Greek roots isos (ίσος "equal") and topos (τόπος "place") and described them as "Put colloquially, their atoms have identical outsides but different insides." Soddy won the Nobel Prize in Chemistry in 9121 for his work.

As stated earlier, not all atoms of a given element are identical. Specifically, the number of neutrons can be variable for many elements. As an example, naturally occurring carbon exists in three forms. Each carbon atom has the same number of protons (6), which is its atomic number. Each carbon atom also contains six electrons in order to maintain electrical neutrality. However the number of neutrons varies as six, seven, or eight. Isotopes are atoms that have the same number 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 $\left({}^{12}_{6}\mathrm{C}\right)$, carbon-13 $\left({}^{13}_{6}\mathrm{C}\right)$, and carbon-14 $\left({}^{14}_{6}\mathrm{C}\right)$. Most elements naturally consist of mixtures of isotopes. Carbon has three natural isotopes, while some heavier elements can have many more. Tin has ten stable isotopes, the most of any element. The term **nuclide** refers to the nucleus of a given isotope of an element. A carbon atom is one of three different nuclides.

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.

Summary

- Isotopes are atoms that have the same number atomic number, but different mass numbers due to a change in the number of neutrons.
- The term nuclide refers to the nucleus of a given isotope of an element.
- The atomic mass of an atom equals the sum of the protons and the neutrons.

Practice

Use the link below to answer the following questions:

http://www.ehow.com/about_4678737_discovered-isotope.html

1. When was the term “isotope” first used?
2. Are isotopes of an element chemically the same or different?
3. How are radioactive isotopes used?

Review

1. What does the term “isotope” mean
2. Define “isotope.”
3. What affects the chemical behavior of an atom?
4. An isotope of yttrium has 39 protons and 59 neutrons. What is the atomic mass of that isotope?
5. An isotope with an atomic mass of 193 has 116 neutrons. What is the atomic number of this isotope?
6. An isotope of barium (atomic number 56) has an atomic mass of 138. How many neutrons are in the nucleus of this isotope?

- **isotope:** Atoms that have the same number atomic number, but different mass numbers due to a change in the number of neutrons.
- **nuclide:** The nucleus of a given isotope of an element. A carbon atom is one of three different nuclides.

4.18 Atomic Mass Unit

- Define atomic mass unit.
- Explain how atomic mass units are determined.

The current system of measurements in the Unites States is a hodge-podge of different units, many of which are hard to interconvert, unlike the metric system. We at least have standardized units these days, unlike centuries past. At one time, measurements of length often were defined as the distance from the end of one appendage to another. For example, the yard would be defined as the distance from the king's nose to the tip of his thumb when his arm was stretched out.

Standardized measurements make it possible for people everywhere to get the same amount of something. Note the red and white labels on the gas pump above. These labels certify that the gas pump has been checked and is pumping an accurate gallon of gas. Standard measurements in science are very important so we can compare experimental data from one lab to another and make sure we all are talking about the same thing.

Atomic Mass

Masses of individual atoms are very, very small. Using a modern device called a mass spectrometer, it is possible to measure such minuscule masses. An atom of oxygen-16, for example, has a mass of 2.66×10^{-23} g. While comparisons of masses measured in grams would have some usefulness, it is far more practical to have a system that will allow us to more easily compare relative atomic masses. Scientists decided on using the carbon-12 nuclide as the reference standard by which all other masses would be compared. By definition, one atom of carbon-12 is assigned a mass of 12 **atomic mass units** (amu). An atomic mass unit is defined as a mass equal to one twelfth the mass of an atom of carbon-12. The mass of any isotope of any element is expressed in relation to the carbon-12 standard. For example, one atom of helium-4 has a mass of 4.0026 amu. An atom of sulfur-32 has a mass of 31.972 amu.

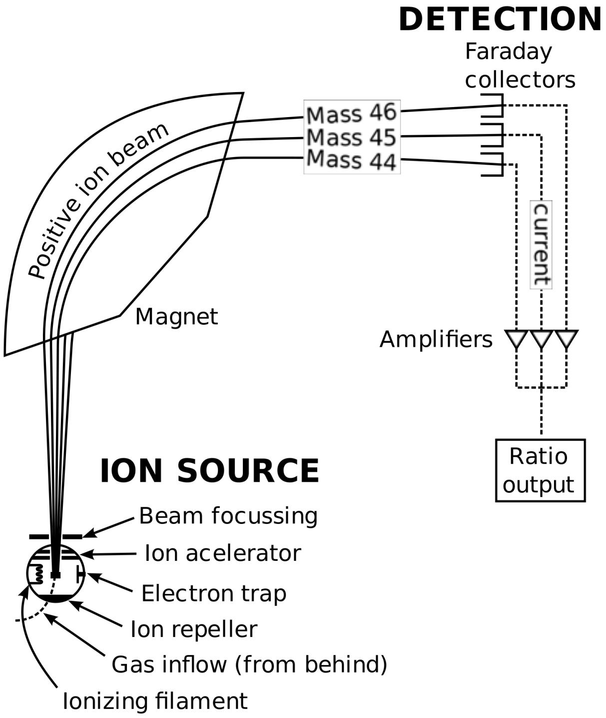


FIGURE 4.21

The carbon-12 atom has six protons and six neutrons in its nucleus for a mass number of 12. Since the nucleus accounts for nearly all of the mass of the atom, a single proton or single neutron has a mass of approximately 1 amu. However, as seen by the helium and sulfur examples, the masses of individual atoms are not whole numbers. This is because an atom's mass is affected very slightly by the interactions of the various particles within the nucleus and also the small mass of the electron is taken into account.

Summary

- Carbon-12 is the reference for all atomic mass calculations.
- An atomic mass unit is defined as a mass equal to one twelfth the mass of an atom of carbon-12.
- The mass of an atom is affected by the interactions of particles within the nucleus.

Practice

Use the link below to answer the following questions:

http://www.wisegeek.com/what-is-the-atomic-mass-unit.htm#lbss

- What is the atomic mass unit based on?
- What is another term for atomic mass unit?
- What mistake is in the second paragraph?

Review

- What instrument is used to measure the mass of atoms?
- How much does a single oxygen-16 atom weigh in grams?

- What is the reference standard for atomic mass units?
- How is an atomic mass unit defined?
- Why are the numbers for atomic mass of individual atoms not whole numbers?

- **atomic mass unit:** Abbreviated as "amu." A mass equal to one twelfth the mass of an atom of carbon-12.

4.19 Calculating Atomic Mass

- Define atomic mass.
- Calculate atomic mass given relevant information about the isotopes.

You have a pile of rocks to move and need to decide what equipment you want to rent to move them. If the rocks are fairly small, you can get a shovel to pick them up. Larger rocks could be moved by hand, but big boulders will need some sort of mechanical scoop. The amount of each kind of rock will also determine how much time you will need to get the job done. Knowing the relative amounts of large, medium, and small rocks can be very useful in deciding how to approach the job.

Most elements occur naturally as a mixture of two or more isotopes. The table below shows the natural isotopes of several elements, along with the **percent natural abundance** of each.

TABLE 4.2: **Atomic Masses and Percent Abundances of Some Natural Isotopes**

Element	Isotope (symbol)	Percent natural abundance	Atomic mass (amu)	Average atomic mass (amu)
Hydrogen	${}^{1}_{1}H$	99.985	1.0078	1.0079
	${}^{2}_{1}H$	0.015	2.0141	
	${}^{3}_{1}H$	negligible	3.0160	
Carbon	${}^{12}_{6}C$	98.89	12.000	12.011
	${}^{13}_{6}C$	1.11	13.003	
	${}^{14}_{6}C$	trace	14.003	
Oxygen	${}^{16}_{8}O$	99.759	15.995	15.999
	${}^{17}_{8}O$	0.037	16.995	
	${}^{18}_{8}O$	0.204	17.999	
Chlorine	${}^{35}_{17}Cl$	75.77	34.969	35.453
	${}^{37}_{17}Cl$	24.23	36.966	

TABLE 4.2: (continued)

Copper	$^{63}_{29}\text{Cu}$	69.17	62.930	63.546
	$^{65}_{29}\text{Cu}$	30.83	64.928	

For some elements, one particular isotope predominates greatly over the other isotopes. Naturally occurring hydrogen is nearly all hydrogen-1 and naturally occurring oxygen is nearly all oxygen-16. For many other elements, however, more than one isotope may exist in more substantial quantities. Chlorine (atomic number 17) is a yellowish-green toxic gas. About three quarters of all chlorine atoms have 18 neutrons, giving those atoms a mass number of 35. About one quarter of all chlorine atoms have 20 neutrons, giving those atoms a mass number of 37. Were you to simply calculate the arithmetic average of the precise **atomic masses**, you would get 36.

$\frac{(34.969+36.966)}{2} = 35.968 \text{ amu}$

Clearly the actual average atomic mass from the last column of the table is significantly lower. Why? We need to take into account the percent natural abundances of each isotope in order to calculate what is called the weighted average. The atomic mass of an element is the weighted average of the atomic masses of the naturally occurring isotopes of that element. The sample problem below demonstrates how to calculate the atomic mass of chlorine.

Sample Problem: Calculating Atomic Mass

Use the atomic masses of each of the two isotopes of chlorine along with their percent abundances to calculate the average atomic mass of chlorine.

Step 1: List the known and unknown quantities and plan the problem.

Known

- chlorine-35: atomic mass = 34.969 amu and % abundance = 75.77%
- chlorine-37: atomic mass = 36.966 amu and % abundance = 24.23%

Unknown

- Average atomic mass of chlorine

Change each percent abundance into decimal form by dividing by 100. Multiply this value by the atomic mass of that isotope. Add together for each isotope to get the average atomic mass.

Step 2: Calculate

$$\begin{array}{ll}
\textit{chlorine-35} & 0.7577 \times 34.969 = 26.50 \; amu \\
\textit{chlorine-37} & 0.2423 \times 36.966 = 8.957 \; amu \\
\textit{average atomic mass} & 26.50 + 8.957 = 35.45 \; amu
\end{array}$$

Note: Applying significant figure rules results in the 35.45 amu result without excessive rounding error. In one step:

$(0.7577 \times 34.969) + (0.2423 \times 36.966) = 35.45 \text{ amu}$

Step 3: Think about your result.

The calculated average atomic mass is closer to 35 than to 37 because a greater percentage of naturally occurring chlorine atoms have the mass number of 35. It agrees with the value from the table above.

Watch these videos to learn more about these calculations:

http://www.kentchemistry.com/links/AtomicStructure/atomicmasscalc.htm

Summary

- The atomic mass of an element is the weighted average of the atomic masses of the naturally occurring isotopes of that element.
- Calculations of atomic mass use the percent abundance of each isotope.

Practice

Click on the link below to get some experience in atomic mass determinations:

http://www.collegeadjuncts.org/javascripts/AtomicMass.html

Review

1. Define atomic mass.
2. What information do you need to calculate atomic mass for an element?
3. Calculate the atomic mass for carbon using the following data:

TABLE 4.3:

mass number	exact weight	percent abundance
12	12.000000	98.90
13	13.003355	1.10

- **atomic mass:** The weighted average of the atomic masses of the naturally occurring isotopes of that element.
- **percent abundance:** To calculate the weighted average, take into account the percent natural abundances of each isotope. The atomic mass of an element is the weighted average of the atomic masses of the naturally occurring isotopes of that element.

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CHAPTER 5

Electrons in Atoms

Chapter Outline

5.1 Properties of Light

- Describe problems with Rutherford's model of the atom.
- List types of electromagnetic radiation

Waves can come in many sizes. Here we see a large wave crashing on the beach. Other waves can be very small and regular. We normally think of waves as being made of water, but there are forms of energy that take on the characteristics of waves. The idea of a wave has played a major role in our understanding of how the atom is put together and why it behaves the way it does.

Properties of Light

The nuclear atomic model proposed by Rutherford was a great improvement over previous models, but was still not complete. It did not fully explain the location and behavior of the electrons in the vast space outside of the nucleus. In fact, it was well known that oppositely charged particles attract one another. Rutherford's model did not explain why the electrons don't simply move toward and eventually collide with the nucleus. Experiments in the early twentieth century began to focus on the absorption and emission of light by matter. These studies showed how certain phenomena associated with light reveal insight into the nature of matter, energy, and atomic structure.

Wave Nature of Light

In order to begin to understand the nature of the electron, we first need to look at the properties of light. Prior to 1900, scientists thought light behaved solely as a wave. As we will see later, this began to change as new experiments demonstrated that light also has some of the characteristics of a particle. First, we will examine the wavelike properties of light.

Visible light is one type of **electromagnetic radiation**, which is a form of energy that exhibits wavelike behavior as it moves through space. Other types of electromagnetic radiation include gamma rays, x-rays, ultraviolet light, infrared light, microwaves, and radio waves. The figure below shows the **electromagnetic spectrum**, which is all forms of electromagnetic radiation. Notice that visible light makes up only a very, very small portion of the entire electromagnetic spectrum. All electromagnetic radiation moves through a vacuum at a constant speed of 2.998×10^8 m/s. While the presence of air molecules slows the speed of light by a very small amount, we will use the value of 3.00×10^8 m/s as the speed of light in air.

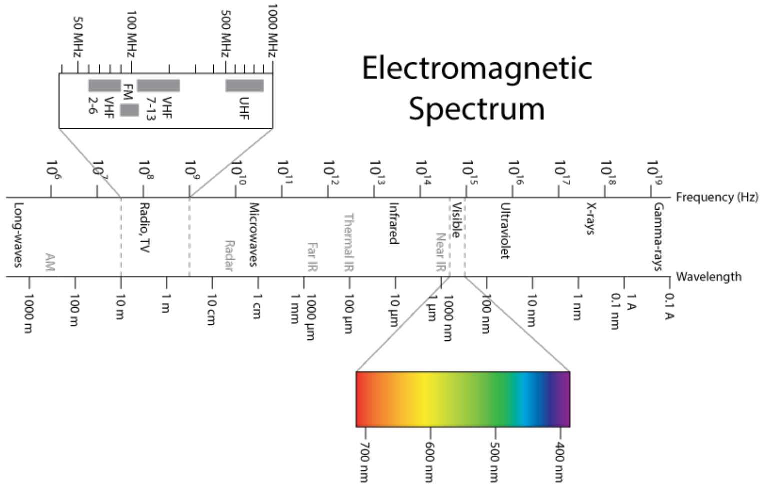


FIGURE 5.1

The electromagnetic spectrum encompasses a very wide range of wavelengths and frequencies. Visible light is only a very small portion of the spectrum with wavelengths from 400-700 nm.

The **Figure** 5.1 shows how the electromagnetic spectrum displays a wide variation in wavelength and frequency. Radio waves have wavelengths of as long as hundreds of meters, while the wavelength of gamma rays are on the order of 10^{-12} m. The corresponding frequencies range from 10^6 to 10^{21} Hz. Visible light can be split into colors with the use of a prism (**Figure** 5.2), yielding the visible spectrum of light. Red light has the longest wavelength and lowest frequency, while violet light has the shortest wavelength and highest frequency. Visible light wavelength ranges from about 400 – 700 nm with frequencies in the range of 10^{14} Hz.

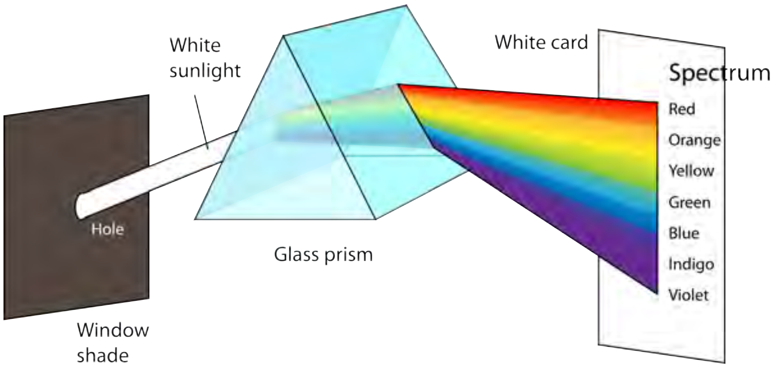


FIGURE 5.2

A small beam of white light is (refracted) bent as it passes through a glass prism. The shorter the wavelength of light, the greater is the refraction, so the light is separated into all its colors.

Summary

- Electromagnetic radiation is a form of energy.
- Visible light has wavelengths from 400-700 nm.

- The speed of light in air is 3.00×10^8 m/s.

Practice

Use the link below to answer the following questions:

http://www.colorado.edu/physics/2000/waves_particles/lightspeed_evidence.html

1. Who first tried to measure the speed of light?
2. How long would it take for light to travel the one mile distance that Galileo studied?
3. What astronomical object did Ole Roemer use to determine the speed of light?
4. What did Roemer determine the speed of light to be?

Review

1. What did Rutherford's nuclear atomic model not explain?
2. Prior to 1900, what did scientists believe about the nature of light?
3. What is visible light?
4. What is the range of wavelengths for visible light?

- **electromagnetic radiation:** A form of energy that exhibits wavelike behavior as it moves through space.
- **electromagnetic spectrum:** All forms of electromagnetic radiation.

5.2 Wavelength and Frequency Calculations

- Define wavelength.
- Define frequency.
- Describe the characteristics of a wave.
- Perform calculations involving wavelength and frequency.

Do you enjoy going to the beach?

During the summer, almost everyone enjoys going to the beach. They can swim, have picnics, and work on their tans. But if you get too much sun, you can burn. A particular set of solar wavelengths are especially harmful to the skin. This portion of the soar spectrum is known as UV B, with wavelengths of 280-320 nm. Sunscreens are effective in protecting the skin against both the immediate skin damage and the long-term possibility of skin cancer.

Waves

Waves are characterized by their repetitive motion. Imagine a toy boat riding the waves in a wave pool. As the water wave passes under the boat, it moves up and down in a regular and repeated fashion. While the wave travels horizontally, the boat only travels vertically up and down. The **Figure** 5.3 shows two examples of waves.

A wave cycle consists of one complete wave – starting at the zero point, going up to a wave **crest**, going back down to a wave **trough**, and back to the zero point again. The **wavelength** of a wave is the distance between any two corresponding points on adjacent waves. It is easiest to visualize the wavelength of a wave as the distance from one wave crest to the next. In an equation, wavelength is represented by the Greek letter lambda (λ). Depending on the type of wave, wavelength can be measured in meters, centimeters, or nanometers (1 m = 10^9 nm). The **frequency**, represented by the Greek letter nu (ν), is the number of waves that pass a certain point in a specified amount of time. Typically, frequency is measured in units of cycles per second or waves per second. One wave per second is also called a Hertz (Hz) and in SI units is a reciprocal second (s^{-1}).

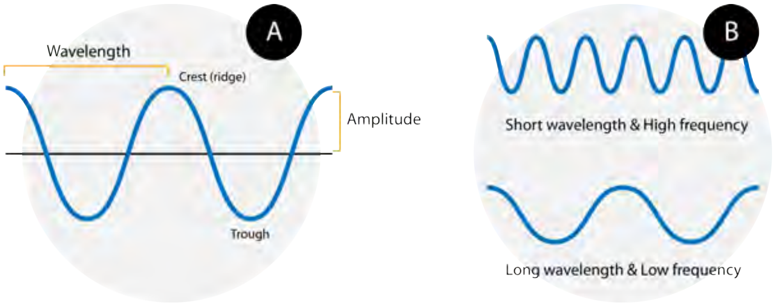


FIGURE 5.3

(A) A wave consists of alternation crests and troughs. The wavelength (λ) is defined as the distance between any two consecutive identical points on the waveform. The amplitude is the height of the wave. (B) A wave with a short wavelength (top) has a high frequency because more waves pass a given point in a certain amount of time. A wave with a longer wavelength (bottom) has a lower frequency.

Figure B above shows an important relationship between the wavelength and frequency of a wave. The top wave clearly has a shorter wavelength than the second wave. However, if you picture yourself at a stationary point watching these waves pass by, more waves of the first kind would pass by in a given amount of time. Thus the frequency of the first waves is greater than that of the second waves. Wavelength and frequency are therefore inversely related. As the wavelength of a wave increases, its frequency decreases. The equation that relates the two is:

$$c = \lambda\nu$$

The variable c is the speed of light. For the relationship to hold mathematically, if the speed of light is used in m/s, the wavelength must be in meters and the frequency in Hertz.

Sample Problem: Wavelength and Frequency

The color orange within the visible light spectrum has a wavelength of about 620 nm. What is the frequency of orange light?

Step 1: List the known quantities and plan the problem.

Known

- wavelength (λ) = 620 nm
- speed of light (c) = 3.00×10^8 m/s
- conversion factor 1 m = 10^9 nm

Unknown

- Frequency

Convert the wavelength to m, then apply the equation $c = \lambda\nu$ and solve for frequency. Dividing both sides of the equation by λ yields:

$$\nu = \frac{c}{\lambda}$$

Step 2: Calculate

$$620\ \text{nm} \times \left(\frac{1\ \text{m}}{10^9\ \text{nm}}\right) = 6.20 \times 10^{-7}\ \text{m}$$
$$\nu = \frac{c}{\lambda} = \frac{3.0 \times 10^8\ \text{m/s}}{6.20 \times 10^{-7}\ \text{m}} = 4.8 \times 10^{14}\ \text{Hz}$$

Step 3: Think about your result.

The value for the frequency falls within the range for visible light.

Summary

- All waves can be defined in terms of their frequency and intensity.
- $c = \lambda\nu$ expresses the relationship between wavelength and frequency.

Practice

Read the material on the link below and answer the questions as they come up:

http://www.absorblearning.com/physics/demo/units/DJFPh064.html

Review

1. Define wavelength.
2. Define frequency.
3. What is the relationship between wavelength and frequency?

- **amplitude:** The height of the wave, the distance between the crest and the trough
- **crest:** The peak of the wave
- **frequency:** Is the number of waves that pass a certain point in a specified amount of time.
- **trough:** The low point of the wave cycle.
- **wavelength:** The distance between two successive peaks.

5.3 Quantization of Energy

- Define quantum.
- Describe the relationship between the amount of energy absorbed or released by an object and the frequency of the radiation observed.

Every so often you hear a commercial or a news story with the words "quantum leap" in it. The quantum leap is supposed to be a major breakthrough, a big change, something extraordinarily large. The reality is far different. Instead of the big, extravagant change the "quantum" that scientists know about is a very small difference in the location of an electron around a nucleus – hardly an enormous shift at all.

Quantization of Energy

German physicist Max Planck (1858-1947) studied the emission of light by hot objects. You have likely seen a heated metal object glow an orange-red color (see **Figure** 5.4).

FIGURE 5.4

A heated object may glow different colors. The atoms in this piece of metal are releasing energy in discrete units called quanta.

Classical physics, which explains the behavior of large, everyday objects, predicted that a hot object would emit electromagnetic energy in a continuous fashion. In other words, every wavelength of light could possibly be emitted. Instead, what Planck found by analyzing the spectra was that the energy of the hot body could only be lost in small discrete units. A **quantum** is the minimum quantity of energy that can either be lost or gained by an atom. An analogy is that a brick wall can only undergo a change in height by units of one or more bricks and not by any possible height. Planck showed that the amount of radiant energy absorbed or emitted by an object is directly proportional to the frequency of the radiation.

$$E = h\nu$$

In the equation, E is the energy, in joules, of a quantum of radiation, v is the frequency, and h is a fundamental constant called **Planck's constant**. The value of Planck's constant is $h = 6.626 \times 10^{-34}$ J $\cdot$ s. The energy of any system must increase or decrease in units of $h \times v$. A small energy change results in the emission or absorption of low-frequency radiation, while a large energy change results in the emission or absorption of high-frequency radiation.

Sample Problem: Quantized Energy

What is the energy of a photon of green light with a frequency of 5.75×10^{14} Hz?

Step 1: List the known quantities and plan the problem.

Known

- frequency $(\nu) = 5.75 \times 10^{14}$ Hz
- Planck's constant $(h) = 6.626 \times 10^{-34}$ J • s

Unknown

- energy (E)

Apply the equation $E = hv$ to solve for the energy.

Step 2: Calculate

$$E = (6.626 \times 10^{-34} \text{ J} \cdot \text{s}) \times (5.75 \times 10^{14} \text{ Hz}) = 3.81 \times 10^{-19} \text{ J}$$

Step 3: Think about your result.

While the resulting energy may seem very small, this is for only one photon of light. Visible quantities of light consist of huge quantities of photons. Recall that a hertz is equal to a reciprocal second, so the units agree in the equation.

Summary

- A quantum relates to the energy gained or absorbed by an object.
- The value of Planck's constant is $h = 6.626 \times 10^{-34}$ J $\cdot$ s.

Practice

Use the link below to answer the following questions:

http://abyss.uoregon.edu/ js/21st_century_science/lectures/lec12.html

1. According to classical physics, what should happen as the electron accelerates around the nucleus?
2. What did Planck assume?
3. How are changes in energy carried out at the sub-atomic level?

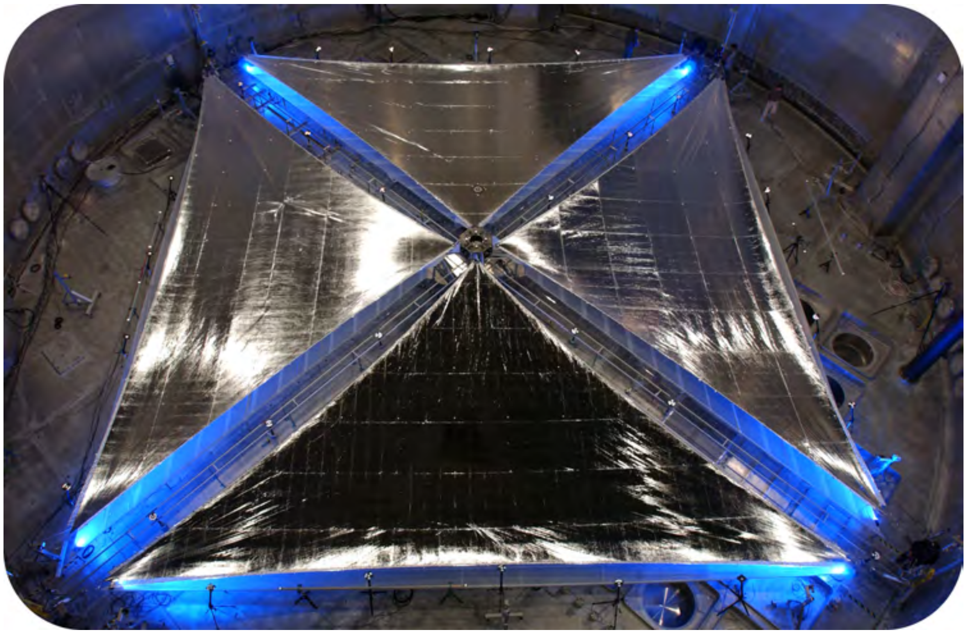
Review

1. What did classical physics predict about hot objects?
2. What did Planck find?
3. What is a quantum?

- **Planck's constant:** $h = 6.626 \times 10^{-34}\ J \cdot s$.
- **quantum:** The minimum quantity of energy that can either be lost or gained by an atom.

5.4 Photoelectric Effect

- Describe the photoelectric effect.



In old science fiction stories (1950s), one of the space travel themes was the use of solar sails for propulsion. The idea was that the photon pressure from the sun would push the sail (like the wind sails) and move the space craft. What once was science fiction is now reality as solar sails are being developed and tested for modern space travel.

Photoelectric Effect and the Particle Nature of Light

In 1905 Albert Einstein (1879-1955) proposed that light be described as quanta of energy that behave as particles. A **photon** is a particle of electromagnetic radiation that has zero mass and carries a quantum of energy. The energy of photons of light is quantized according to the $E = h\nu$ equation. For many years light had been described using only wave concepts, and scientists trained in classical physics found this wave-particle duality of light to be a difficult idea to accept. A key experiment that was explained by Einstein using light's particle nature was called the photoelectric effect.

The **photoelectric effect** is a phenomenon that occurs when light shined onto a metal surface causes the ejection of electrons from that metal. It was observed that only certain frequencies of light are able to cause the ejection of electrons. If the frequency of the incident light is too low (red light, for example), then no electrons were ejected even if the intensity of the light was very high or it was shone onto the surface for a long time. If the frequency of the light was higher (green light, for example), then electrons were able to be ejected from the metal surface even if the intensity of the light was very low or it was shone for only a short time. This minimum frequency needed to cause electron ejection is referred to as the **threshold frequency**.

Classical physics was unable to explain the photoelectric effect. If classical physics applied to this situation, the electron in the metal could eventually collect enough energy to be ejected from the surface even if the incoming light was of low frequency. Einstein used the particle theory of light to explain the photoelectric effect as shown in the **Figure** 5.5.

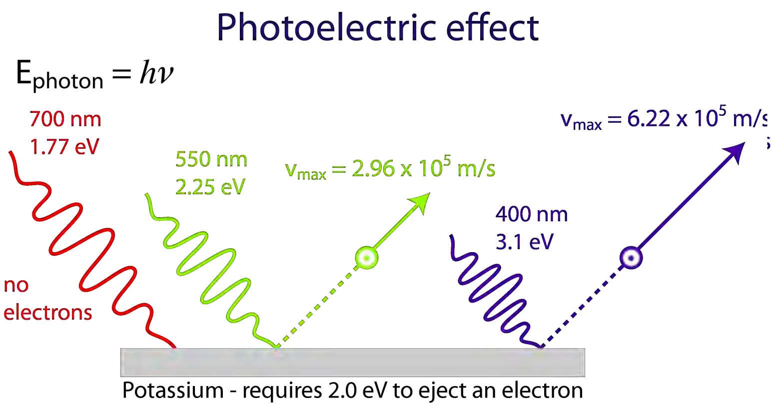


FIGURE 5.5

Low frequency light (red) is unable to cause ejection of electrons from the metal surface. At or above the threshold frequency (green) electrons are ejected. Even higher frequency incoming light (blue) causes ejection of the same number of electrons but with greater speed.

Consider the $E = hv$ equation. The E is the minimum energy that is required in order for the metal's electron to be ejected. If the incoming light's frequency, v, is below the threshold frequency, there will never be enough energy to cause electron to be ejected. If the frequency is equal to or higher than the threshold frequency, electrons will be ejected. As the frequency increases beyond the threshold, the ejected electrons simply move faster. An increase in the intensity of incoming light that is above the threshold frequency causes the number of electrons that are ejected to increase, but they do not travel any faster. The photoelectric effect is applied in devices called **photoelectric cells**, which are commonly found in everyday items such as a calculator which uses the energy of light to generate electricity.

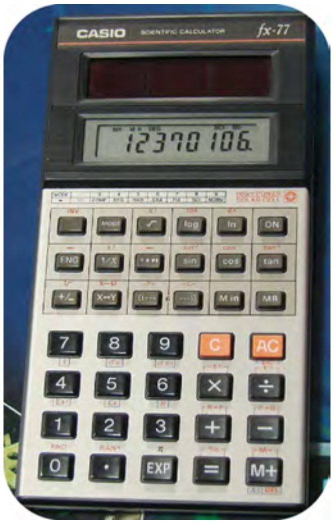


FIGURE 5.6

Photoelectric cells convert light energy into electrical energy which powers this calculator.

Summary

- Light has properties of both a wave and a particle.
- The photoelectric effect is produced by light striking a metal and dislodging electrons form the surface of the metal.

Practice

Use the link below to answer the following questions:

http://www.citycollegiate.com/physicsXII_photocell.htm

1. What is the emitting material in this photocell?
2. What causes photoelectrons to be emitted?
3. Does the current increase or decrease with an increase in light intensity?
4. What happens if light does not strike the cathode?

Review

1. What are the properties of a photon?
2. What does the photoelectric effect show about the properties of light?
3. How does the frequency of light affect the release of photons?

- **photoelectric cell:** Use energy of light to generate electricity.
- **photoelectric effect:** A phenomenon that occurs when light shined onto a metal surface causes the ejection of electrons from that metal.
- **photon:** A particle of electromagnetic radiation that has zero mass and carries a quantum of energy.
- **threshold frequency:** Minimum frequency needed to cause electron ejection.

5.5 Atomic Emission Spectra

- Define ground state.
- Define excited state.
- Describe how atomic emission spectra are produced.

Archery as a sport or a means of defense has existed for centuries. At rest, there is no tension on the bowstring and no force on the arrow. When the string and arrow are pulled back, we now have a situation where kinetic energy (pulling of the string) has been converted to potential energy (the tension on the string). The archer releases the arrow and the potential energy is translated into kinetic energy as the arrow moves. It turns out that electrons behave the same way when energy is put into the system or released from the system.

Atomic Emission Spectra

The electrons in an atom tend to be arranged in such a way that the energy of the atom is as low as possible. The **ground state** of an atom is the lowest energy state of the atom. When those atoms are given energy, the electrons absorb the energy and move to a higher energy level. These energy levels of the electrons in atoms are quantized, meaning again that the electron must move from one energy level to another in discrete steps rather than continuously. An **excited state** of an atom is a state where its potential energy is higher than the ground state. An atom in the excited state is not stable. When it returns back to the ground state, it releases the energy that it had previously gained in the form of electromagnetic radiation.

So how do atoms gain energy in the first place? One way is to pass an electric current through an enclosed sample of a gas at low pressure. Since the electron energy levels are unique for each element, every gas discharge tube will glow with a distinctive color depending on the identity of the gas (see **Figure** 5.7).

"Neon" signs are familiar examples of gas discharge tubes. However, only signs that glow with the red-orange color seen in the figure are actually filled with neon. Signs of other colors contain different gases or mixtures of gases.

FIGURE 5.7

Gas discharge tubes are enclosed glass tubes filled with a gas at low pressure through which an electric current is passed. Electrons in the gaseous atoms first become excited, and then fall back to lower energy levels, emitting light of a distinctive color in the process. Shown are gas discharge tubes of helium, neon, argon, krypton, and xenon.

Scientists studied the distinctive pink color of the gas discharge created by hydrogen gas. When a narrow beam of this light was viewed through a prism, the light was separated into four lines of very specific wavelengths (and frequencies since λ and v are inversely related). An **atomic emission spectrum** is the pattern of lines formed when light passes through a prism to separate it into the different frequencies of light it contains. The **Figure** 5.8 shows the atomic emission spectrum of hydrogen.

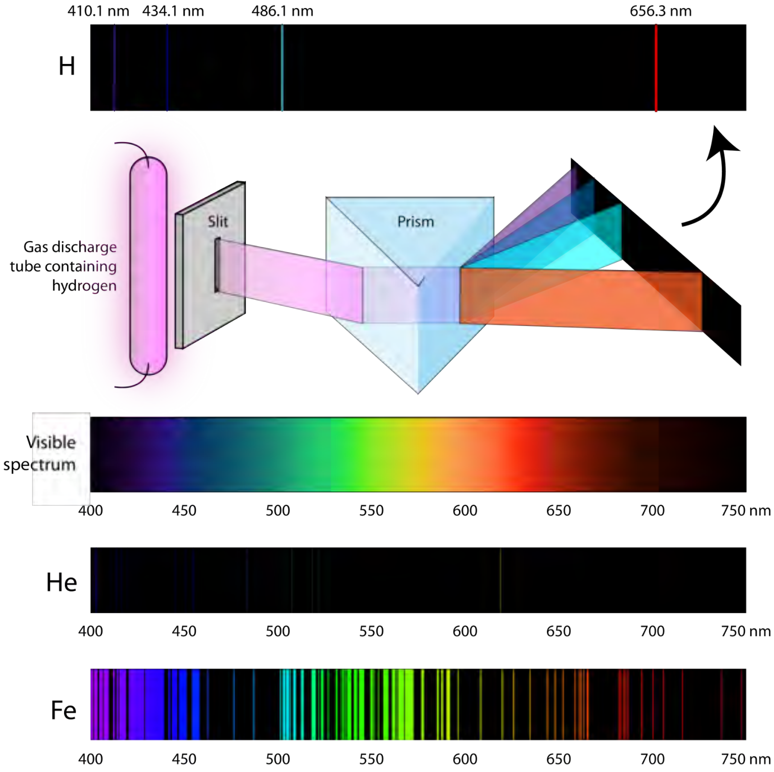


FIGURE 5.8

When light from a hydrogen gas discharge tube is passed through a prism, the light is split into four visible lines. Each of these spectral lines corresponds to a different electron transition from a higher energy state to a lower energy state. Every element has a unique atomic emission spectrum, as shown by the examples of mercury (Hg) and strontium (Sr).

Classical theory was unable to explain the existence of atomic emission spectra, also known as line-emission spectra. According to classical physics, a ground state atom would be able to absorb any amount of energy rather than only discrete amounts. Likewise, when the atoms relaxed back to a lower energy state, any amount of energy could be released. This would result in what is known a **continuous spectrum**, where all wavelengths and frequencies are represented. White light viewed through a prism and a rainbow are examples of continuous spectra. Atomic emission spectra were more proof of the quantized nature of light and led to a new model of the atom based on quantum theory.

Summary

- Atomic emission spectra re produced when excited electrons return to ground state.
- The emitted light corresponds to energies of the specific electrons.

Practice

Use the link below to answer the following questions:

http://chemistry.bd.psu.edu/jircitano/periodic4.html

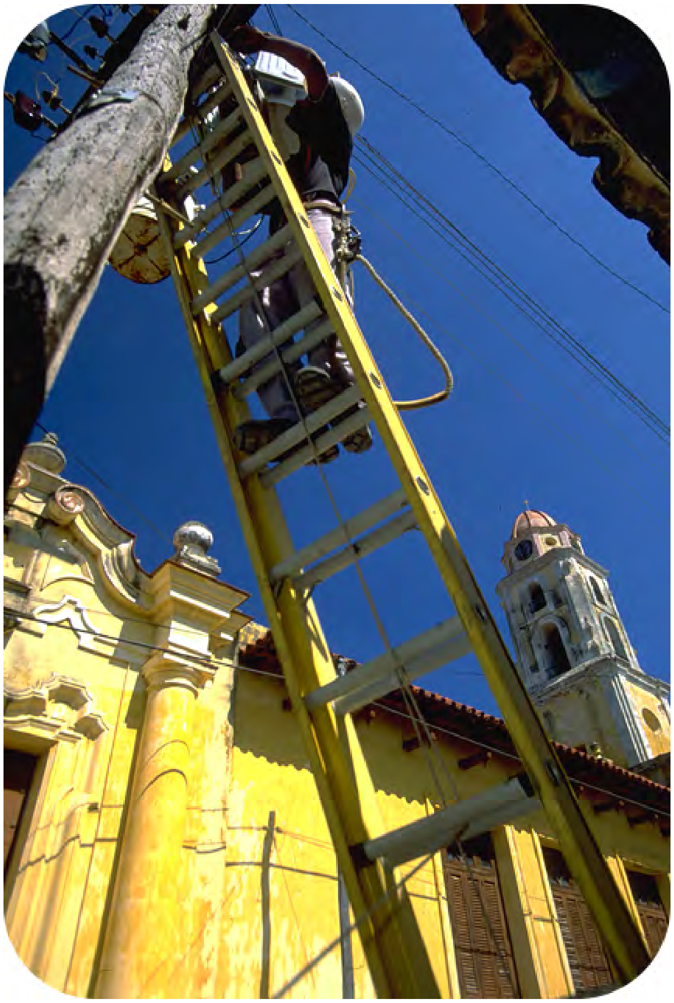
1. How many spectral lines are there for lithium?
2. How many spectral lines are there for beryllium?
3. Which element would you expect to have more lines: Na or Mg?

Review

1. What is the ground state of an atom?
2. What is an excited state?
3. Why do we see emission lines when electrons return to the ground state?

- **atomic emission spectrum:** The pattern of lines formed when light passes through a prism to separate it into the different frequencies of light it contains.
- **continuous spectrum:** All wavelengths of light are present.
- **excited state:** A state where the potential energy of the atom is higher than the ground state.
- **ground state:** The lowest energy state of the atom.

5.6 Bohr's Atomic Model



Climbing a ladder takes energy. At every step you are pushing yourself up against gravity, accumulating potential energy. Coming back down releases that potential energy as you descend step by step. If you are not careful, you can release that potential energy all at once when you fall off the ladder (never a good idea). In addition, you take the climb or descent in steps. There is no "in-between" position on the ladder – your foot either hits a rung or it hits empty space and you are in trouble until you find a rung to stand on.

Bohr's Atomic Model

Following the discoveries of hydrogen emission spectra and the photoelectric effect, the Danish physicist Niels Bohr (1885 – 1962) proposed a new model of the atom in 1915. Bohr proposed that electrons do not radiate energy as they orbit the nucleus, but exist in states of constant energy which he called **stationary states**, orbiting at fixed distances from the nucleus (see **Figure** 5.9). Bohr's work was primarily based on the emission spectra of hydrogen. This is also referred to as the planetary model of the atom. It explained the inner workings of the hydrogen atom. Bohr was awarded the Nobel Prize in physics in 1922 for his work.

Bohr explained that electrons can be moved into different orbits with the addition of energy. When the energy is removed, the electrons return back to their ground state, emitting a corresponding amount of energy – a quantum of

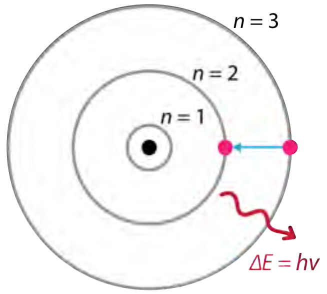


FIGURE 5.9

Bohr's atomic model hydrogen emission spectra.

light, or photon. This was the basis for what later became known as **quantum theory**. This is a theory based on the principle that matter and energy have the properties of both particles and waves. It accounts for a wide range of physical phenomena, including the existence of discrete packets of energy and matter, the uncertainty principle, and the exclusion principle.

According to the Bohr model, often referred to as a **planetary model**, the electrons encircle the nucleus of the atom in specific allowable paths called orbits. When the electron is in one of these orbits, its energy is fixed. The ground state of the hydrogen atom, where its energy is lowest, is when the electron is in the orbit that is closest to the nucleus. The orbits that are further from the nucleus are all of successively greater energy. The electron is not allowed to occupy any of the spaces in between the orbits. An everyday analogy to the Bohr model is the rungs of a ladder. As you move up or down a ladder, you can only occupy specific rungs and cannot be in the spaces in between rungs. Moving up the ladder increases your potential energy, while moving down the ladder decreases your energy.

Bohr's work had a strong influence on our modern understanding of the inner workings of the atom. However, his model worked well for an explanation for the emissions of the hydrogen atom, but 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.

Summary

- The Bohr model postulates electrons orbiting the nucleus at fixed energy levels.
- Orbits further from the nucleus exist at higher energy levels.
- When electrons return to a lower energy level, they emit energy in the form of light.

Practice

Use the link below to answer the following questions:

http://www.universetoday.com/46886/bohrs-atomic-model/

1. How does an electron change orbits?
2. What was the Bohr model based on?
3. What did Bohr believe about the orbits?
4. Does Bohr's model work for all atoms?

Review

1. When did Bohr propose his model of the atom?
2. What is a stationary state?
3. What is the ground state?

4. Can the electron occupy any space between the orbits?

- **planetary model:** A way to describe Bohr's model of the atom.
- **quantum theory:** Matter and energy have the properties of both particles and waves.
- **stationary state:** Electrons orbit at fixed distance from the nucleus.

5.7 Spectral Lines of Hydrogen

- List the electron transition lines according to energy levels.
- Explain the presence of emission lines and relate them to electron transitions

It's not as common any more, but there was a time when many people could work on their own cars if there was a problem. Today, engines are computerized and require specialized training and tools in order to be fixed. When people did their own repairs, it was sometimes a trial and error process. Maybe the parks plugs needed to be replaced. No, that didn't fix the problem completely, but it was a start in the right direction. Science operates the same way. A theory is developed that works for a while, but then there are data that the theory cannot explain. Then it's time for a newer and more inclusive theory.

Spectral Lines of Hydrogen

Bohr's model explains the spectral lines of the hydrogen atomic emission spectrum. While the electron of the atom remains in the ground state, its energy is unchanged. When the atom absorbs one or more quanta of energy, the electron moves from the ground state orbit to an excited state orbit that is further away. Energy levels are designated with the variable n. The ground state is $n = 1$, the first excited state is $n = 2$, and so on. The energy that is gained by the atom is equal to the difference in energy between the two energy levels. When the atom relaxes back to a lower energy state, it releases energy that is again equal to the difference in energy of the two orbits (see **Figure** 5.10).

The change in energy, ΔE, then translates to light of a particular frequency being emitted according to the equation $E = h\nu$. Recall that the atomic emission spectrum of hydrogen had spectral lines consisting of four different frequencies. This is explained in the Bohr model by the realization that the electron orbits are not equally spaced. As the energy increases further and further from the nucleus, the spacing between the levels gets smaller and smaller.

Based on the wavelengths of the spectral lines, Bohr was able to calculate the energies that the hydrogen electron would have in each of its allowed energy levels. He then mathematically showed which energy level transitions corresponded to the spectral lines in the atomic emission spectrum (**Figure** 5.11).

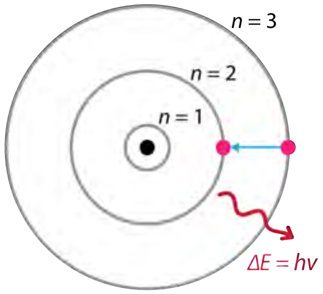


FIGURE 5.10

Bohr model of the atom: electron is shown transitioning from the n = 3 energy level to the n = 2 energy level. The photon of light that is emitted has a frequency that corresponds to the difference in energy between the two levels.

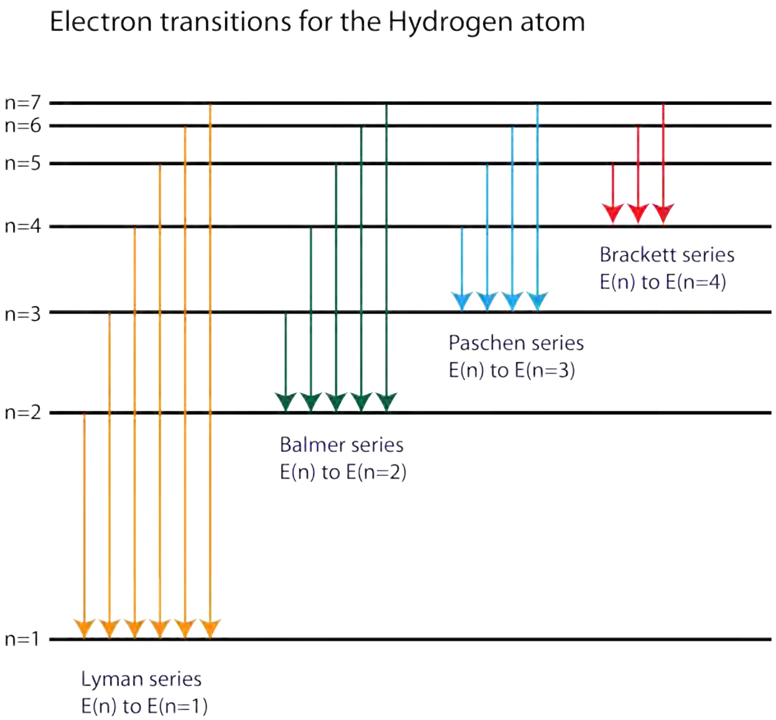


FIGURE 5.11

The electron energy level diagram for the hydrogen atom.

He found that the four visible spectral lines corresponded to transitions from higher energy levels down to the second energy level $(n = 2)$. This is called the Balmer series. Transitions ending in the ground state $(n = 1)$ are called the Lyman series, but the energies released are so large that the spectral lines are all in the ultraviolet region of the spectrum. The transitions called the Paschen series and the Brackett series both result in spectral lines in the infrared region because the energies are too small.

Bohr's model was a tremendous success in explaining the spectrum of the hydrogen atom. Unfortunately, when the mathematics of the model was applied to atoms with more than one electron, it was not able to correctly predict the frequencies of the spectral lines. While Bohr's model represented a great advancement in the atomic model and the concept of **electron transitions** between energy levels is valid, improvements were needed in order to fully understand all atoms and their chemical behavior.

Summary

- Emission lines for hydrogen correspond to energy changes related to electron transitions.
- The Bohr model works only for the hydrogen atom.

Practice

Use the link below to answer the following questions:

http://www.chemguide.co.uk/atoms/properties/hspectrum.html

1. How many volts can be used to generate a hydrogen line spectrum?
2. Can you see the Lyman series with the naked eye?
3. Which series can we at least partially see?
4. What happens to the hydrogen gas in a discharge tube?

Review

1. What happens when a hydrogen atoms absorbs one or more quanta of energy?
2. How do we detect the change in energy?
3. What electron transitions are presented by the lines of the Paschen series?
4. Does the Bohr model work for atoms other than hydrogen?

- **electron transition:** Movement of an electron from one energy level to another.

5.8 de Broglie Wave Equation

- State the de Broglie wave equation.
- Use this equation to calculate the wavelength of a moving object.

Bohr's model of the atom was valuable in demonstrating how electrons were capable of absorbing and releasing energy and how atomic emission spectra were created. However, the model did not really explain why electrons should exist only in fixed circular orbits rather than being able to exist in a limitless number of orbits all with different energies. In order to explain why atomic energy states are quantized, scientists needed to rethink the way in which they viewed the nature of the electron and its movement.

de Broglie Wave Equation

Planck's investigation of the emission spectra of hot objects and the subsequent studies into the photoelectric effect had proven that light was capable of behaving both as a wave and as a particle. It seemed reasonable to wonder if electrons could also have a dual wave-particle nature. In 1924, French scientist Louis de Broglie (1892-1987) derived an equation that described the wave nature of any particle. Particularly, the wavelength (λ) of any moving object is given by:

$$\lambda = \frac{h}{mv}$$

In this equation, h is Planck's constant, m is the mass of the particle in kg, and v is the velocity of the particle in m/s. The problem below shows how to calculate the wavelength of the electron.

Sample Problem: de Broglie Wave Equation

An electron of mass 9.11×10^{-31} kg moves at nearly the speed of light. Using a velocity of 3.00×10^{8} m/s, calculate the wavelength of the electron.

Step 1: List the known quantities and plan the problem.

Known

- mass $(m) = 9.11 \times 10^{-31}$ kg
- Planck's constant $(h) = 6.6262\ \ 10^{-34} \times \mathrm{J} \bullet \mathrm{s}$
- velocity $(v) = 3.00 \times 10^{8}$ m/s

Unknown

- wavelength (λ)

Apply the **de Broglie wave equation** $\lambda = \frac{h}{mv}$ to solve for the wavelength of the moving electron.

Step 2: Calculate

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}\ \mathrm{J \cdot s}}{(9.11 \times 10^{-31}\ \mathrm{kg}) \times (3.00 \times 10^{8}\ \mathrm{m/s})} = 2.42 \times 10^{-12}\ \mathrm{m}$$

Step 3: Think about your result.

This very small wavelength is about 1/20th of the diameter of a hydrogen atom. Looking at the equation, as the speed of the electron decreases, its wavelength increases. The wavelengths of everyday large objects with much greater masses should be very small.

If we were to calculate the wavelength of a 0.145 kg baseball thrown at a speed of 40 m/s, we would come up with an extremely short wavelength on the order of 10^{-34} m. This wavelength is impossible to detect even with advanced scientific equipment. Indeed, while all objects move with wavelike motion, we never notice it because the wavelengths are far too short. On the other hand, particles with measurable wavelengths are all very small. However, the wave nature of the electron proved to be a key development in a new understanding of the nature of the electron. An electron that is confined to a particular space around the nucleus of an atom can only move around that atom in such a way that its electron wave "fits" the size of the atom correctly. This means that the frequencies of electron waves are **quantized**. Based on the $E = hv$ equation, the quantized frequencies means that electrons can only exist in an atom at specific energies, as Bohr had previously theorized.

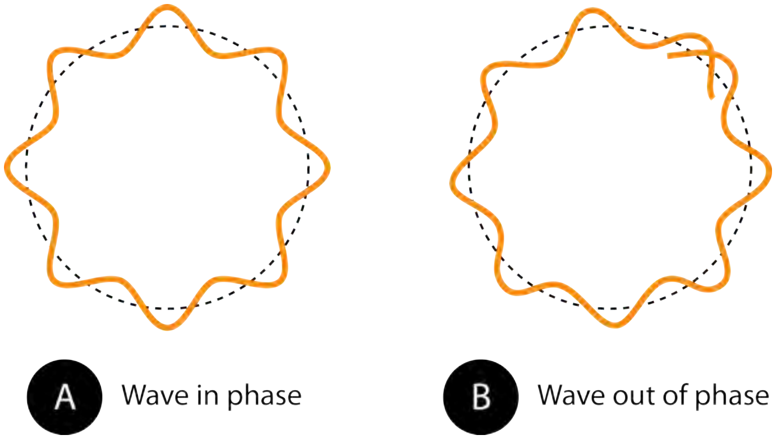


FIGURE 5.12

The circumference of the orbit in (A) allows the electron wave to fit perfectly into the orbit. This is an allowed orbit. In (B), the electron wave does not fit properly into the orbit, so this orbit is not allowed.

Summary

- The deBroglie wave equations allows calculation of the wavelength of any moving object.
- As the speed of the electron decreases, its wavelength increases.

Practice

Use the link below to practice calculations using the deBroglie wave equation:

http://science.widener.edu/svb/tutorial/debrogliecsn7.html

Review

1. What did the Bohr model not explain?
2. State the deBroglie wave equation.
3. What happens as the speed of the electron decreases?

- **de Broglie wave equation:** $\lambda = \frac{h}{mv}$.
- **quantize:** Limit the possible values of (a magnitude or quantity) to a discrete set of values by quantum mechanical rules.

5.9 Quantum Mechanics

How do you study something that seemingly makes no sense? We talk about electrons being in orbits and it sounds like we can tell where that electron is at any moment. We can draw pictures of electrons in orbit, but the reality is that we just don't know exactly where they are. We are going to take a quick look at an area of science that even leaves scientists puzzled. When asked about quantum mechanics, Niels Bohr (who proposed the Bohr model of the atom) said: "Anyone who is not shocked by quantum theory has not understood it". Richard Feynman (one of the founders of modern quantum theory) stated: "I think I can safely say that nobody understands quantum theory". So, let's take a short trip into a land that challenges our every-day world.

Quantum Mechanics

The study of motion of large objects such as baseballs is called mechanics, or more specifically classical mechanics. Because the quantum nature of the electron and other tiny particles moving at high speeds, classical mechanics is inadequate to accurately describe their motion. **Quantum mechanics** is the study of the motion of objects that are atomic or subatomic in size and thus demonstrate wave-particle duality. In classical mechanics, the size and mass of the objects involved effectively obscures any quantum effects so that such objects appear to gain or lose energies in any amounts. Particles whose motion is described by quantum mechanics gain or lose energy in the small pieces called **quanta**.

One of the fundamental (and hardest to understand) principles of quantum mechanics is that the electron is both a particle and a wave. In the everyday macroscopic world of things we can see, something cannot be both. But this duality can exist in the quantum world of the submicroscopic at the atomic scale.

At the heart of quantum mechanics is the idea that we cannot specify accurately the location of an electron. All we can say is that there is a probability that it exists within this certain volume of space. The scientist Erwin Schrödinger developed an equation that deals with these calculations, which we will not pursue at this time.

FIGURE 5.13

Erwin Schrödinger

Summary

- Quantum mechanics involves the study of material at the atomic level.
- This field deals with probabilities since we cannot definitely locate a particle.

Practice

Use the link below to answer the following questions:

http://www.nobelprize.org/nobel_prizes/physics/laureates/1933/schrodinger-bio.html

1. What were the scientific interests of Schrödinger's father?
2. When did Schrödinger discover his wave equation?
3. What award did he receive for this work?
4. In what other areas did Schrödinger carry out research?

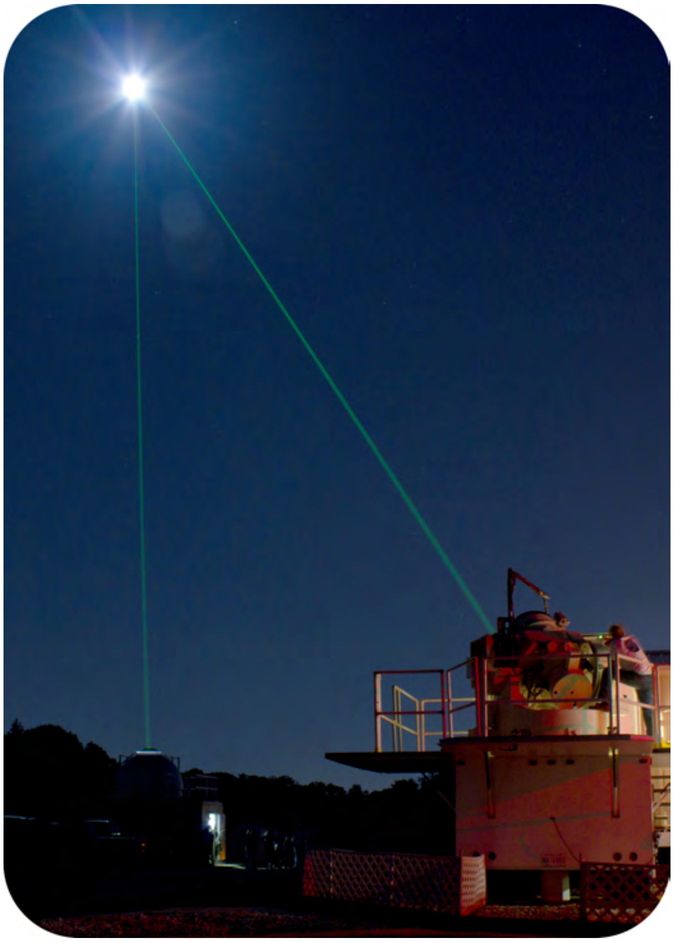
Review

1. What does quantum mechanics deal with?
2. How would you describe an electron?
3. What did Schrödinger demonstrate about the location of a particle?

- **quanta:** Plural of quantum, smallest amount of energy that can exist independently.
- **quantum mechanics:** The study of the motion of objects that are atomic or subatomic in size and thus demonstrate wave-particle duality.

5.10 Heisenberg Uncertainty Principle

- State the Heisenberg Uncertainty Principle.



Lasers are finding numerous applications outside the physics lab. These devices can be employed to measure distances accurately and many commercial instruments are used in construction for laying out a building site. When the light beam strikes a solid object, it is reflected back and the device determines how far away the object is. There is such a significant difference between the mass of the light beam (photons) and the mass of the object, the beam does not disturb the object at all. One measurement of interest was the use of a laser to measure the distance from the Earth to the moon (see figure above). The impact of the photons from the laser on the moon had absolutely no effect on the moon's orbit.

Heisenberg Uncertainty Principle

Another feature that is unique to quantum mechanics is the uncertainty principle. The **Heisenberg Uncertainty Principle** states that it is impossible to determine simultaneously both the position and the velocity of a particle. The detection of an electron, for example, would be made by way of its interaction with photons of light. Since photons and electrons have nearly the same energy, any attempt to locate an electron with a photon will knock the electron off course, resulting in uncertainty about where the electron is located (see **Figure** 5.14). We do not have to worry about the uncertainty principle with large everyday objects because of their mass. If you are looking for something with a flashlight, the photons coming from the flashlight are not going to cause the thing you are looking for to move. This is not the case with atomic-sized particles, leading scientists to a new understanding about how to envision the location of the electrons within atoms.

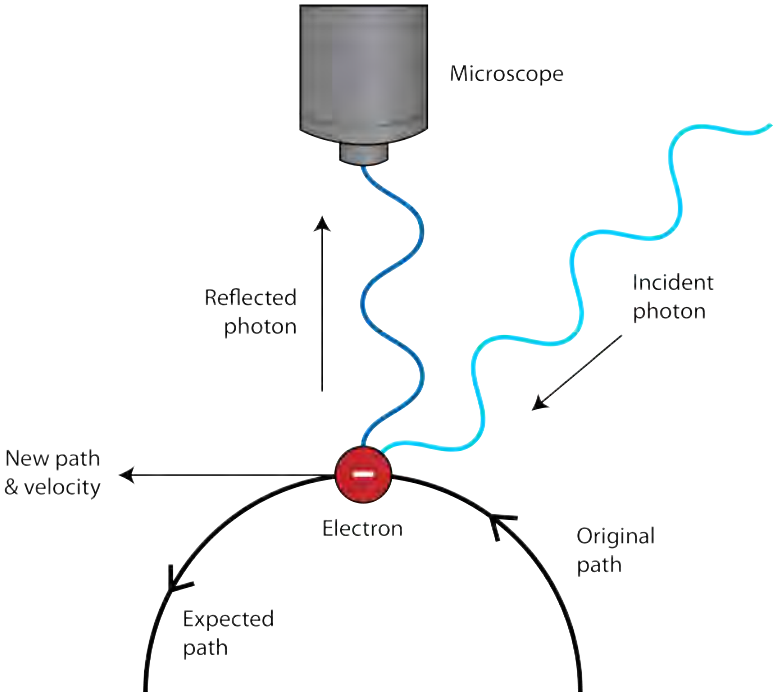


FIGURE 5.14

Heisenberg Uncertainty Principle: The observation of an electron with a microscope requires reflection of a photon off of the electron. This reflected photon causes a change in the path of the electron.

Summary

- The Heisenberg Uncertainty principle explains why we cannot simultaneously determine both the precise velocity and position of a particle.
- This principle is only applicable at the atomic level.

Practice

Use the link below to answer the following questions:

1. When did Heisenberg get his Ph.D?
2. What idea of Niels Bohr did Heisenberg disprove?
3. When did he win his Nobel Prize?

Review

1. Why is the Heisenberg Uncertainty Principle true at the atomic level?
2. Is the principle valid at the macroscopic level?

- **Heisenberg Uncertainty Principle:** It is impossible to determine simultaneously both the position and the velocity of a particle.

5.11 Quantum Mechanical Atomic Model

The news flash interrupts your favorite TV program. “There has been a hold-up at the First National Bank. The suspect fled in a car and is believed to be somewhere in the downtown district. Everyone is asked to be on the alert.” The robber can be located only within a certain area – the police do not have an exact location, just a general idea as to the where abouts of the thief.

Quantum Mechanical Atomic Model

In 1926, Austrian physicist Erwin Schrödinger (1887-1961) used the wave-particle duality of the electron to develop and solve a complex mathematical equation that accurately described the behavior of the electron in a hydrogen atom. **The quantum mechanical model** of the atom comes from the solution to Schrödinger’s equation. Quantization of electron energies is a requirement in order to solve the equation. This is unlike the Bohr model, in which quantization was simply assumed with no mathematical basis.

Recall that in the Bohr model, the exact path of the electron was restricted to very well-defined circular orbits around the nucleus. The quantum mechanical model is a radical departure from that. Solutions to the Schrödinger wave equation, called **wave functions**, give only the probability of finding an electron at a given point around the nucleus. Electrons do not travel around the nucleus in simple circular orbits.

The location of the electrons in the quantum mechanical model of the atom is often referred to as an **electron cloud**. The electron cloud can be thought of in the following way. Imagine placing a square piece of paper on the floor with a dot in the circle representing the nucleus. Now take a marker and drop it onto the paper repeatedly, making small marks at each point the marker hits. If you drop the marker many, many times, the overall pattern of dots will be roughly circular. If you aim toward the center reasonably well, there will be more dots near the nucleus and progressively fewer dots as you move away from it. Each dot represents a location where the electron could be at any given moment. Because of the uncertainty principle, there is no way to know exactly where the electron is. An electron cloud has variable densities: a high density where the electron is most likely to be and a low density where the electron is least likely to be (**Figure** 5.15).

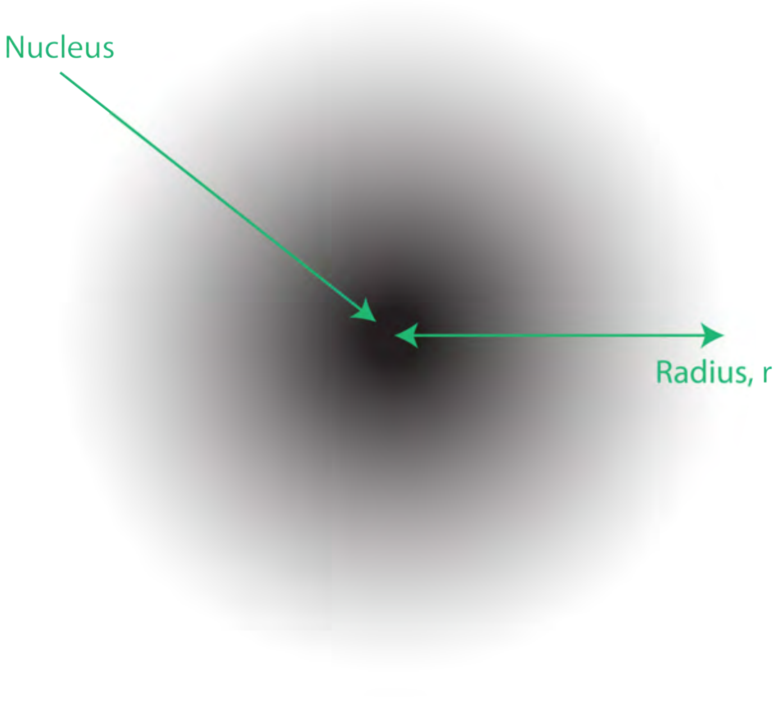


FIGURE 5.15

An electron cloud: the darker region nearer the nucleus indicates a high probability of finding the electron, while the lighter region further from the nucleus indicates a lower probability of finding the electron.

In order to specifically define the shape of the cloud, it is customary to refer to the region of space within which there is a 90% probability of finding the electron. This is called an **orbital**, the three-dimensional region of space that indicates where there is a high probability of finding an electron.

Summary

- The Schrödinger wave equation replaced the Bohr ideas about electron location with an uncertainty factor.
- The location of the electron can only be given as a probability that the electron is somewhere in a certain area.

Practice

Use the link below to answer the following questions:

http://science.howstuffworks.com/atom8.htm

1. What was one problem with the Bohr model of the atom?
2. What did Heisenberg show about electrons?
3. What did Schrödinger derive?

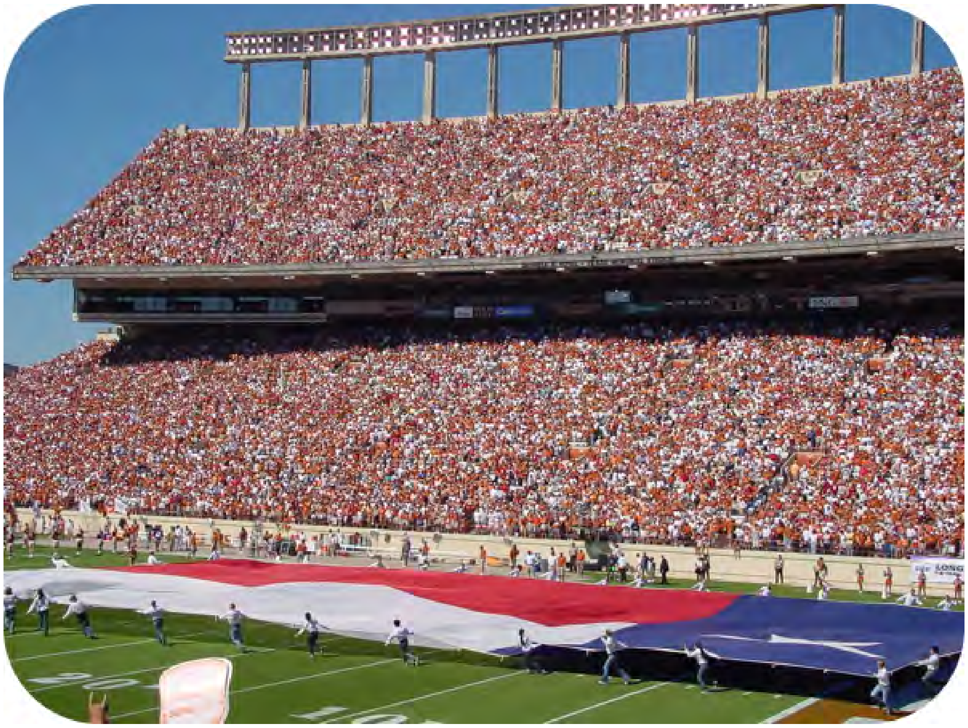
Review

1. What does the quantum mechanical view of the atom require?
2. What is a wave function?
3. What does a high density electron cloud suggest?

- **electron cloud:** The location of the electrons in the quantum mechanical model of the atom.
- **orbital:** The three-dimensional region of space that indicates where there is a high probability of finding an electron.
- **quantum mechanical model:** A model of the atom that derives from the Schrödinger wave equation and deals with probabilities.
- **wave function:** Give only the probability of finding an electron at a given point around the nucleus.

5.12 Quantum Numbers

- Define the four quantum numbers.
- Determine quantum numbers for specific electrons when given appropriate data.



If you attend a college or professional football game, you need a ticket to get in. It is very likely that your ticket may specify a gate number, a section number, a row, and a seat number. No other ticket can have the same four parts to it. It may have the same gate, section, and seat number, but it would have to be in a different row. Each seat is unique and allows only one occupant to fill it.

Quantum Numbers

We use a series of specific numbers, called **quantum numbers**, to describe the location of an electron in an associated atom. Quantum numbers specify the properties of the atomic orbitals and the electrons in those orbitals. 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. Energy levels are fixed distances from the nucleus of a given atom. They are described in whole number increments (e.g., 1, 2, 3, 4, 5, 6, ...). At location $n = 1$, an electron would be closest to the nucleus, while $n = 2$ the electron would be farther, and $n = 3$ farther yet. As we will see, the principal quantum number corresponds to the row number for an atom on the periodic table.

Angular Momentum Quantum Number (l)

The **angular momentum quantum number**, signified as (l), describes the general shape or region an electron occupies – its orbital shape. The value of l depends on the value of the principle quantum number n. The angular momentum quantum number can have positive values of zero to $(n-1)$. If $n=2$, l could be either 0 or 1.

Magnetic Quantum Number (m_l)

The **magnetic quantum number**, signified as (m_l), describes the orbital orientation in space. Electrons can be situated in one of three planes in three dimensional space around a given nucleus $(x, y$, and $z)$. For a given value of the angular momentum quantum number l, there can be $(2l+1)$ values for m_l. As an example:

$n=2$

$l=0$ or 1

for $l=0,\ m_l=0$

for $l=1,\ m_l=-1,\ 0,\ +1$

TABLE 5.1: Principal Energy Levels and Sublevels

Principal energy level	**Number of possible sub-levels**	**Possible Angular Momentum Quantum Numbers**	**Orbital Designation by Principal Energy Level and Sublevel**
$n=1$	1	$l=0$	1*s*
$n=2$	2	$l=0$ $l=1$	2*s* 2*p*
$n=3$	3	$l=0$ $l=1$ $l=2$	3*s* 3*p* 3*d*
$n=4$	4	$l=0$ $l=1$ $l=2$ $l=3$	4*s* 4*p* 4*d* 4*f*

The table above shows the possible magnetic quantum number values (m_l) for the corresponding angular momentum quantum numbers (l) of $l=0,\ l=1,\ l=2$, and $l=3$.

Spin Quantum Number (m_s)

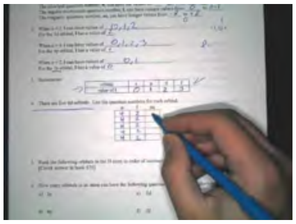
The **spin quantum number** describes the spin for a given electron. An electron can have one of two associated spins, $\left(+\frac{1}{2}\right)$ spin, or $\left(-\frac{1}{2}\right)$ spin. An electron cannot have zero spin. We also represent spin with arrows $\uparrow$ or $\downarrow$. A single orbital can hold a maximum of two electrons and each must have opposite spin.

Summary

- Quantum numbers specify the arrangements of electrons in orbitals.
- There are four quantum numbers that provide information about various aspects of electron behavior.

Practice

Watch the video, pause at each question and try to calculate the quantum number before you see the answer written in. Do not try to answer the orbital questions, just the quantum number ones.



MEDIA

Click image to the left for more content.

http://www.youtube.com/watch?v=DvlfMO3QlQw

Review

1. What do quantum numbers do?
2. What is the principal quantum number?
3. What does the spin quantum number represent?

- **angular momentum quantum number** (l)**:** Describes the general region occupied by the electron.
- **magnetic quantum number** (m)**:** Describes the orbital orientation of the electron in space.
- **principal quantum number** (n)**:** Specifies the main energy level occupied by the electron.
- **quantum numbers:** Describe the location of an electron in an atom.
- **spin quantum number** (m_s)**:** Describes the spin for a given electron.

5.13 Orbitals

- Draw the shapes of s, p, d, and f orbitals.
- Relate the four quantum numbers for an electron to a specific orbital.

The flight path of a commercial airliner is carefully regulated by the Federal Aviation Administration. Each airplane must maintain a distance of five miles from another plane flying at the same altitude and 2,000 feet above and below another aircraft (1,000 feet if the altitude is less than 29,000 feet). So, each aircraft only has certain positions it is allowed to maintain while it flies. As we explore quantum mechanics, we see that electrons have similar restrictions on their locations.

Orbitals

We can apply our knowledge of quantum numbers to describe the arrangement of electrons for a given atom. We do this with something called **electron configurations**. They are effectively a map of the electrons for a given atom. We look at the four quantum numbers for a given electron and then assign that electron to a specific orbital.

s Orbitals

For any value of n, a value of $l = 0$ places that electron in an **s orbital**. This orbital is spherical in shape:

p Orbitals

From the table below we see that we can have three possible orbitals when $l = 1$. These are designated as **p orbitals** and have dumbbell shapes. Each of the p orbitals has a different orientation in three-dimensional space.

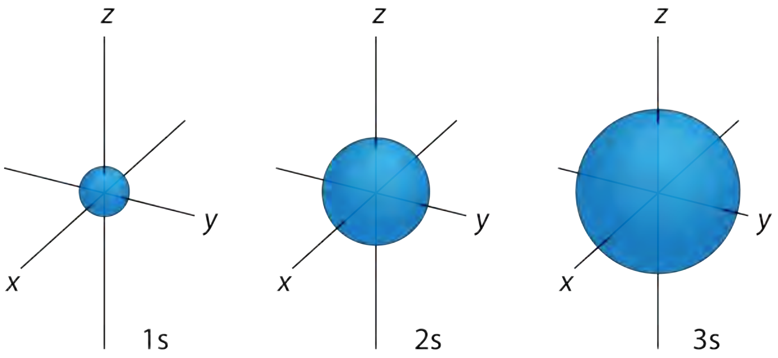


FIGURE 5.16
s orbital

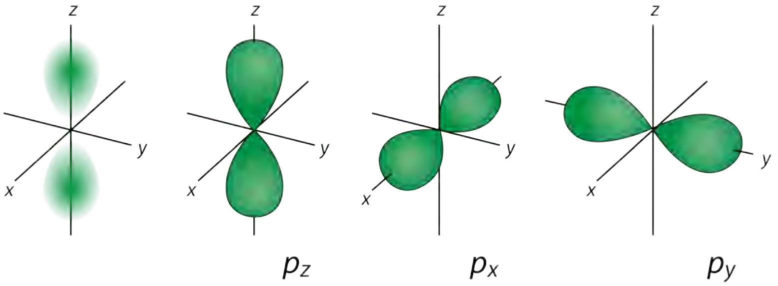


FIGURE 5.17
p orbital – general shape and configuration of individual p orbitals.

d Orbitals

When $l = 2$, m_l values can be -2, -1, 0, +1, +2 for a total of five **d orbitals**. Note that all five of the orbitals have specific three-dimensional orientations.

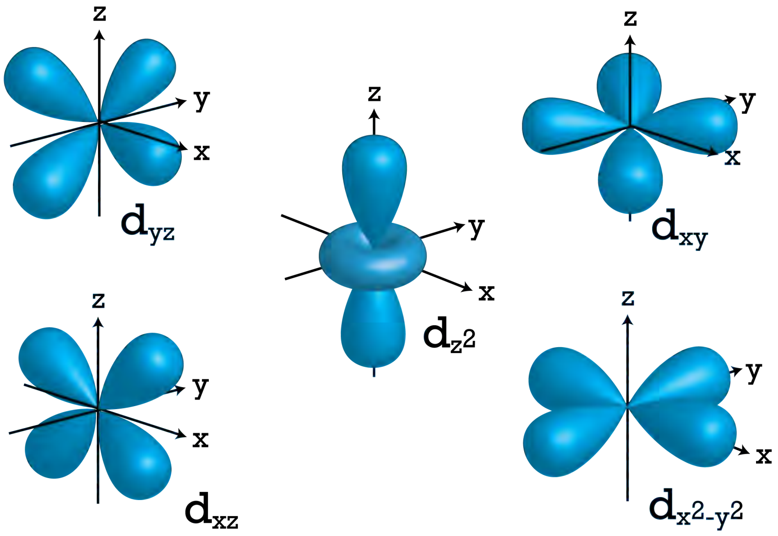


FIGURE 5.18
Geometry of d orbitals.

f Orbitals

The most complex set of orbitals are the **f orbitals**. When $l = 3$, m_l values can be -3, -2, -1, 0, +1, +2, +3 for a total of seven different orbital shapes. Again, note the specific orientations of the different f orbitals.

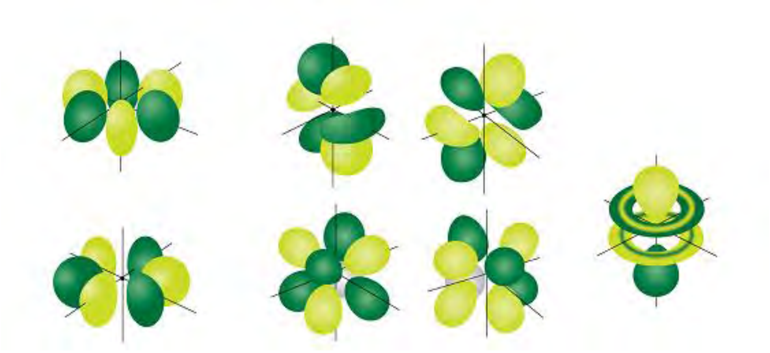


FIGURE 5.19

Geometry of f orbitals.

TABLE 5.2: Electron Arrangement Within Energy Levels

Principal Quantum Number (n)	Allowable Sub-levels	Number of Orbitals per Sub-level	Number of Orbitals per Principal Energy Level	Number of Electrons per Sublevel	Number of Electrons per Principal Energy Level
1	*s*	1	1	2	2
2	*s* *p*	1 3	4	2 6	8
3	*s* *p* *d*	1 3 5	9	2 6 10	18
4	*s* *p* *d* *f*	1 3 5 7	16	2 6 10 14	32

Summary

- There are four different classes of electron orbitals.
- These orbitals are determined by the value of the angular momentum quantum number l.

Practice

Use the link below to answer the following questions:

http://www.chem4kids.com/files/atom_orbital.html

1. What is a shell?
2. What do the letters K-Q stand for?
3. How many electrons does the K shell hold?

4. What is the maximum number of electrons any shell can hold?

Review

1. What is an electron configuration?
2. How many electrons are in the $n = 1$ orbital?
3. What is the total number of electrons in a p orbital?
4. How many electrons does it take to completely fill a d orbital?

- **electron configuration:** A map of the electrons for a given atom.
- **d orbital:** Five orbitals characterized by $l = 2$.
- **f orbitals:** The most complex set of orbitals with seven orbital shapes for $l = 3$.
- **p orbitals:** Three dumbbell shaped orbitals for $l = 1$.
- **s orbitals:** Spherical orbitals where $l = 0$.

5.14 Aufbau Principle

- State the Aufbau principle.
- Use the Aufbau principle to determine the electron configuration of an atom.

Construction of a building begins at the bottom. The foundation is laid and the building goes up step by step. You obviously cannot start with the roof since there is no place to hang it on. The building goes from the lowest level to the highest in a systematic way.

Aufbau Principle

In order to create ground state electron configurations for any element, it is necessary to know the way in which the atomic sublevels are organized in order of increasing energy. The **Figure** 5.20 shows the order of increasing energy of the 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 proceed with atoms with multiple electrons, those electrons are added to the next lowest sublevel: $2s$, $2p$, $3s$, and so on. The **Aufbau principle** states that an electron occupies orbitals in order from lowest energy to highest. The Aufbau (German: "building up, construction") 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 and that this method is merely an aid for us to understand the end result.

As seen in the **Figure** 5.20, 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 and thus fills first. Following the filling of

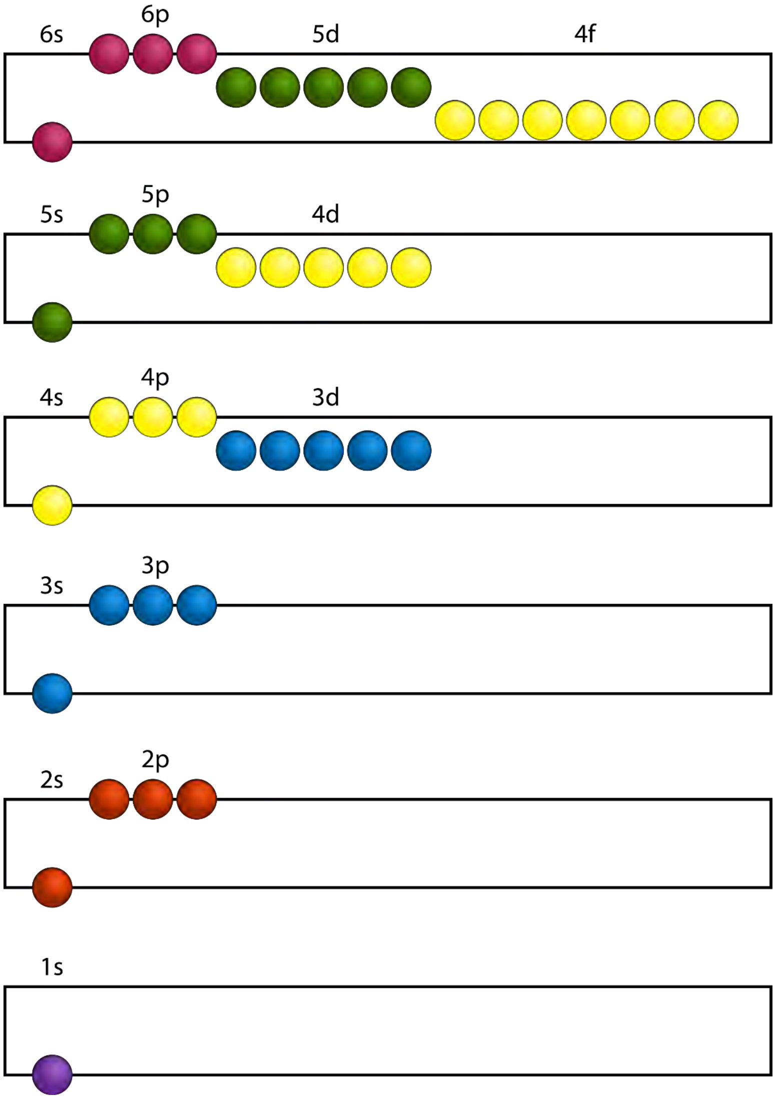


FIGURE 5.20
Electrons are added to atomic orbitals in order from low energy (bottom of graph) to high (top of graph) according to the Aufbau principle. Principal energy levels are color coded, while sublevels are grouped together and each circle represents an orbital capable of holding two electrons.

the $3d$ sublevel is the $4p$, then the $5s$ and the $4d$. Note that the $4f$ sublevel does not fill until just after the $6s$ sublevel. The **Figure** 5.21 is a useful and simple aid for keeping track of the order of fill of the atomic sublevels.

Summary

- The Aufbau principle gives the order of electron filling in an atom.
- It can be used to describe the locations and energy levels of every electron in a given atom.

Practice

Use the link below to answer the following questions:

http://ths.talawanda.net/ BrambleN/classroom/Chemistry/Notes/Section%202A/Exceptions&Shortcut.htm

1. Do the electrons in all atoms follow the Aufbau rule?
2. What happens to electrons in copper to make the atom more stable?
3. How does silver become more stable?

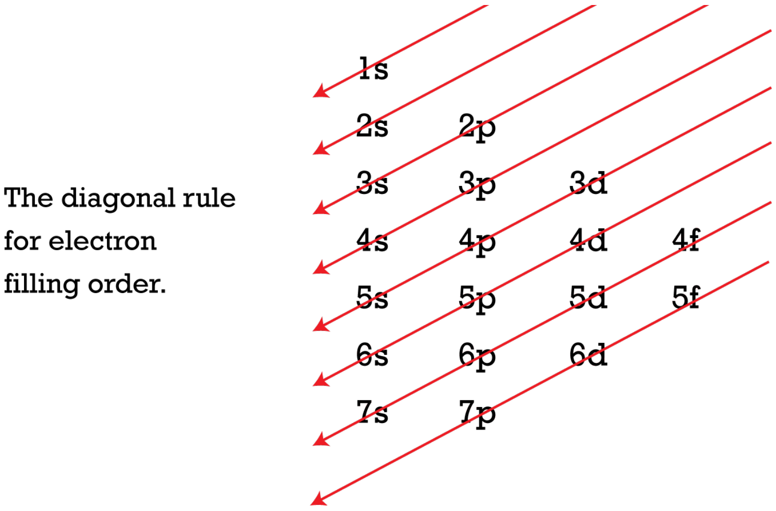


FIGURE 5.21

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

Review

1. What is the Aufbau principle?
2. Which orbital is filled after the $2p$?
3. Which orbital is filled after $4s$?
4. Which orbital is filled after $6s$?

- **Aufbau principle:** An electron occupies orbitals in order from lowest energy to highest.

5.15 Pauli Exclusion Principle

- State the Pauli exclusion principle.

Can you name one thing that easily distinguishes you from the rest of the world?

And we're not talking about DNA – that's a little expensive to sequence. For many people, it is their email address. My email address allows people all over the world to contact me. It does not belong to anyone else, but serves to identify me. Electrons also have a unique set of identifiers in the quantum numbers that describe their location and spin.

Pauli Exclusion Principle

When we look at the orbital possibilities for a given atom, we see that there are different arrangements of electrons for each different type of atom. Since each electron must maintain its unique identity, we intuitively sense that the four quantum numbers for any given electron must not match up exactly with the four quantum numbers for any other electron in that atom.

For the hydrogen atom, there is no problem since there is only one electron in the H atom. However, when we get to helium we see that the first three quantum numbers for the two electrons are the same: same energy level, same spherical shape. What differentiates the two helium electrons is their spin. One of the electrons has $a+\frac{1}{2}$ spin while the other electron has $a-\frac{1}{2}$ spin. So the two electrons in the 1s orbital are each unique and distinct from one another because their spins are different. This observation leads to the **Pauli exclusion principle**, which states that no two electrons in an atom can have the same set of four quantum numbers. The energy of the electron is specified by the principal, angular momentum, and magnetic quantum numbers. If those three numbers are identical for two electrons, the spin numbers must be different in order for the two electrons to be differentiated from one another. The two values of the spin quantum number allow each orbital to hold two electrons. The figure below shows how the electrons are indicated in a diagram.

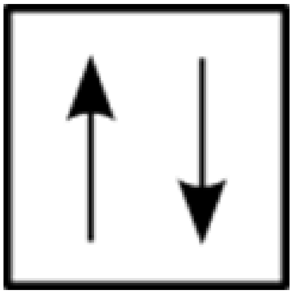


FIGURE 5.22

In an orbital filling diagram, a square represents an orbital, while arrows represent electrons. An arrow pointing upward represents one spin direction, while an arrow pointing downward represents the other spin direction.

Summary

- The Pauli exclusion principle specifies limits on how identical quantum numbers can be for two electrons in the same atom.

Practice

Use the link below to answer the following questions:

http://www.nobelprize.org/nobel_prizes/physics/laureates/1945/pauli-bio.html

1. When was Pauli born?
2. How old was he when he received his doctorate?
3. What was he the first to recognize?
4. When did he win his Nobel Prize in Physics?

Review

1. What is the difference between the two helium electrons?
2. What does the Pauli exclusion principle state?
3. What does the two values for the spin quantum number allow?

- **Pauli exclusion principle:** No two electrons in an atom can have the same set of four quantum numbers.

5.16 Hund's Rule and Orbital Filling Diagrams

- State Hund's rule.
- Apply Hund's rule to the filling of orbitals.
- Use orbital filling diagrams to describe the locations of electrons in an atom.

Have you ever wondered what those load limit signs mean on a bridge?

The sign above says that nothing over five tons is allowed because it will do damage to the structure. There are limits to the amount of weight that a bridge can support, there are limits to the number of people that can safely occupy a room, and here are limits to what can go into an electron orbital.

Hund's Rule

The last of the three rules for constructing electron arrangements requires electrons to be placed one at a time in a set of orbitals within the same sublevel. This minimizes the natural repulsive forces that one electron has for another. **Hund's rule** states that orbitals of equal energy are each occupied by one electron before any orbital is occupied by a second electron and that each of the single electrons must have the same spin. The **Figure** 5.23 shows how a set of three *p* orbitals is filled with one, two, three, and four electrons.

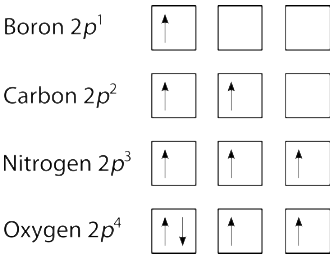


FIGURE 5.23

The 2p sublevel, for the elements boron (Z = 5), carbon (Z = 6), nitrogen (Z = 7), and oxygen (Z = 8). According to Hund's rule, as electrons are added to a set of orbitals of equal energy, one electron enters each orbital before any orbital receives a second electron.

Orbital Filling Diagrams

An **orbital filling diagram** is the more visual way to represent the arrangement of all the electrons in a particular atom. In an orbital filling diagram, the individual orbitals are shown as circles (or squares) and orbitals within a sublevel are drawn next to each other horizontally. Each sublevel is labeled by its principal energy level and sublevel. 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 in **Figure** 5.24.

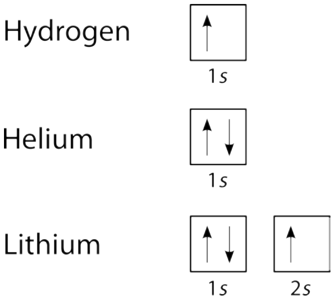


FIGURE 5.24

Orbital filling diagrams for hydrogen, helium, and lithium.

According to the Aufbau process, 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 is lithium and necessitates the use of the next available sublevel, the 2*s*.

The filling diagram for carbon is shown in the **Figure** 5.25. There are two 2*p* electrons for carbon and each occupies its own 2*p* orbital.

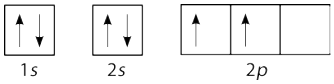


FIGURE 5.25

Orbital filling diagram for carbon.

Oxygen has four 2*p* electrons. After each 2*p* orbital has one electron in it, the fourth electron can be placed in the first 2*p* orbital with a spin opposite that of the other electron in that orbital.

Summary

- Hund's rule specifies the order of electron filling within a set of orbitals.
- Orbital filling diagrams are a way of indicating electron locations in orbitals.

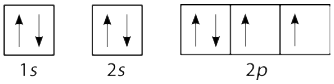


FIGURE 5.26

Orbital filling diagram for oxygen.

Practice

Use the link below to carry out the following exercise:

https://www.caymanchem.com/app/template/chemAssistant,Tool.vm/itemid/4001

1. Select an atom from the list (you will probably want to do lower atomic numbers). Leave the number set a zero.
2. Look up the atom on a periodic table and determine the number of electrons present.
3. Draw the orbital filling diagram for the atom.
4. Click on the "Calculate" button and compare your answer with the one provided.

Review

1. State Hund's rule.
2. What is an orbital filling diagram?
3. Is the diagram in the **Figure** 5.27correct? Explain your answer.

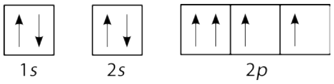


FIGURE 5.27

4. Is the diagram in the **Figure** 5.28correct? Explain your answer.

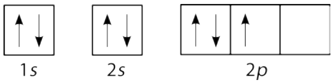
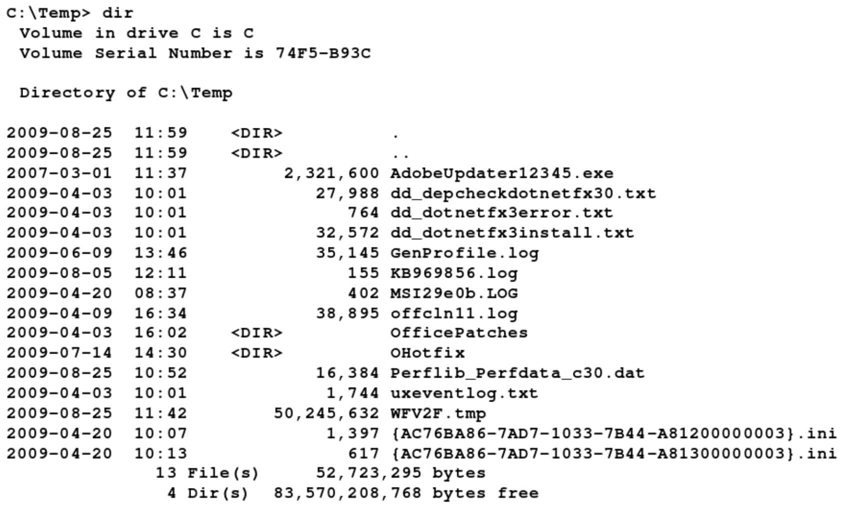


FIGURE 5.28

- **Hund's rule:** Orbitals of equal energy are each occupied by one electron before any orbital is occupied by a second electron and that each of the single electrons must have the same spin.
- **orbital filling diagram:** A visual way to represent the arrangement of all the electrons in a particular atom.

5.17 Electron Configurations

- Use electron configuration notation to indicate the electron configuration of an atom.



```
C:\Temp> dir
 Volume in drive C is C
 Volume Serial Number is 74F5-B93C

 Directory of C:\Temp

2009-08-25  11:59    <DIR>          .
2009-08-25  11:59    <DIR>          ..
2007-03-01  11:37         2,321,600 AdobeUpdater12345.exe
2009-04-03  10:01            27,988 dd_depcheckdotnetfx30.txt
2009-04-03  10:01               764 dd_dotnetfx3error.txt
2009-04-03  10:01            32,572 dd_dotnetfx3install.txt
2009-06-09  13:46            35,145 GenProfile.log
2009-08-05  12:11               155 KB969856.log
2009-04-20  08:37               402 MSI29e0b.LOG
2009-04-09  16:34            38,895 offcln11.log
2009-04-03  16:02    <DIR>          OfficePatches
2009-07-14  14:30    <DIR>          OHotfix
2009-08-25  10:52            16,384 Perflib_Perfdata_c30.dat
2009-04-03  10:01             1,744 uxeventlog.txt
2009-08-25  11:42        50,245,632 WFV2F.tmp
2009-04-20  10:07             1,397 {AC76BA86-7AD7-1033-7B44-A81200000003}.ini
2009-04-20  10:13               617 {AC76BA86-7AD7-1033-7B44-A81300000003}.ini
              13 File(s)     52,723,295 bytes
               4 Dir(s)  83,570,208,768 bytes free
```

How big is a file?

If you keep your papers in manila folders, you can pick up a folder and see how much it weighs. If you want to know how many different papers (articles, bank records, or whatever else you keep in a folder), you have to take everything out and count. A computer directory, on the other hand, tells you exactly how much you have in each file. We can get the same information on atoms. If we use an orbital filling diagram, we have to count arrows. When we look at electron configuration data, we simply add up the numbers.

Electron Configurations

Electron configuration notation eliminates the boxes and arrows of orbital filling diagrams. Each occupied sublevel designation is written followed by a superscript that is the number of electrons in that sublevel. For example, the hydrogen configuration is $1s^1$, while the helium configuration is $1s^2$. Multiple occupied sublevels are written one after another. The electron configuration of lithium is $1s^2 2s^1$. The sum of 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.

Sample Problem: Orbital Filling Diagrams and Electron Configurations

Draw the orbital filling diagram for carbon and write its electron configuration.

Step 1: List the known quantities and plan the problem.

Known

- atomic number of carbon, Z = 6

Use the order of fill diagram to draw an orbital filling diagram with a total of six electrons. Follow Hund's rule. Write the electron configuration.

Step 2: Construct Diagram

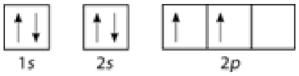


FIGURE 5.29

Orbital filling diagram for carbon.

Electron configuration $1s^2 2s^2 2p^2$

Step 3: Think about your result.

Following the $2s$ sublevel is the $2p$, and p sublevels always consist of three orbitals. All three orbitals need to be drawn even if one or more is unoccupied. According to Hund's rule, the sixth electron enters the second of those p orbitals and with the same spin as the fifth electron.

Second Period Elements

Periods refer to the horizontal rows of the periodic table. Looking at a periodic table you will see that the first period contains only the elements hydrogen and helium. This is because the first principal energy level consists of only the s sublevel and so only two electrons are required in order to fill the entire principal energy level. Each time a new principal energy level begins, as with the third element lithium, a new period is started on the periodic table. As one moves across the second period, electrons are successively added. With beryllium (Z = 4), the $2s$ sublevel is complete and the $2p$ sublevel begins with boron (Z = 5). Since there are three $2p$ orbitals and each orbital holds two electrons, the $2p$ sublevel is filled after six elements. The **Table** 5.3 shows the electron configurations of the elements in the second period.

TABLE 5.3: **Electron Configurations of Second-Period Elements**

Element Name	Symbol	Atomic Number	Electron Configuration
Lithium	Li	3	$1s^2 2s^1$
Beryllium	Be	4	$1s^2 2s^2$
Boron	B	5	$1s^2 2s^2 2p^1$
Carbon	C	6	$1s^2 2s^2 2p^2$
Nitrogen	N	7	$1s^2 2s^2 2p^3$
Oxygen	O	8	$1s^2 2s^2 2p^4$
Fluorine	F	9	$1s^2 2s^2 2p^5$
Neon	Ne	10	$1s^2 2s^2 2p^6$

Summary

- Electron configuration notation simplifies the indication of where electrons are located in a specific atom.
- Superscripts are used to indicate the number of electrons in a given sublevel.

Practice

Use the link below to practice solving electron configuration problems.

http://www.sciencegeek.net/Chemistry/taters/Unit2ElectronNotations.htm

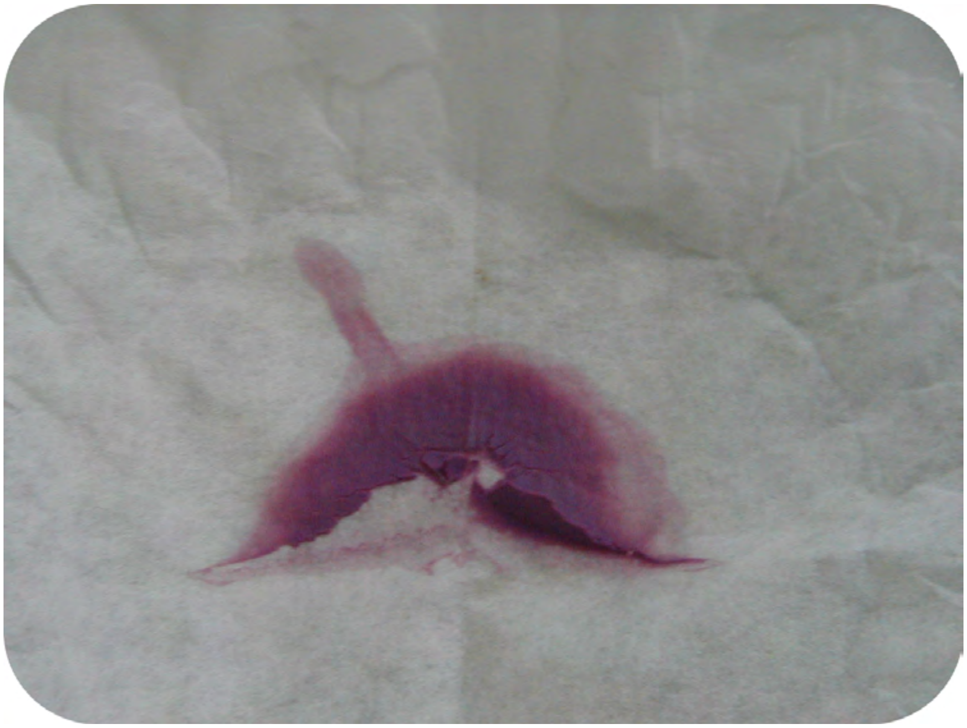
Review

1. What does electron configuration notation eliminate?
2. How do we know how many electrons are in each sublevel?
3. An atom has the electron configuration of $1s^2 2s^2 2p^5$. How many electrons are in that atom?
4. Which element has the electron configuration of $1s^2 2s^2 2p^6 3s^2$?

- **electron configuration notation:** Each occupied sublevel designation is written followed by a superscript that is the number of electrons in that sublevel.

5.18 Valence Electrons

- Define valence electron.
- Be able to indicate valence electrons when given the electron configuration for an atom.



What makes a particular element very reactive and another element non-reactive?

A chemical reaction involves either electron removal, electron addition, or electron sharing. The path a specific element will take depends on where the electrons are in the atom and how many there are.

TABLE 5.4: **Electron Configurations of Second-Period Elements**

Element Name	**Symbol**	**Atomic Number**	**Electron Configuration**
Lithium	Li	3	$1s^22s^1$
Beryllium	Be	4	$1s^22s^2$
Boron	B	5	$1s^22s^22p^1$
Carbon	C	6	$1s^22s^22p^2$
Nitrogen	N	7	$1s^22s^22p^3$
Oxygen	O	8	$1s^22s^22p^4$
Fluorine	F	9	$1s^22s^22p^5$
Neon	Ne	10	$1s^22s^22p^6$

In the study of chemical reactivity, we will find that the electrons in the outermost principal energy level are very important and so they are given a special name. **Valence electrons** are the electrons in the highest occupied principal energy level of an atom. In the second period elements listed above, the two electrons in the $1s$ sublevel are called

inner-shell electrons and are not involved directly in the element's reactivity or in the formation of compounds. Lithium has a single electron in the second principal energy level and so we say that lithium has one valence electron. Beryllium has two valence electrons. How many valence electrons does boron have? You must recognize that the second principal energy level consists of both the $2s$ and the $2p$ sublevels and so the answer is three. In fact, the number of valence electrons goes up by one for each step across a period until the last element is reached. Neon, with its configuration ending in s^2p^6, has eight valence electrons.

Summary

- Valence electrons are the outer-shell electrons of an atom.
- Valence electrons determine the reactivity of an atom.

Practice

Use the link below to answer questions about valence electrons:

http://www.sciencegeek.net/Chemistry/taters/Unit3ValenceElectrons.htm

Review

1. Define valence electron.
2. Define inner shell electron.
3. How many valence electrons are there in fluorine?
4. What are the $2s$ electrons in nitrogen?
5. How many inner shell electrons are there in beryllium?

- **inner-shell electrons:** Those electrons that are not in the outer shell and are not involved in the reactivity of the element.
- **valence electrons:** The electrons in the highest occupied principal energy level of an atom.

5.19 Noble Gas Configuration

- Use the noble gas configuration approach to write electron configurations for the elements.

How does it feel to be full after a meal?

You had a great meal, but cannot put another bite in your mouth because there is no place for it to go. The noble gases have the same problem – there is no room for any more electrons in their outer shells. They are completely full and cannot handle any more.

Noble Gas Configurations

Sodium, element number eleven, is the first element in the third period of the periodic table. Its electron configuration is $1s^22s^22p^63s^1$. The first ten electrons of the sodium atom are the inner-shell electrons and the configuration of just those ten electrons is exactly the same as the configuration of the element neon (Z = 10). This provides the basis for a shorthand notation for electron configurations called the noble gas configuration. The elements that are found in the last column of the periodic table are an important group of elements that are called the noble gases. They are helium, neon, argon, krypton, xenon, and radon. A **noble gas configuration** of an atom consists of the elemental symbol of the last noble gas prior to that atom, followed by the configuration of the remaining electrons. So for sodium, we make the substitution of [Ne] for the $1s^22s^22p^6$ part of the configuration. Sodium's noble gas configuration becomes [Ne]$3s^1$. **Table** 5.5 shows the noble gas configurations of the third period elements.

TABLE 5.5: **Electron Configurations of Third-Period Elements**

Element Name	Symbol	Atomic Number	Noble Gas Electron Configuration

TABLE 5.5: (continued)

Sodium	Na	11	[Ne]$3s^1$
Magnesium	Mg	12	[Ne]$3s^2$
Aluminum	Al	13	[Ne]$3s^2 3p^1$
Silicon	Si	14	[Ne]$3s^2 3p^2$
Phosphorus	P	15	[Ne]$3s^2 3p^3$
Sulfur	S	16	[Ne]$3s^2 3p^4$
Chlorine	Cl	17	[Ne]$3s^2 3p^5$
Argon	Ar	18	[Ne]$3s^2 3p^6$

Again, the number of valence electrons increases from one to eight across the third period.

The fourth and subsequent periods follow the same pattern except for using a different noble gas. Potassium has nineteen electrons, one more than the noble gas argon, so its configuration could be written as [Ar]$4s^1$. In a similar fashion, strontium has two more electrons than the noble gas krypton, which would allow us to write its electrons distribution as [Kr]$5s^2$. All the elements can be represented in this fashion.

Summary

- The noble gas configuration system allows some shortening of the total electron configuration by using the symbol for the noble gas of the previous period as part of the pattern of electrons.

Practice

Use the link below to practice writing noble gas configurations:

http://www.sciencegeek.net/Chemistry/taters/Unit2ElectronNotations.htm

Review

1. What is the element represented by [Ne]$3s^2 3p^2$?
2. What element has this electron configuration [Ar]$3d^7 4s^2$?
3. What noble gas would be part of the electron configuration notation for Mn?
4. How would you write the electron configuration for Ba?

- **noble gas configuration:** Consists of the elemental symbol of the last noble gas prior to that atom, followed by the configuration of the remaining electrons.

5.20 References

1. Jon Sullivan / pdphoto.org. http://commons.wikimedia.org/wiki/File:Beach_3_bg_121402-1-.jpg. Public Domain
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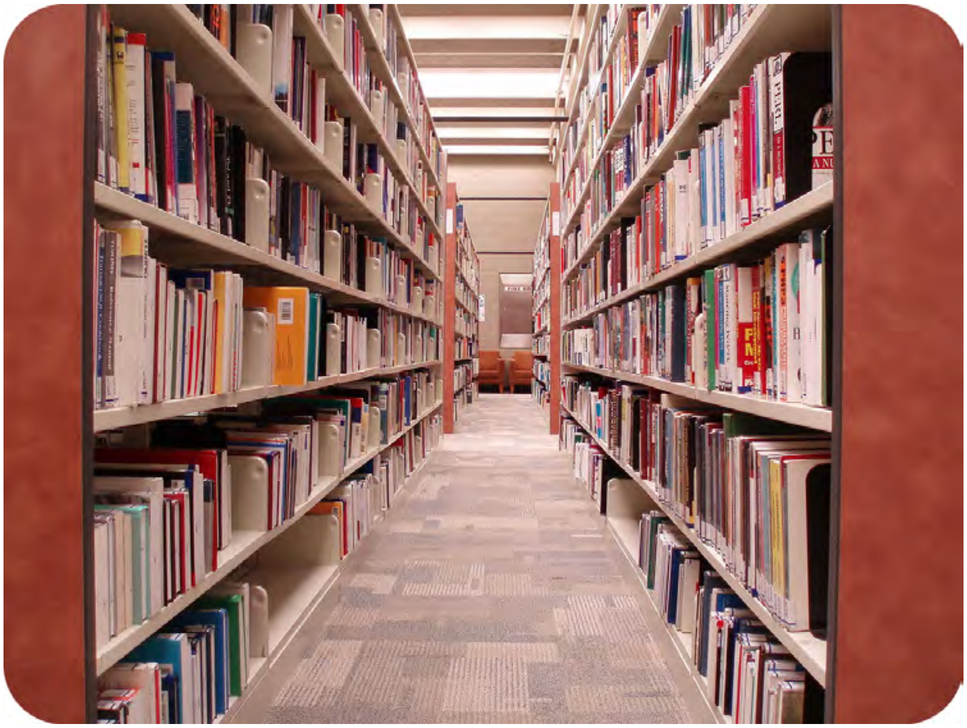
CHAPTER 6 The Periodic Table

Chapter Outline

6.1 Early History of the Periodic Table

- Describe Dobereiner's triad approach to organizing elements.
- Describe Newland's Law of Octaves.



When you go to the library to find a book, how do you locate it?

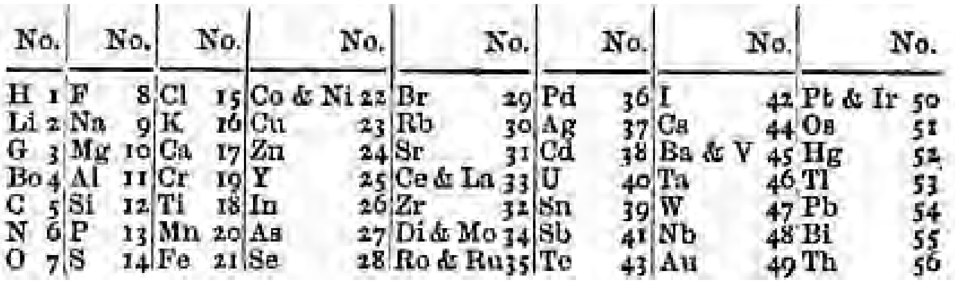
If it is a fiction book, you look by author since the fiction materials are filed by the author's last name. If you are looking for a non-fiction publication, you look in a catalog (most likely on a computer these days). The book you are looking for will have a number by the title. This number could refer to the Dewey Decimal system, developed by Melvil Dewy in 1876 and used in over 200,000 libraries throughout the world. Another system in wide use is the Library of Congress approach, developed in the late 1800s-early 1900s to organize the materials in the federal Library of Congress. This method is one of the most widely used ways to organize libraries in the world. Both approaches organize information so that people can easily find what they are looking for. Chemistry information also needs to be organized so we can see patterns of properties in elements.

Early Attempts to Organize Elements

By the year 1700, only a handful of elements had been identified and isolated. Several of these, such as copper and lead, had been known since ancient times. As scientific methods improved, the rate of discovery dramatically increased. With the ever-increasing number of elements, chemists recognized that there may be some kind of systematic way to organize the elements. The question was: how?

A logical way to begin to group elements together was by their chemical properties. In other words, putting elements in separate groups based on how they reacted with other elements. In 1829, a German chemist, Johann Dobereiner (1780-1849), placed various groups of three elements into groups called **triads**. One such triad was lithium, sodium, and potassium. Triads were based on both physical as well as chemical properties. Dobereiner found that the atomic masses of these three elements, as well as other triads, formed a pattern. When the atomic masses of lithium and potassium were averaged together $\frac{(6.94+39.10)}{2} = 23.02$, it was approximately equal to the atomic mass of sodium (22.99). These three elements also displayed similar chemical reactions, such as vigorously reacting with the members of another triad: chlorine, bromine, and iodine. While Dobereiner's system would pave the way for future ideas, a limitation of the triad system was that not all of the known elements could be classified in this way.

English chemist John Newlands (1838-1898) ordered the elements in increasing order of atomic mass and noticed that every eighth element exhibited similar properties. He called this relationship the "Law of **Octaves**." Unfortunately, there were some elements that were missing and the law did not seem to hold for elements that were heavier than calcium. Newlands's work was largely ignored and even ridiculed by the scientific community in his day. It was not until years later that another more extensive periodic table effort would gain much greater acceptance and the pioneering work of John Newlands would be appreciated.



	No.		No.		No.		No.		No.		No.		No.		No.
H	1	F	8	Cl	15	Co & Ni	22	Br	29	Pd	36	I	42	Pt & Ir	50
Li	2	Na	9	K	16	Cu	23	Rb	30	Ag	37	Cs	44	Os	51
G	3	Mg	10	Ca	17	Zn	24	Sr	31	Cd	38	Ba & V	45	Hg	52
Bo	4	Al	11	Cr	19	Y	25	Ce & La	33	U	40	Ta	46	Tl	53
C	5	Si	12	Ti	18	In	26	Zr	32	Sn	39	W	47	Pb	54
N	6	P	13	Mn	20	As	27	Di & Mo	34	Sb	41	Nb	48	Bi	55
O	7	S	14	Fe	21	Se	28	Ro & Ru	35	Te	43	Au	49	Th	56

Summary

- Johann Dobereiner organized elements in groups called triads.
- John Newland proposed the "Law of Octaves" for organizing the elements.

Practice

Use the link below to answer the following questions:

http://www.bpc.edu/mathscience/chemistry/history_of_the_periodic_table.html

1. Who discovered the first element through scientific inquiry and what was the element?
2. Describe the triad approach to constructing a periodic table.
3. What contribution did A.E.Beguyer de Chancourtois make to the development of the periodic table?
4. Why did John Newlands call his approach the Law of Octaves?

Review

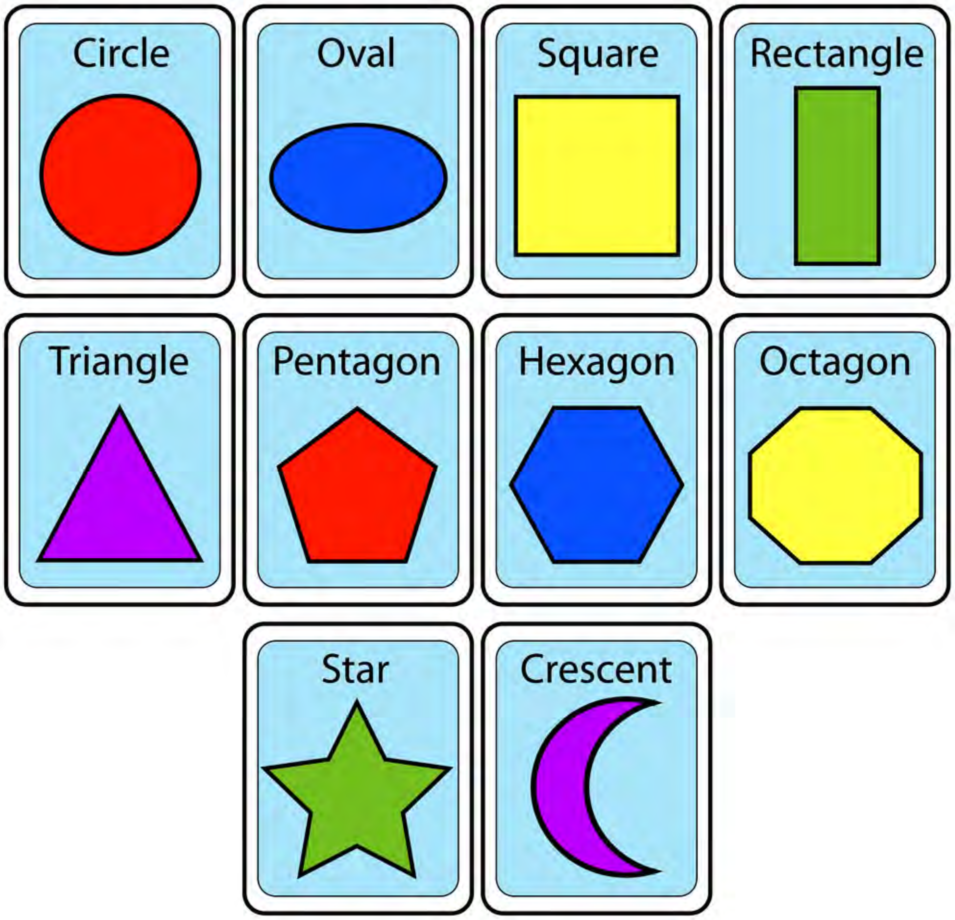
1. List some elements known since ancient times?
2. What properties were the basis of the triad system?
3. Why did Dobereiner believe that lithium, sodium, and potassium belonged in a triad?
4. What was a shortcoming of the triad system?
5. How did Newlands arrange the element?
6. What was a problem with the "Law of Octaves"?

- **triad:** In 1829, a German chemist, Johann Dobereiner (1780-1849), placed various groups of three elements into groups called triads. One such triad was lithium, sodium, and potassium. Triads were based on both physical as well as chemical properties. Dobereiner found that the atomic masses of these three elements, as well as other triads, formed a pattern.

- **octave:** English chemist John Newlands (1838-1898) ordered the elements in increasing order of atomic mass and noticed that every eighth element exhibited similar properties. He called this relationship the "Law of Octaves."

6.2 Mendeleev's Periodic Table

- Describe Mendeleev's organization of the periodic table.
- State predictions made possible by this table.



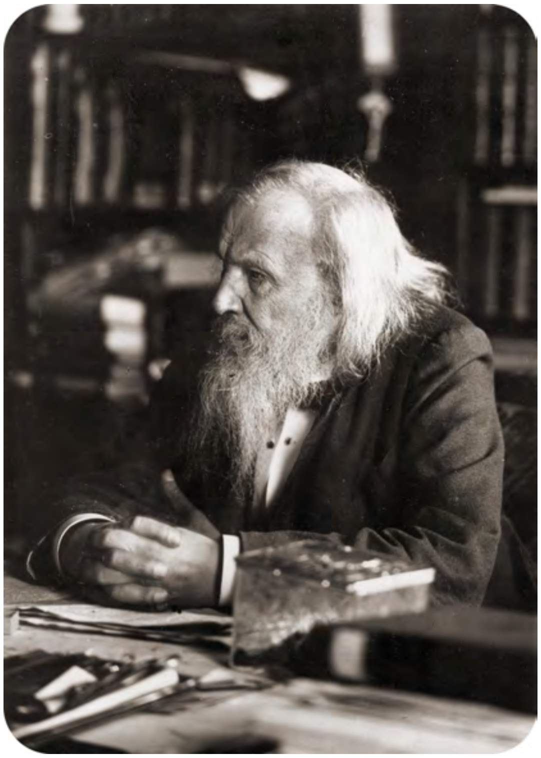
When you study for a test, how do you approach the task?

One useful way is to use flash cards. You write down the vocabulary words, the foreign language terms, the math formulas, the chemistry reactions – anything you want to learn. Then you sort these cards into categories, topics that go together. This organization of information helps you see patterns in the material so you can tie different ideas together and make better sense of them.

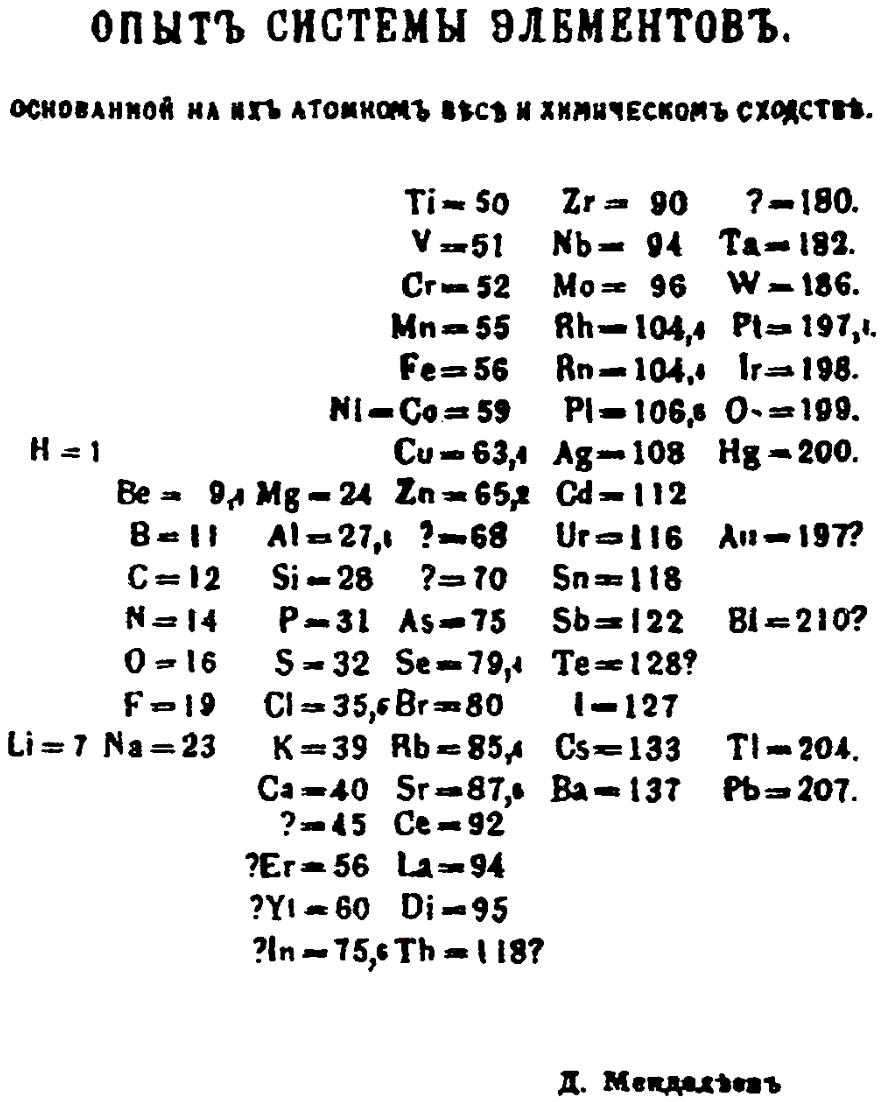
The periodic table was first built using a set of cards. With this strategy, Mendeleev could organize and rearrange material until patterns emerged.

Mendeleev's Periodic Table

In 1869, Russian chemist and teacher Dmitri Mendeleev (1836-1907) published a periodic table of the elements. The following year, German chemist Lothar Meyer independently published a very similar table. Mendeleev is generally given more credit than Meyer because his table was published first and because of several key insights that he made regarding the table.



Mendeleev was writing a chemistry textbook for his students and wanted to organize all of the known elements at that time according to their chemical properties. He famously organized the information for each element on to separate note cards that were then easy to rearrange as needed. He discovered that when he placed them in order of increasing atomic mass, certain similarities in chemical behavior repeated at regular intervals. This type of a repeating pattern is called "periodic." A pendulum that swings back and forth in a given time interval is periodic, as is the movement of the moon around the Earth.



ОПЫТЪ СИСТЕМЫ ЭЛЕМЕНТОВЪ.

ОСНОВАННОЙ НА ИХЪ АТОМНОМЪ ВѢСѢ И ХИМИЧЕСКОМЪ СХОДСТВѢ.

			Ti = 50	Zr = 90	? = 180.
			V = 51	Nb = 94	Ta = 182.
			Cr = 52	Mo = 96	W = 186.
			Mn = 55	Rh = 104,4	Pt = 197,4.
			Fe = 56	Rn = 104,4	Ir = 198.
			Ni = Co = 59	Pl = 106,6	Os = 199.
H = 1			Cu = 63,4	Ag = 108	Hg = 200.
	Be = 9,4	Mg = 24	Zn = 65,2	Cd = 112	
	B = 11	Al = 27,4	? = 68	Ur = 116	Au = 197?
	C = 12	Si = 28	? = 70	Sn = 118	
	N = 14	P = 31	As = 75	Sb = 122	Bi = 210?
	O = 16	S = 32	Se = 79,4	Te = 128?	
	F = 19	Cl = 35,5	Br = 80	I = 127	
Li = 7	Na = 23	K = 39	Rb = 85,4	Cs = 133	Tl = 204.
		Ca = 40	Sr = 87,6	Ba = 137	Pb = 207.
		? = 45	Ce = 92		
		?Er = 56	La = 94		
		?Yt = 60	Di = 95		
		?In = 75,6	Th = 118?		

Д. Менделѣевъ

In this table, atomic mass increases from top to bottom of vertical columns, with successive columns going left to right. As a result, elements that are in the same horizontal row are groups of elements that were known to exhibit similar chemical properties. One of Mendeleev's insights is illustrated by the elements tellurium (Te) and iodine (I). Notice that tellurium is listed before iodine even though its atomic mass is higher. Mendeleev reversed the order 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. As we will see shortly, this turned out not to be the case, but Mendeleev was indeed correct to group these two elements as he did.

Notice that there are several places in the table that have no chemical symbol, but are instead labeled with a question mark. Between zinc (Zn) and arsenic (As) are two such missing elements. Mendeleev believed that elements with atomic masses of 68 and 70 would eventually be discovered and that they would fit chemically into each of those spaces. Listed below are other properties that Mendeleev predicted for the first of these two missing elements, which he called "eka-aluminum," compared with the element gallium.

TABLE 6.1:

	Eka-Aluminum (Ea)	Gallium (Ga)
Atomic mass	68 amu	69.9 amu

TABLE 6.1: (continued)

Melting point	Low	30.15°C
Density	5.9 g/cm^3	5.94 g/cm^3
Formula of oxide	Ea_2O_3	Ga_2O_3

The element gallium was discovered four years after the publication of Mendeleev's table, and its properties matched up remarkably well with eka-aluminum, fitting into the table exactly where he had predicted. This was also the case with the element that followed gallium, which was named eventually named germanium.

Mendeleev's periodic table gained wide acceptance with the scientific community and earned him credit as the discoverer of the periodic law. Element number 101, synthesized in 1955, is named **mendelevium** after the founder of the periodic table. It would, however, be several years after Mendeleev died before the several discrepancies with the atomic masses could be explained and before the reasons behind the repetition of chemical properties could be fully explained.

Some historic periodic tables:

http://freezeray.com/flashFiles/periodicHistory.htm

Discovery dates of the elements:

http://freezeray.com/flashFiles/discoveryDates.htm

Summary

- Mendeleev published his periodic table in 1869.
- His organization of elements was based on atomic mass.
- Mendeleev's periodic table made it possible to predict properties of elements that had not yet been discovered.

Practice

1. Where was Mendeleev born?
2. Where did he teach?
3. What is one important thing about Mendeleev's table?
4. What other contributions to chemistry did Mendeleev make?

Review

1. When did Mendeleev publish his periodic table?
2. Who else came out with a periodic table at about the same time?
3. Why was Mendeleev's table considered to be superior?
4. What element did Mendeleev predict to exist?
5. What element was named after Mendeleev?

- **Mendelevium:** Element number 101, synthesized in 1955, is named mendelevium after Dmitri Mendeleev (1836-1907), the founder of the periodic table.

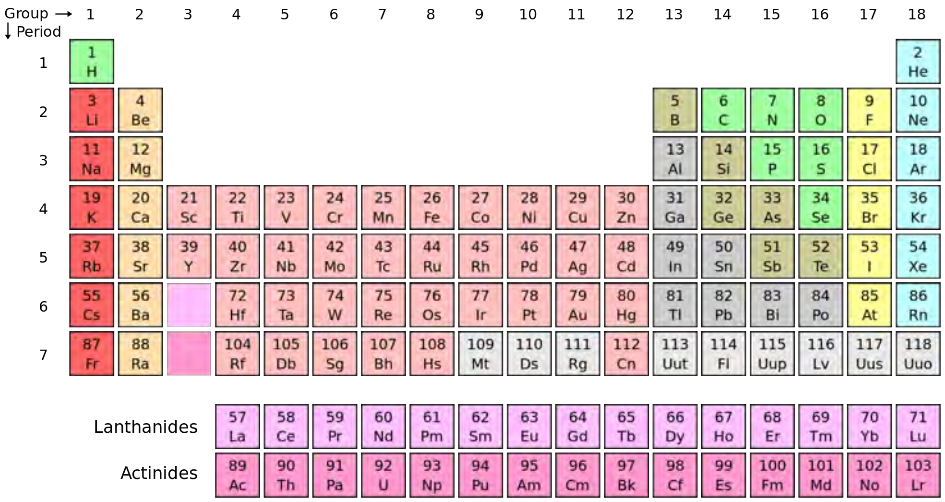
6.3 Periodic Law

- State the periodic law.
- Describe the organization of the periodic table.

We have all enjoyed playing the game "Clue." The object of the game is to obtain information about a murder – who did it, where they did it, and what was used as the murder weapon. As the game progresses, clues are obtained by each player and they then must assemble these clues into a guess as to the criminal. Individual pieces of information takes on broader significance when put together with other parts of the puzzle.

The Periodic Law

When Mendeleev put his periodic table together, nobody knew about the existence of the nucleus. It was not until 1911 that Rutherford conducted his gold foil experiment that demonstrated the presence of the nucleus in the atom. Just two years later, in 1913, English physicist Henry Moseley (1887-1915) examined x-ray spectra of a number of chemical elements. He would shoot X-rays through crystals of the element and study the wavelengths of the radiation he detected. Moseley found that there was a relationship between wavelength and atomic number. 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 rather than 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. So even though tellurium does indeed have a greater atomic mass than iodine, it is properly placed before iodine in the periodic table. Mendeleev and Moseley are credited with being most responsible for the modern **periodic law**: When elements are arranged in order of increasing atomic number, there is a periodic repetition of their chemical and physical properties. The result is the periodic table as we know it today. Each new horizontal row of the periodic table corresponds to the beginning of a new **period** because a new principal energy level is being filled with electrons. Elements with similar chemical properties appear at regular intervals, within the vertical columns called **groups**.

Summary

- Elements of the periodic table are arranged in order of increasing atomic number.
- The periodic law states "When elements are arranged in order of increasing atomic number, there is a periodic repetition of their chemical and physical properties."

Practice

Use the link below to answer the following questions:

http://www.famousscientists.org/henry-moseley/

1. Where did Moseley attend college?
2. Who did he do research with after graduating from college?
3. What is Moseley's law?

Review

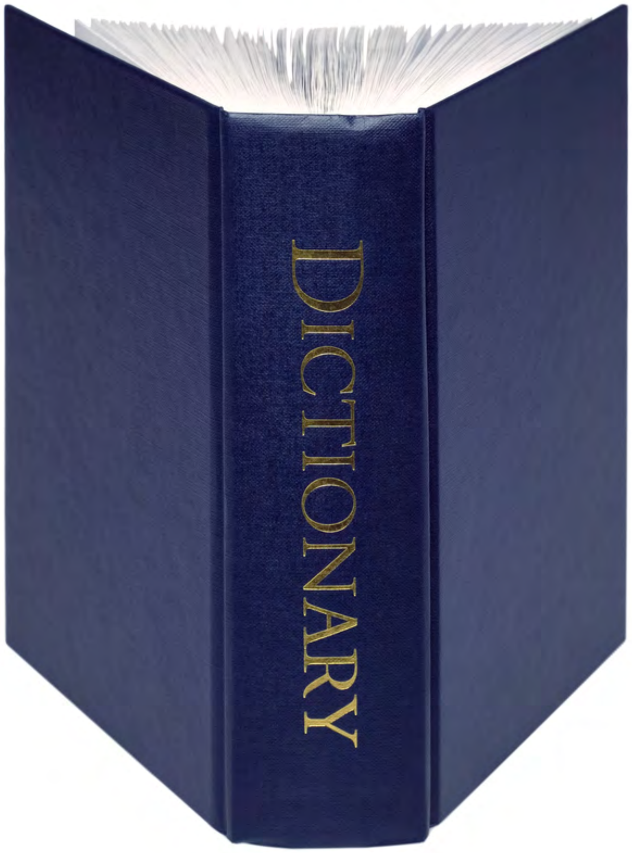
1. Did Mendeleev know about the nucleus of an atom?
2. Who discovered the relationship between wavelength of X-rays and atomic number?
3. What did Moseley conclude from his research?
4. What is the "periodic law"?
5. What do the vertical columns (groups) in the periodic table represent?

- **group:** Elements with similar chemical properties appear at regular intervals, within the vertical columns.

- **period:** A period is a horizontal row of the periodic table.
- **periodic law:** When elements are arranged in order of increasing atomic number, there is a periodic repetition of their chemical and physical properties.

6.4 Modern Periodic Table: Periods and Groups

- Describe the organization of the modern periodic table.

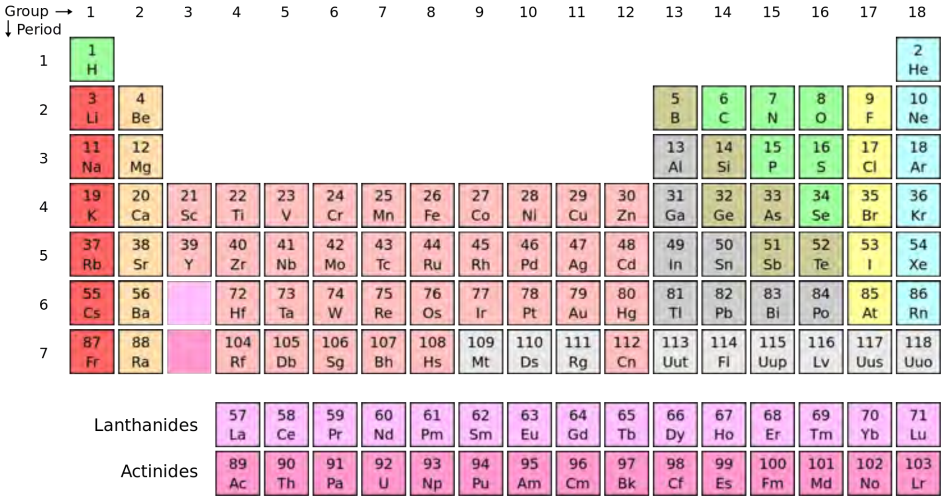


Language changes with time. New words enter the language and old words often disappear from lack of use. Dictionaries are published so that people can keep up with changes in language and know how to use words properly. These publications may be in print, as is the law dictionary below, or they may be electronic. Dictionaries can be found on the internet and apps are available for smartphones. Dictionaries are invaluable for good, reliable communication.

The Modern Periodic Table

The periodic table has undergone extensive changes in the time since it was originally developed by Mendeleev and Moseley. Many new elements have been discovered, while others have been artificially synthesized. Each fits properly into a **group** of elements with similar properties. The periodic table is an arrangement of the elements in order of their atomic numbers so that elements with similar properties appear in the same vertical column or group.

The figure below shows the most commonly used form of the periodic table. Each square shows the chemical symbol of the element along with its name. Notice that several of the symbols seem to be unrelated to the name of the element: Fe for iron, Pb for lead, etc. Most of these are the elements that have been known since ancient times and have symbols based on their Latin names. The atomic number of each element is written above the symbol. Each square on this version of the periodic table also shows the average atomic mass of the element.



A **period** is a horizontal row of the periodic table. There are seven periods in the periodic table, with each one beginning at the far left. A new period begins when a new principal energy level begins filling with electrons. Period 1 has only two elements (hydrogen and helium), while periods 2 and 3 have 8 elements. Periods 4 and 5 have 18 elements. Periods 6 and 7 have 32 elements because the two bottom rows that are separated from the rest of the table belong to those periods. They are pulled out in order to make the table itself fit more easily onto a single page.

A group is a vertical column of the periodic table, based on the organization of the outer shell electrons. There are a total of 18 groups. There are two different numbering systems that are commonly used to designate groups and you should be familiar with both. The traditional system used in the United States involves the use of the letters A and B. The first two groups are 1A and 2A, while the last six groups are 3A through 8A. The middle groups use B in their titles. Unfortunately, there was a slightly different system in place in Europe. To eliminate confusion the International Union of Pure and Applied Chemistry (IUPAC) decided that the official system for numbering groups would be a simple 1 through 18 from left to right. Many periodic tables show both systems simultaneously.

Summary

- The periodic table is arranged in order of atomic number
- A period is a horizontal row of the periodic table.
- A group is a vertical row of the periodic table.

Practice

Use the link below to answer the following questions:

http://pontotriplo.org/triplepoint/2007/05/the_best_55_online_periodic_tables.html

1. Select the periodic table from the "best" column that you like the most. Why did you choose that table?
2. Which periodic table in the "specific" section do you like the most? Why?
3. Which of the "funny" periodic tables do you like most? Why?

Review

1. How is today's periodic table different from the one that Mendeleev published?
2. Are all the elements in today's periodic table naturally occurring? Explain your answer.
3. What is a "period?" What does it represent?
4. What is a "group?" What does it represent?
5. Why are there two different numbering systems for groups?

- **group:** Elements with similar chemical properties appear at regular intervals, within the vertical columns.
- **period:** A period is a horizontal row of the periodic table.

6.5 Metals

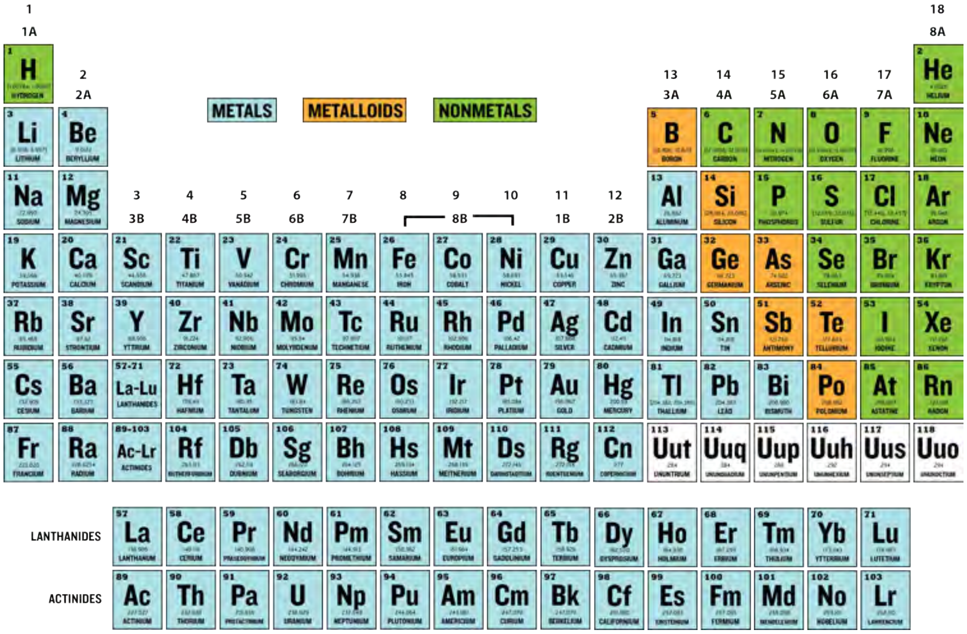
- List properties of metals.
- List common metals and their uses.

Screws come in all sizes and shapes. They are all (well, almost all) made of some kind of metal. But they have differences in size, shape, and type of metal. Physical characteristics also differ. Some screws are long, and others are short. One screw may have a flat-head slot while another screw may have a Phillips-head. Some of the screws in the picture below are used to fasten things together, and others are used to hang heavy objects on a wall.

Chemists classify materials in many ways. We can sort elements on the basis of their electron arrangements. The way the electrons are distributed determines the chemical properties of the element. Another way is to classify elements based on physical properties. Some common physical properties are color, volume, and density. Other properties that allow us to sort on the basis of behavior are conduction of heat and electricity, malleability (the ability to be hammered into very thin sheets), ductility (the ability to be pulled into then wires), melting point, and boiling point. Three broad classes of elements based on physical properties are metals, nonmetals, and metalloids.

Metals

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. They are 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 is called luster. All metals are solid at room temperature with the exception of mercury (Hg), which is a liquid. Melting points of metals display a very wide variance. The melting point of mercury is -39°C, while the highest melting metal is tungsten (W), with a melting point of 3422°C. The elements in blue in the periodic table below are metals. About 80 percent of the elements are metals.



Gold has been used by many civilizations for making jewelry. This metal is soft and easily shaped into a variety of items. Since gold is very valuable and often used as currency, gold jewelry has also often represented wealth.

Copper is a good conductor of electricity and is very flexible and ductile. This metal is widely used to conduct electric current in a variety of appliances, from lamps to stereo systems to complex electronic devices.

Mercury is the only metal to exist as a liquid at room temperature. This metal was extensively used in thermometers for decades until information about its toxicity became known. Mercury switches were once common, but are no longer used. However, new federally-mandated energy-efficient light bulbs that are now used contain trace amounts of mercury and represent a hazardous waste.

Summary

- Metals are good conductors of heat and electricity.
- Metals are malleable and ductile
- All metals are solids at room temperature with the exception of mercury
- Gold, silver, iron, and mercury are typical metals.

Practice

Select two metals from the periodic table that have not been mentioned. Locate information to answer the following questions:

1. What color is this metal?
2. Describe its ductility and malleability
3. List three current uses for this metal.

Review

1. What properties of an element are affected by electron distribution?
2. Define malleability.
3. Define ductility.
4. State one reason gold is used in jewelry.
5. Why is mercury no longer used in many devices?

- **conductor:** A material that allows the flow of an electric current.

- **ductile:** A material that can be drawn into wires.
- **malleable:** Means that the material can be hammered into very thin sheets without breaking.
- **metal:** An element that is a good conductor of heat and electricity.

6.6 Nonmetals

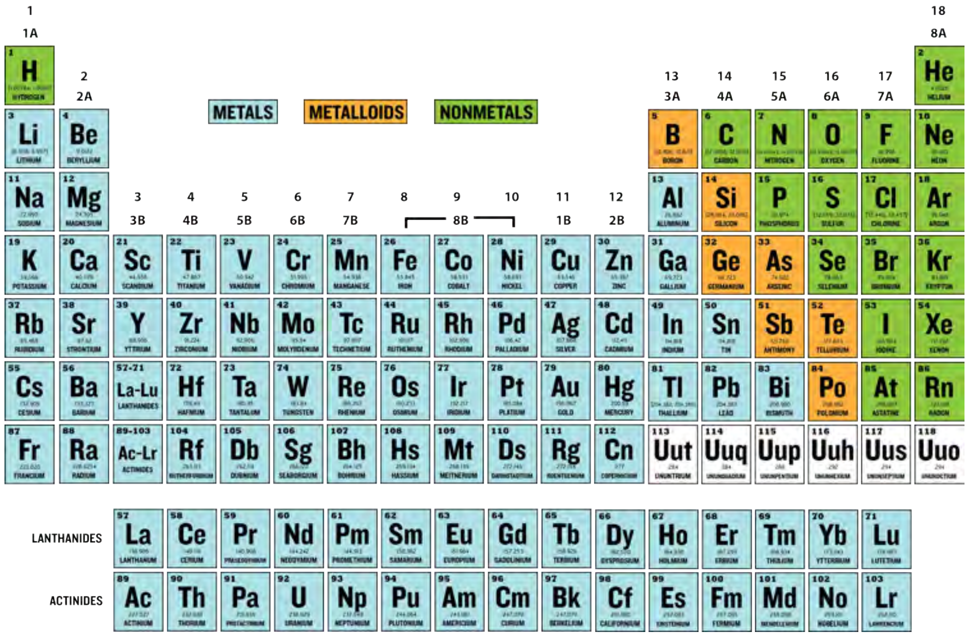
- Define non-metal.
- List typical non-metals and their uses.

When we sort parts in our shop or garage, we often classify them in terms of common properties. One container might hold all the screws (possibly sub-divided by size and type). Another container would be for nails. Maybe there is a set of drawers for plumbing parts.

When you get finished, you could also have a collection of things that don't nicely fit a category. You define them in terms of what they are not. They are not electrical components, or sprinkler heads for the yard, or parts for the car. These parts may have some common properties, but are a variety of items.

Non-Metals

In the chemical world, these "spare parts" would be considered non-metals, loosely defined as not having the properties of metals. A **nonmetal** is an element that is generally a poor conductor of heat and electricity. Most properties of nonmetals are the opposite of metals. There is a wider variation in properties among the nonmetals than among the metals. Nonmetals exist in all three states of matter. The majority are gases, such as nitrogen and oxygen. Bromine is a liquid. 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. Melting points are generally much lower than those of metals. The green elements in the table below are non-metals.



Non-metals have a wide variety of uses. Sulfur can be employed in gunpowder, fireworks, and matches to facilitate ignition. This element is also widely used as an insecticide, a fumigant, or a means of eliminating certain types of fungus. An important role for sulfur is the manufacture of rubber for tires and other materials. First discovered in 1839 by Charles Goodyear, the process of vulcanization makes the rubber more flexible and elastic as well as being more resistant to changes in temperature. A major use of sulfur is for the preparation of sulfur-containing compounds such as sulfuric acid.

Bromine is a versatile compound, used mainly in manufacture of flame-retardant materials, especially important for children's clothing. For treatment of water in swimming pools and hot tube, bromine is beginning to replace chlorine as a disinfectant because of its higher effectiveness. When incorporated into compounds, bromine atoms play important roles in pharmaceuticals for treatment of pain, cancer, and Alzheimer's disease.

Helium is one of the many non-metals that is a gas. Other non-metal gases include hydrogen, fluorine, chlorine, and all the period eighteen noble (or inert) gases. Helium is chemically non-reactive, so it is useful for applications such as balloons and lasers, where non-flammability is extremely important. Liquid helium exists at an extremely low temperature and can be used to cool superconducting magnets for imaging studies (MRI, magnetic resonance imaging). Leaks in vessels and many types of high-vacuum apparatus can be detected using helium. Inhaling helium changes the speed of sound, producing a higher pitch in your voice. This is definitely an unsafe practice and can lead to physical harm and death.

Summary

- Non-metals are generally poor conductors of heat and electricity.
- Properties of non-metals are usually the opposite of properties of metals
- Non-metals can be solid, liquid, or gas at room temperature depending upon the element.
- Sulfur, bromine, and helium are typical non-metals.

Practice

Select two non-metals from the periodic table that have not been mentioned. Locate information to answer the following questions:

1. What are the physical properties of this non-metal?
2. List three current uses for this element.

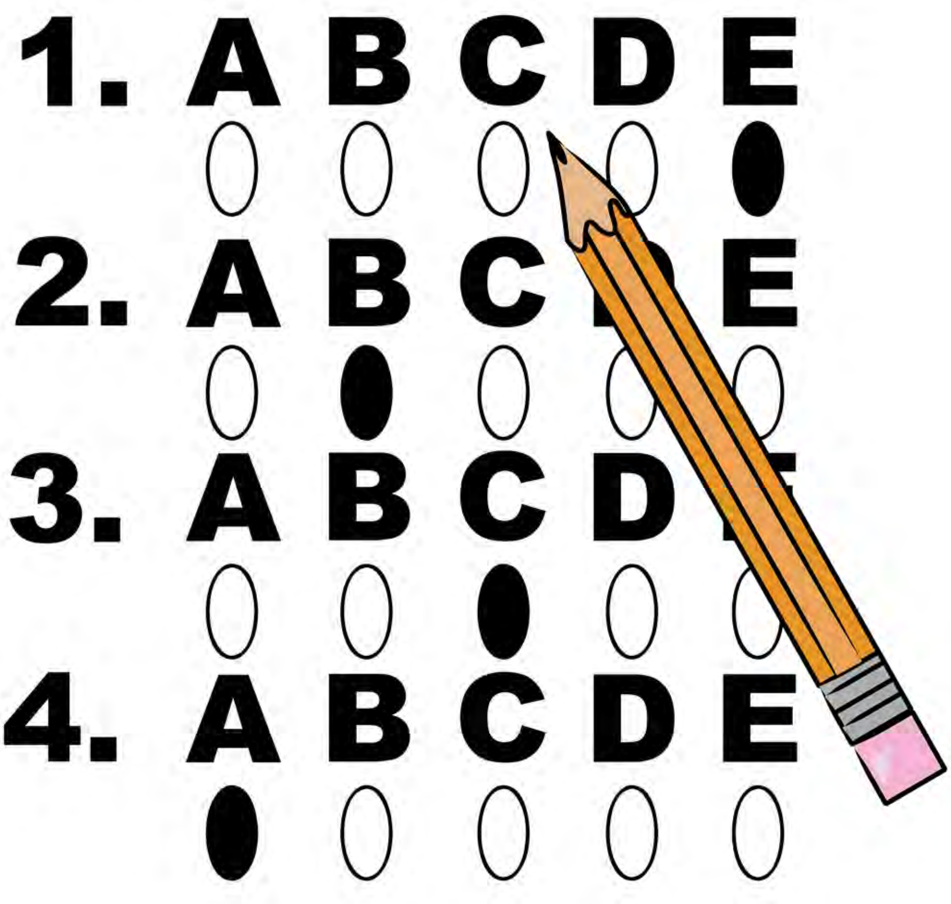
Review

1. What are the properties of non-metals?
2. List the states of matter in which non-metals can exist and give one example of each state
3. What are the physical properties and uses of sulfur?
4. What are the physical properties and uses of bromine?
5. What are the physical properties and uses of helium?

- **non-metal:** An element that is generally a poor conductor of heat and electricity.
- **brittle:** Shatters easily.

6.7 Metalloids

- Define metalloid.
- List common metalloids and give their uses.

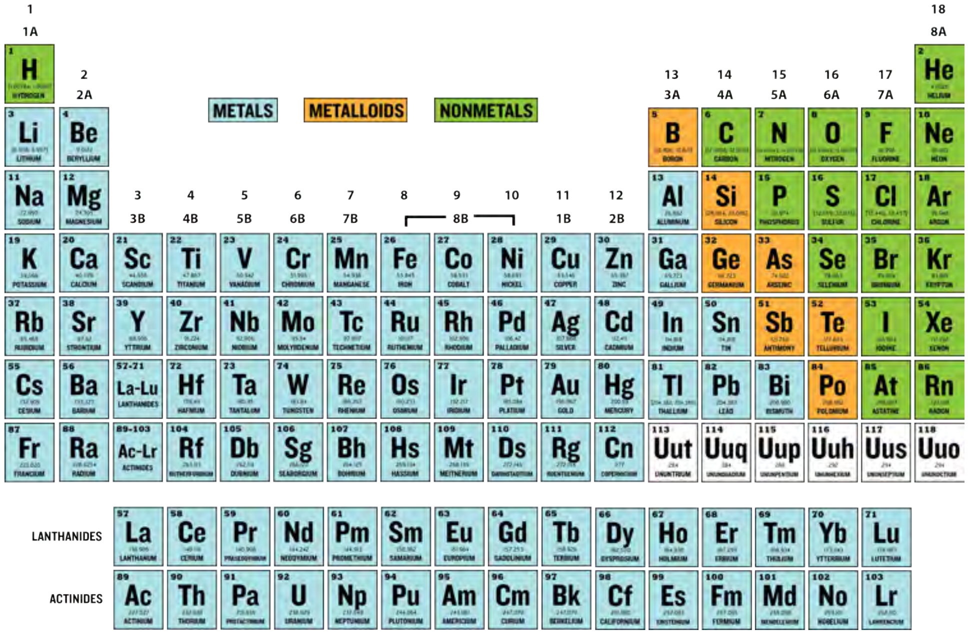


Have you ever taken a multiple-choice test?

Most of the time the answers are specific choices – is the answer possibility a or possibility b? Quite often you can “think through” the choices to come up with the correct answer. More frustrating is the choice “none of the above.” You feel very uncertain checking that possibility.

Metalloids

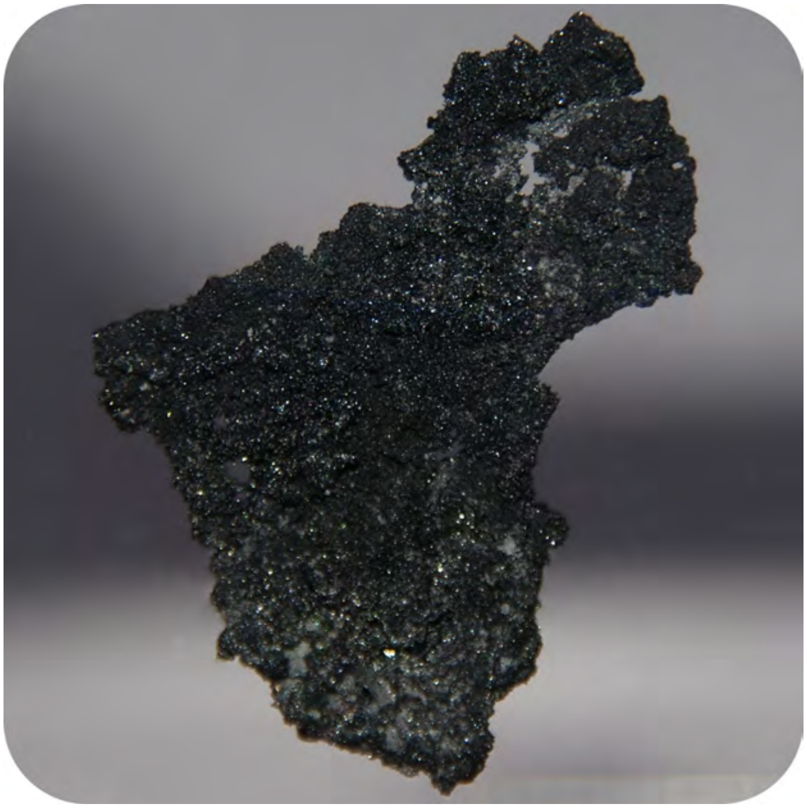
Some elements are “none of the above.” They don’t fit neatly into the categories of metal or non-metal because of their characteristics. A **metalloid** is an element that has properties that are intermediate between those of metals and nonmetals. Metalloids can also be called semimetals. On the periodic table, the elements colored yellow, which generally border the stair-step line, are considered to be metalloids. Notice that aluminum borders the line, but it is considered to be a metal since all of its properties are like those of metals.



Examples of Metalloids

Silicon is a typical metalloid. 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.

Boron is a versatile element that can be incorporated into a number of compounds. Borosilicate glass is extremely resistance to thermal shock. Extreme changes in the temperature of objects containing borosilicates will not create any damage to the material, unlike other glass compositions, which would crack or shatter. Because of their strength, boron filaments are used as light, high-strength materials for airplanes, golf clubs, and fishing rods. Sodium tetraborate is widely used in fiberglass as insulation and also is employed in many detergents and cleaners.



Arsenic has long played a role in murder mysteries, being used to commit the foul deed. This use of the material is not very smart since arsenic can be easily detected on autopsy. We find arsenic in pesticides, herbicides, and insecticides, but the use of arsenic for these applications is decreasing due to the toxicity of the metal. Its effectiveness as an insecticide has led arsenic to be used as a wood preservative.

Antimony is a brittle, bluish-white metallic material that is a poor conductor of electricity. Used with lead, antimony increases the hardness and strength of the mixture. This material plays an important role in the fabrication of electronic and semiconductor devices. About half of the antimony used industrially is employed in the production of batteries, bullets, and alloys.

Summary

- Metalloids are elements with properties intermediate between those of metals and non-metals
- Silicon is a metalloid because it has luster, but is brittle.
- Boron, arsenic, and antimony are metalloids with a variety of uses.

Practice

Use the link below to answer the following:

http://www.buzzle.com/articles/uses-of-metalloids.html

1. Describe the physical properties of two metalloids of your choosing.
2. List two uses for each of these metalloids.

Review

1. Define “metalloid.”
2. Why would it be difficult to decide whether or not an element was a metalloid?
3. Why is silicon used extensively in electronics?
4. What are borosilicates used for?
5. Why is the use of arsenic as an insecticide decreasing?
6. What is a main application of antimony?

- **metalloid:** An element that has properties that are intermediate between those of metals and nonmetals.
- **luster:** A reflective surface.

6.8 Blocks of the Periodic Table

- Identify blocks of the periodic table.
- Determine the block each element belongs in by its electron configuration.

We all enjoy music of some sort. Some people like classical music, others like jazz or country. Music styles change from one period of time to the next, and from one region to another. Each type of music has its language that describes it. Classical music has a certain structure, style, and content. There are different expressions of classical music – the symphony, concerto, sonata. We have ballet and opera as well as choral music. Jazz has a different set of characteristics from classical and different styles of performance. Each type of music can be described and compared to other types on the basis of certain common qualities like notes, chords, and melodic styles.

The elements in the periodic table could be considered to be similar to types of music. Each set of elements has its unique set of properties, with different sets of elements having some common characteristics in terms of electron arrangements. We can see patterns of electronic structure and reactivity in the periodic table that allow us to understand better the behavior of individual elements.

Periods and Blocks

There are seven horizontal rows of the periodic table, called **periods**. The length of each period is determined by the number of electrons that are capable of occupying the **sublevels** that fill during that period, as seen in the table below.

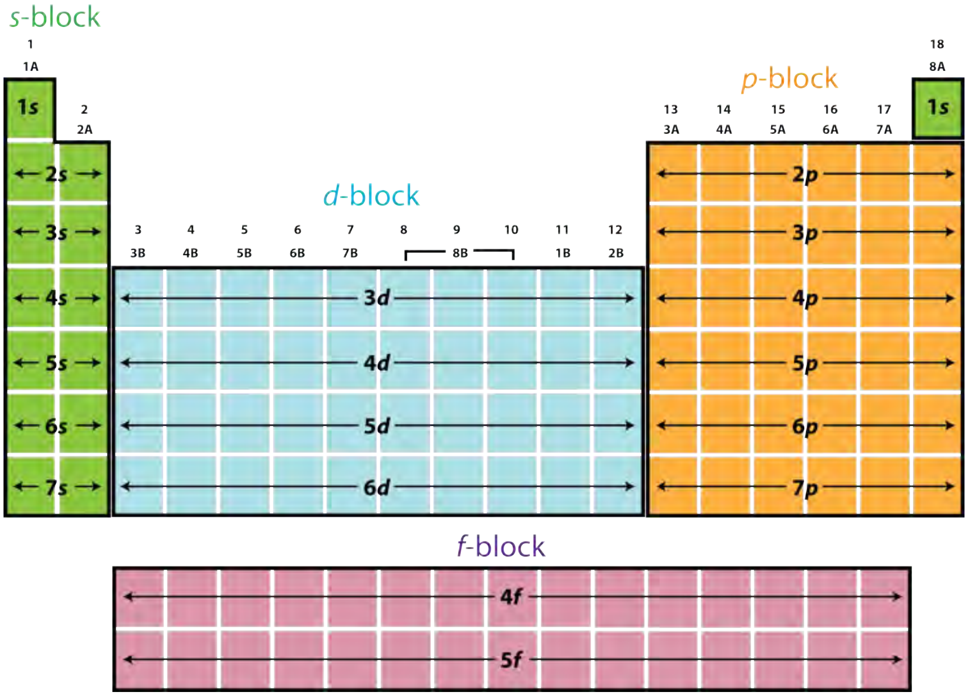
TABLE 6.2: **Period Length and Sublevels in the Periodic Table**

Period	Number of elements in period	Sublevels in order of fill
1	2	1*s*
2	8	2*s* 2*p*
3	8	3*s* 3*p*
4	18	4*s* 3*d* 4*p*
5	18	5*s* 4*d* 5*p*
6	32	6*s* 4*f* 5*d* 6*p*
7	32	7*s* 5*f* 6*d* 7*p*

Recall that the four different sublevels 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 1*s* 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 2*s* sublevel, with two electrons, and the 2*p* sublevel with six electrons, are being filled. Consequently, the second period contains eight elements. The third period is similar to the second, filling the 3*s* and 3*p* sublevels. Notice that the 3*d* sublevel does not actually fill until after the 4*s* sublevel. This results in the fourth period containing 18 elements due to the additional 10 electrons that are contributed by the *d* sublevel. The fifth period is similar to the fourth. After the 6*s* sublevel fills, the 4*f* sublevel with its 14 electrons fills. This is followed by the 5*d* and the 6*p*. The total number of elements in the sixth period is 32. The later elements in the seventh period are still being created. So while there are a possible of 32 elements in the period, the current number is slightly less.

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 $[Ar]3d^8 4s^2$. The highest occupied principal energy level is the fourth, 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.

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.



The figure also illustrates how the *d* sublevel is always one principal level behind the period in which that sublevel occurs. In other words, the 3*d* sublevel fills during the fourth period. The *f* sublevel is always two levels behind. The 4*f* sublevel belongs to the sixth period.

Summary

- The horizontal rows of the periodic table are called periods.
- The length of a period depends on how many electrons are needed to occupy the sublevels that fill the period.
- Blocks indicate which sublevel is being filled.

Practice

Use the link below to answer the following questions:

http://en.wikibooks.org/wiki/High_School_Chemistry/The_Periodic_Table_and_Electron_Configurations

1. How many elements are in the second period? The fourth? The sixth?
2. Use a periodic table to identify the block that each of these elements would be found.

    a. rubidium
    b. holmium
    c. palladium
    d. tellurium

Review

1. What are the horizontal rows of the periodic table called?
2. Which sublevel is being filled in period 1?
3. Which sublevel is being filled in period 7?
4. How does the electron configuration of an element give information about the period it is in?
5. What block of elements has the *d* sublevels being filled?

- **block:** The periodic table can be divided into blocks denoting which sublevel is in the process of being filled.
- **period:** Each horizontal row of the seven rows of the periodic table.
- **sublevel:** Electron orbitals s, p, d or f.

6.9 Hydrogen and Alkali Metals

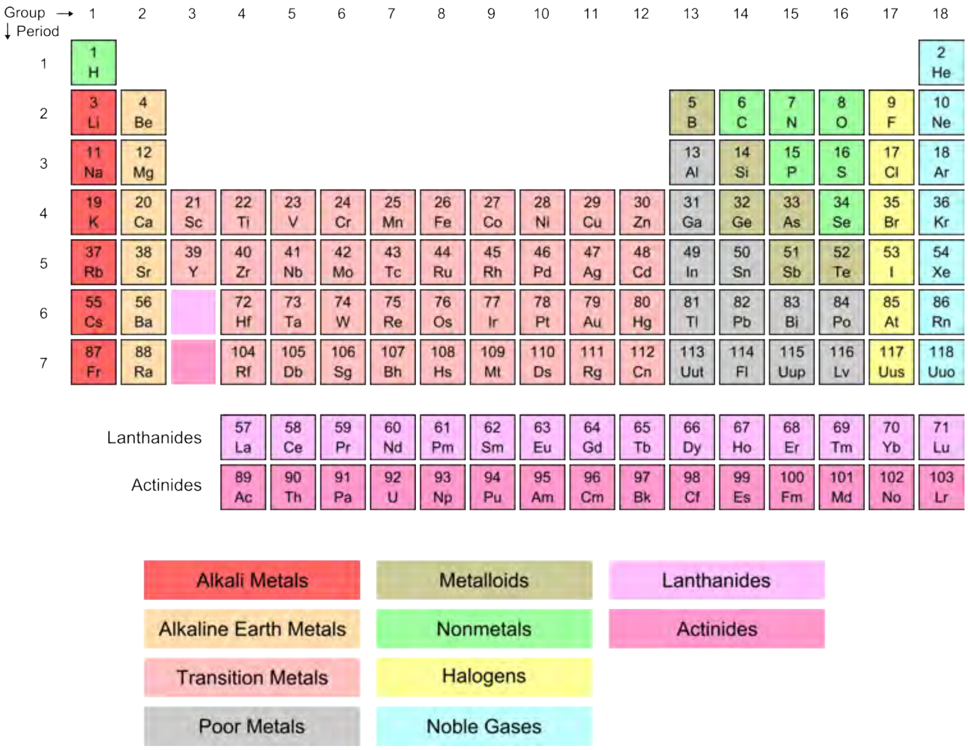
- Indicate the group in which the alkali metals are located.
- List the alkali metals.
- Describe the valence shell electron configuration for the hydrogen atom and the alkali metal elements.

Some chemistry students just enjoy learning about the science, while others are intrigued by the violent reactions that sometimes can occur. Many chemistry classes have been enlivened by the demonstration of how reactive sodium is with water. In some instances, the demonstration has gone off safely. Unfortunately, in other situations students and instructor have incurred serious injury due to their failure to observe proper safety precautions.

One of the values of the periodic table is the ability to make predictions about the behavior of individual elements. By knowing which group an element is in, we can determine the number of reactive electrons and say something about how that element will behave.

Hydrogen and the Alkali Metals

The periodic table is arranged on the basis of atomic numbers (number of protons in the nucleus). One of the valuable consequences of this arrangement is that we can learn a lot about the electron distribution in these atoms. The colors in the table below indicate the different groupings of atoms based on the location and number of electrons in the atom.

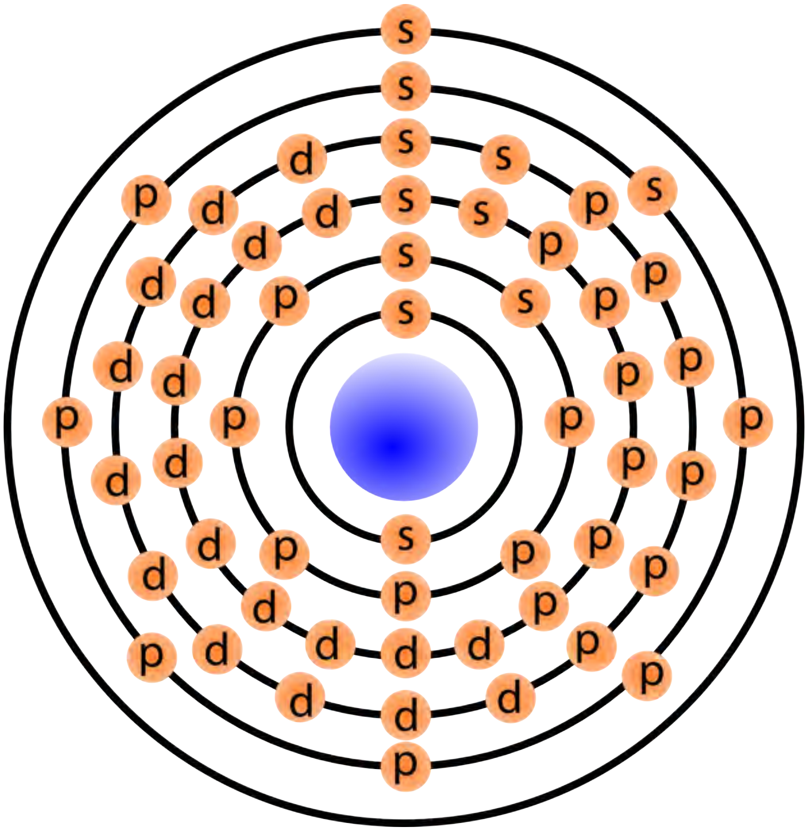


If we look at Group I (red column), we see that it is labeled **alkali metals**. Also note the green H above the alkali metals. All these elements have a similar configuration of outer-shell electrons. In each case, there is one electron in the outer orbital and that is an *s*-orbital electron. In the case of hydrogen (one proton in the nucleus and one electron), the arrangement is very simple. The lone electron exists in a *s*-orbital around the nucleus. For lithium, there are two 1*s* electrons in an inner orbit and one 2*s* electron in the outer orbit. The same pattern holds for sodium and potassium.

TABLE 6.3:

Element	Symbol	Electron Configuration
hydrogen	H	$1s^1$
lithium	Li	$[He]2s^1$
sodium	Na	$[Ne]3s^1$
potassium	K	$[Ar]4s^1$
rubidium	Rb	$[Kr]5s^1$
cesium	Cs	$[Xe]6s^1$
francium	Fr	$[Rn]7s^1$

Even an atom with a very complex electron composition such as cesium still has the single *s* electron in its outer orbital.



This one electron is very easily removed during chemical reactions. The group I elements react rapidly with oxygen to produce metal oxides. They are very soft metals, with the exception of cesium which is a liquid at room temperature. The alkali metals also react readily with water to produce hydrogen gas and metal hydroxides in the following video.

http://youtu.be/QSZ-3wScePM

Li reacts with water to produce hydrogen gas. Sodium also reacts the same way, just more rapidly. Potassium reacts rapidly with water producing hydrogen gas and heat which ignites the hydrogen gas. Rubidium and cesium react yet more vigorously and explode on contact with water.

Summary

1. Group I (alkali metals and H) elements all have one electron in their outer shell.
2. This electron is in a s orbital.
3. The Group I metals are all very reactive with water.

Practice

Use the link below to answer the following questions:

http://chemed.chem.wisc.edu/chempaths/GenChem-Textbook/Group-IA-Alkali-Metals-544.html

1. How is hydrogen similar to the alkali metals? How is it different?
2. Why don't we know much about francium (atomic number 87)?
3. Describe the physical properties of the alkali metals.

Review

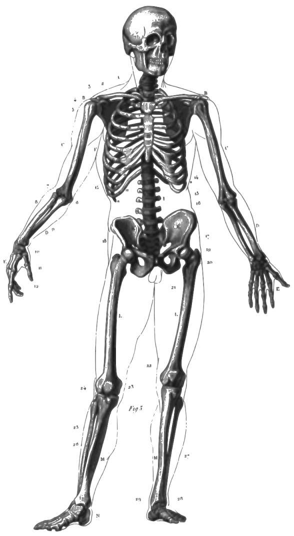
1. What group are the alkali metals and hydrogen in?
2. What is the outer shell electron configuration in this group?
3. Which alkali metal is a liquid at room temperature?
4. How reactive are the alkali metals with oxygen?
5. How reactive are these metals with water?

- **alkali metal:** Has one electron in their outer shell and can be found in Group I in the periodic table.

6.10 Alkaline Earth Metals

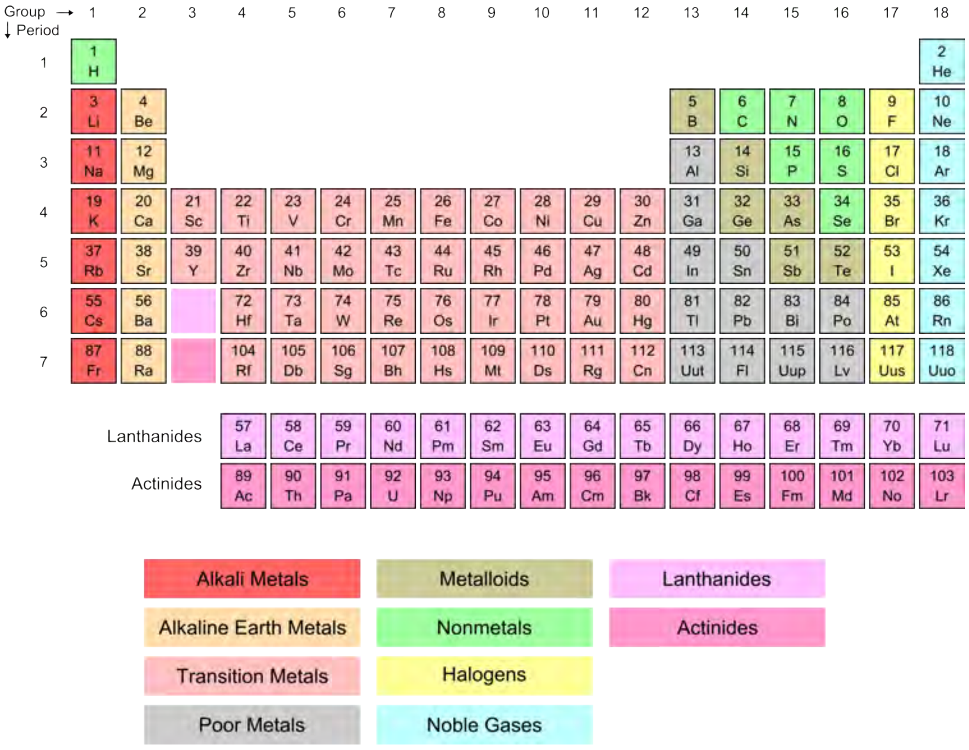
- List the alkaline earth elements.
- Give the electron configuration of this group.
- Describe reaction of the alkaline earth elements.

We take a lot of chemistry for granted. Very few of us think about the chemistry of bone or oyster shells. Both of these materials have large amounts of calcium compounds in them and play important roles in maintaining the structure of the organism. The shell provides a solid surrounding for the oyster. Bones give support to the body so the person can move around and not just be a soft mass of tissue.



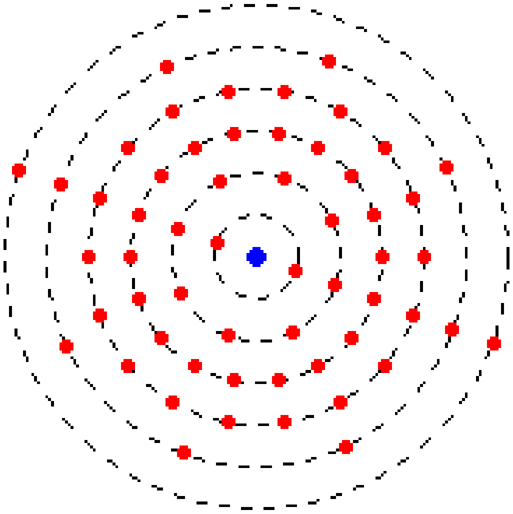
Alkaline Earth Metals

Group II elements are referred to as "**alkaline earth**" metals (tan column below). The name "**alkaline**" comes from the fact that compounds of these elements form **basic** (pH greater than 7) or alkaline solutions when dissolved in water. If the Group I elements all have one s electron in their outer orbital, we can predict that the Group II elements will have two electrons in that outer shell.



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

The beryllium atom, the first element of Group II, has an atomic number of four. The atom has the $1s$ shell filled as well as the $2s$ shell, giving a total of four electrons ($1s^2 2s^2$). Note that there are two s electrons in the outer shell, a structure that is characteristic of the Group II elements. Barium (atomic number 56) has the same outer shell structure of two electrons in the s orbital, even though the internal electron structure for barium is quite complicated.



Radium (atomic number 88) technically falls in the Group II category, but is usually not considered as far as the chemistry goes. Radium is a radioactive element and is generally under the category of radioisotopes since it is not a stable element.

The Group II elements tend to be less reactive than their Group I counterparts. The need to remove two electrons in order for the material to react means more energy is needed for electron removal. However, these elements are reactive enough that they do not exist in their elemental forms in nature, but are present as compounds.

Uses of Alkaline Earth Compounds

Since magnesium burns brightly, it is used in flares and fireworks. Magnesium alloys with aluminum provide light weight and sturdy materials for airplanes, missiles, and rockets. Several antacids use magnesium hydroxide to neutralize excess stomach acid.

Calcium compounds are widely found in limestone, marble, and chalk. Calcium is an important constituent of cement. Other uses include calcium chloride as a deicer and limestone as a white pigment in paints and toothpaste.

Strontium is widely used in fireworks and magnets. Barium compounds can be used in paints, filler for rubber, plastic, and resins, and as a contrast medium for X-rays. Many beryllium compounds are toxic, but these materials have been employed in metal alloys.

Summary

- The alkaline earth elements are in Group II of the periodic table.
- These elements each have two *s* electrons in their outer shell.
- The alkaline earth elements are less reactive than the alkali metals.

Practice

Use the link below to answer the following questions:

http://www.rsc.org/chemsoc/visualelements/pages/data/intro_groupii_data.html

1. What color are all the alkaline earth elements?
2. In what compounds is magnesium found in nature?
3. In what compounds is calcium found in nature?

Review

1. Why are these elements known as "alkaline earth" elements?
2. How many electrons are in the outer shell of the alkaline earth elements?
3. Are the alkaline earth elements more or less reactive than the alkali metals? Explain your answer?
4. Is radium usually considered as part of the alkaline earth category in terms of chemistry? Explain your answer.

- **alkaline:** Comes from the fact that compounds of these elements from basic or alkaline solutions when dissolved in water.
- **alkaline earth:** Group II elements in the periodic table.
- **basic:** pH greater than 7.

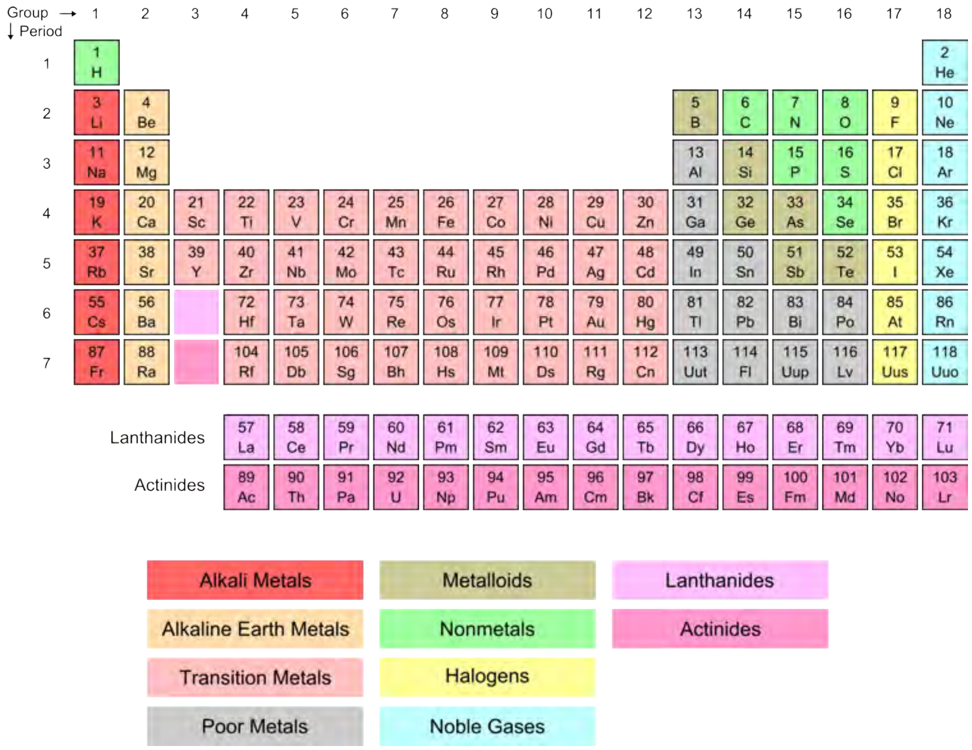
6.11 Noble Gases

- List the noble gases.
- Describe the electron configuration of the noble gases.
- Describe compounds of the noble gases.

Cities at night would be rather boring without all the bright lights. They provide colorful Illuminations and help make things much more visible. We call these lights "neon lights," but they use several gases to make the differenet colors.

Noble Gases

The reactivity of an element can give us important clues as to the electron configuration of that material. If an element is extremely unreactive, this suggests that the electron configuration is such that adding or removing electrons is very unlikely. There must be a stable electron configuration that resists further reaction.



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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

Alkali Metals	Metalloids	Lanthanides
Alkaline Earth Metals	Nonmetals	Actinides
Transition Metals	Halogens	
Poor Metals	Noble Gases	

The Group VIII (new group 18) elements are essentially chemically **inert** (light blue column on the right). All these elements exist as **monatomic** gases at room temperature. If we look at the electron configurations, we see that helium (atomic number 2) has a full shell of two *s* electrons. Since there are no electrons shielding this shell from the nucleus, these two electrons will be very difficult to remove, making helium unreactive.

The remaining elements in the group have full outer shells consisting of two *s* electrons and 6*p* electrons for an outer shell content of eight electrons. This particular arrangement renders the atoms fairly unreactive. This group has been referred to as the "inert" gases, indicating that they are chemically inert, or unreactive. Another popular term is "**noble gases**," suggesting that these gases do not like to have much to do with the other, more common materials (or that they don't do a lot of work).

Noble Gas Compounds

In more recent years, a number of reactions using the noble gas elements have been discovered. Although the conventional wisdom was that the complete outer shells of these elements would not allow them to react, some scientists believed that the outer electrons of the larger elements (such as Rn, Xe, and Kr) were far enough away from the nucleus that they should be able to be displaced under the right set of conditions. The first compound ($XePtF_6$) was made with xenon in 1962. Since then, several compounds have been made with radon, xenon, krypton, and argon. Only helium and neon have not formed compounds at this time.

Colors of Noble Gases

The different gases glow when an electric current is passed through them. Many of these gases are used in displays because of their chemical inertness. They are stable and will not react with other materials in the system. Radon also will give a reddish glow, but is not used because it is radioactive and will not retain its structure as radon for any significant length of time.

Summary

- The noble gases are in Group VIII of the periodic table.
- Helium has a full outer shell of two *s* electrons.
- The other gases have full outer shells of two *s* and six *p* electrons.
- Compounds have been formed with Rn, Xe, Kr, and Ar.

Practice

Use the link below to answer the following questions:

http://www.learner.org/interactives/periodic/groups4.html

1. Where was helium discovered? What does the name mean?
2. What does krypton react with?
3. What does xenon react with?
4. List present-day uses for each of the noble gases.

Review

1. What elements comprise the noble elements?
2. What state are they in at room temperature?
3. Why is helium non-reactive?
4. Why were the other noble gases believed to be non-reactive?
5. When was the first compound formed from xenon?
6. What happens when an electric current is passed through these gases?

- **inert:** Chemically unreactive and can be found in Group VIII in the period table.
- **monatomic:** Has one atom.
- **noble gas:** Another term for inert gas.

6.12 Halogens

- Name the halogens.
- Describe the physical properties of the halogens.
- Describe the chemical properties of the halogens.

How do you study a gas that does not exist as such in nature? It's not as easy as you think. Fluorine is so reactive that we cannot find it free. None of the halogens exist free in nature (unlike some of the metals suchas gold and silver) because they are very reactive. The video below shows how violently elemental fluorine reacts with other materials.

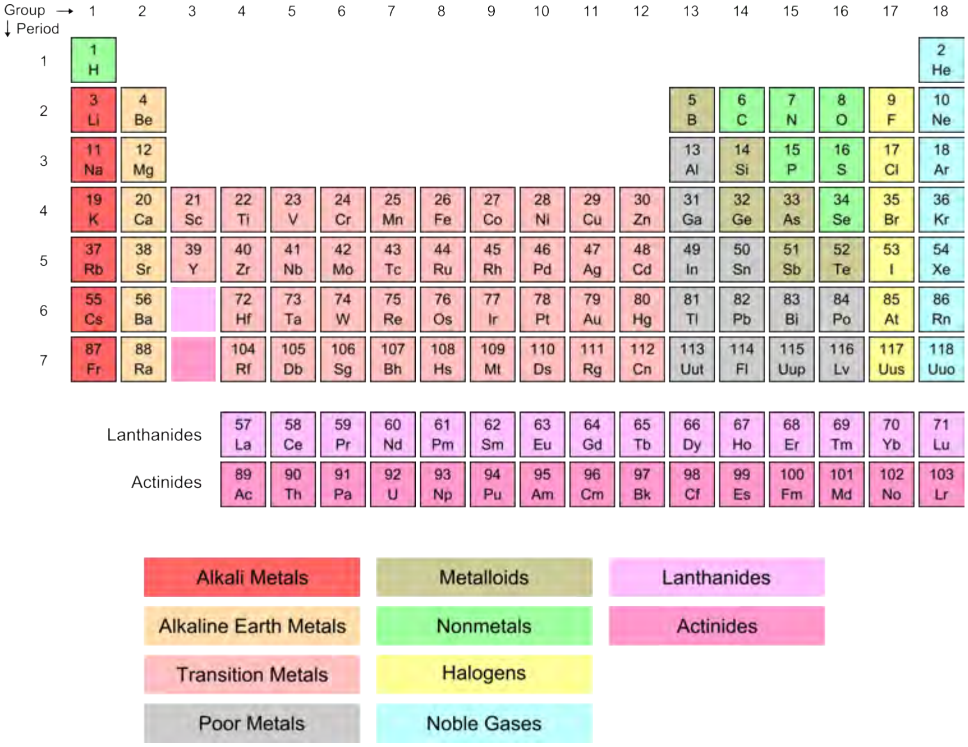
http://www.youtube.com/watch?v=vtWp45Eewtw

MEDIA

Click image to the left for more content.

Halogens

Some elements are much more reactive than others. The Group I (red) and Group II (tan) elements can easily lose electrons during a reaction. Elements of other groups are much more likely to accept electrons as they react.



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
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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

The elements of Group VII (new Group 17 - fluorine, chlorine, bromine, iodine, and astatine) are called the **halogens** (tan column). The term "halogen" means "salt-former" because these elements will readily react with alkali metal and alkaline earth metals to form halide salts. The halogens all have the general electron configuration ns^2np^5, giving them seven valence electrons. They are one electron short of having the full outer s and p sublevel, which makes them very reactive.

Physical Properties of Halogens

As elements, 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. In the picture below we see chlorine gas on the left (green), bromine solid and vapor in the middle (orange), and solid iodine (grey) on the right. Fluorine is not shown in the picture below because it is too corrosive and will destroy the glass container.

None of these elements are found free in nature because of their reactivity. Fluorine is found in combination with cations in several minerals. Chlorine is found in table salt, in the oceans (which are about 2% chloride ion by weight) and in lakes such as the Great Salt Lake in Utah. Small amounts of bromide and iodide salts can be found in the oceans and in brine wells in several states.

Watch video experiments of *p* block elements:

http://youtu.be/zZAiYc3WVXM - video of bromine reaction with aluminum

http://youtu.be/cbFCWFksYoM - halogen reactions

Summary

- The halogens all have seven electrons in their outer shells.
- The electron configuration in the outer shell is ns^2np^5.
- As the atomic number increases, the reactivity of the halogens decreases.
- Fluorine and chlorine exist as gases at room temperature, while bromine is a liquid, and iodine is a solid.

Practice

Use the link below to answer the following questions:

http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch10/group7.php

1. Are the halogen elements monatomic or diatomic molecules?
2. Why do we not know very much about astatine?
3. Describe the reactivity of elemental fluorine.
4. List one use for fluorine, chlorine, bromine, and iodine compounds.

Review

1. List the halogens by name, chemical symbol, and atomic weight.
2. What does the term “halogen” mean?
3. What is the outer shell electron configuration for the halogens?
4. What is the physical state of each halogen at room temperature?
5. Where are the halogens found?

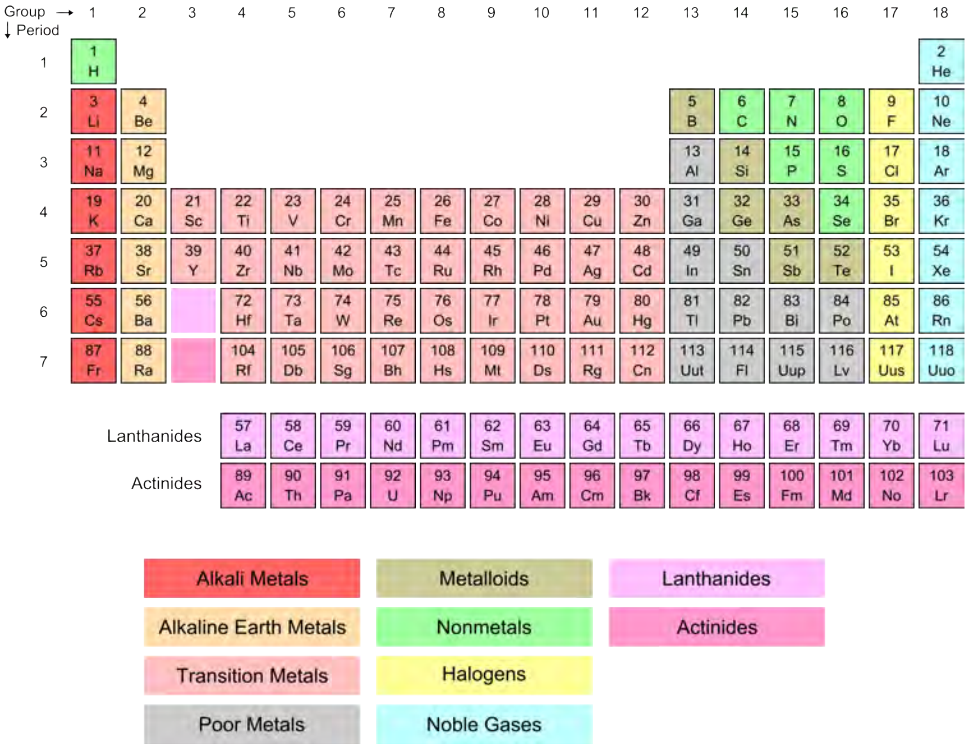
- **halogen:** The term "halogen" means "salt-former" because these elements will readily react with alkali metal and alkaline earth metals to form halide salts. These elements can be found in Group VII in the periodic table.

6.13 Transition Elements

- Identify the transition metals on the periodic table.
- Describe the characteristic electron configuration of the transition elements.

From the outside, the two cars above look the same (except for the flashy paint job on the racing model). They are the same model of the car, but one is a stock edition for regular driving while the other one is built for high-speed racing. We really can't tell much from the external view. To see the differences, we need to go under the hood, take the engines apart, and look at the braking and suspension systems in order to see how the two cars differ.

Many electron configurations of elements are simple and straighforward. We can look at the outer shell and easily understand how that set of elements will react in terms of electron gain or loss. However, there are sets of elements that are more complex in their behavior. One such group is called the **transition elements**.



Group → ↓ Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
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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

Transition elements are the elements that are found in Groups 3-12 (old groups IIA-IIB) on the periodic table (salmon-colored block in the middle of the table). The term refers to the fact that the *d* **sublevel**, which is in the process of being filled, 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]3 $d^1 4s^2$. Remember that the configuration is reversed from the fill order – the 4*s* filled before the 3*d* begins. Because they are all metals, the transition elements are often called the transition metals. As a group, they display typical metallic properties and are less reactive than the metals in Groups 1 and 2. Some of the more familiar ones are so unreactive that they can be found in nature in their free, or uncombined state. These include platinum, gold, and silver. Because of this unique filling order, the transition elements are often referred to as "*d*-block" elements.

FIGURE 6.1

Piece of silver.

Compounds of many transition elements are distinctive for being widely and vividly colored. Electron transitions that occur within the *d* sublevel release energies that result in the emission of visible light of varied wavelengths.

FIGURE 6.2

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.

Summary

- The transition elements are found in groups IIIA-IIB (new groups 3-12).
- These elements are characterized by having unfilled *d* sublevels.
- In general, the next higher *s* sublevel is already filled or has one electron missing.
- Many transition element compounds are brightly colored due to the inner-level *d* electron transitions.

Practice

Use the link below to answer the following questions:

http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch12/trans.php

1. Why are the transition metals named "transition?"
2. How do the properties of transition metals and main-group metals overlap?
3. Which electrons are more likely to be removed from transition metals as they react?

Review

1. List five different transition elements, giving their name, chemical symbol, and atomic number.
2. What is unique about the transition elements in terms of electron configurations?
3. Why are these elements often referred to as "*d*-block" elements?
4. Which transition group elements can be found in their free state in nature?
5. Why do many transition element compounds have bright colors?

- **transition element:** Elements can be found in Groups 3-12 (old groups IIA-IIB) on the period table. The term refers to the fact that the d sublevel, which is in the process of being filled, is in a lower principal energy level than the s sublevel filled before it.
- **sublevel:** Electron orbitals known as s, p, d, or f.

6.14 Lanthanides and Actinides

- Describe the electron configurations of the lanthanide and actinide elements.
- List uses for lanthanides and actinides.

Russian "nesting dolls" (often known as matryoshka dolls) have a long history in Russia. These dolls are designed to nest inside of one another. When we open the largest doll, we find a somewhat smaller doll inside it. These dolls can often go down seven or eight layers. The set seen above is unusual in that it has over thirty-five layers.

Lanthandies and Actinides

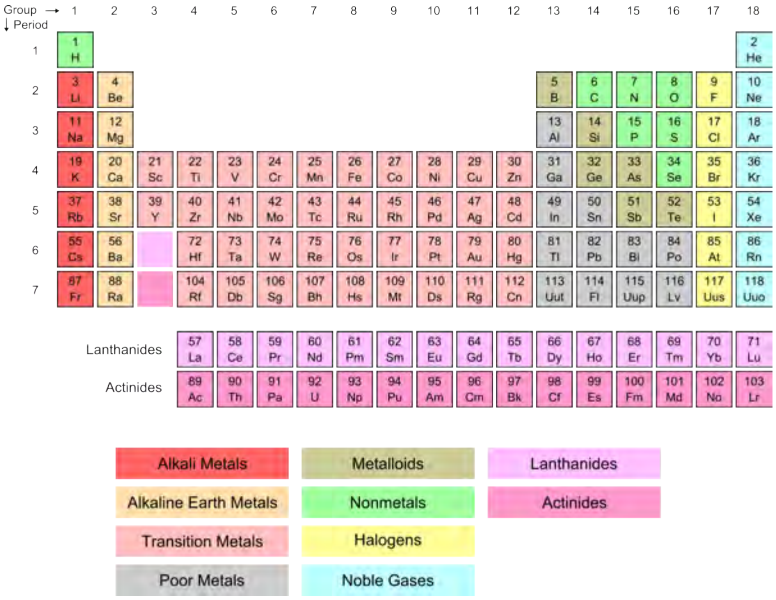
We see some hidden "layers" in chemistry. As we look at the periodic table below, we see two pink boxes – one between Ba (element 56) and Hf (element 72) and the other between Ra (88) and Rf (104). These elements all have unfilled *f*-sublevels. Because of the uniqueness of the electron configurations, these elements fit into the two boxes in the larger periodic table.

As the number of elecrons in an atom increases, we begin to see some strange behaviors. Due to the way the electron energy levels work, some inner levels fill after one or more outer levels do. We see this in two similar groups of elements – the **lanthanides** and the **actinides**.

The *f*-Block

The first of the *f* sublevels to begin filling is the 4*f* sublevel. It fills after the 6*s* 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 accommodate 14 electrons, so the *f* block is 14 elements in length. It is pulled out of the main body of the period table and is shown at the very bottom. Because of that, the elements of the *f* block do not belong to a group, being wedged in between Groups 3 and 4. The lanthanides are the 14 elements from cerium (atomic number 58) to lutetium (atomic number 71). The word comes from the Greek "lanthanein" meaning "to be hidden." The name probably arose because these elements all hide behind one another in the periodic table. The 4*f* sublevel is in the process of being filled for the lanthanides. 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). The 5*f* sublevel is in the process of being filled. The actinides are all radioactive elements and only the first four have been



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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
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Alkali Metals	Metalloids	Lanthanides
Alkaline Earth Metals	Nonmetals	Actinides
Transition Metals	Halogens	
Poor Metals	Noble Gases	

FIGURE 6.3

Periodic table.

found naturally on Earth. All of the others have only been artificially made in the laboratory. The lanthanides and actinides together are sometimes called the inner transition elements.

Uses of Lanthanides

Lanthanides have been widely used as alloys to impart strength and harness to metals. The main lanthanide used for this purpose is cerium, mixed with small amounts of lanthanum, neodymium, and praseodymium. These metals are also widely used in the petroleum industry for refining of crude oil into gasoline products.

FIGURE 6.4

Oil refinery.

Erbium and other lanthanides are widely used in some optical devices, such as night vision goggles, laser beams, and phosphorescent materials.

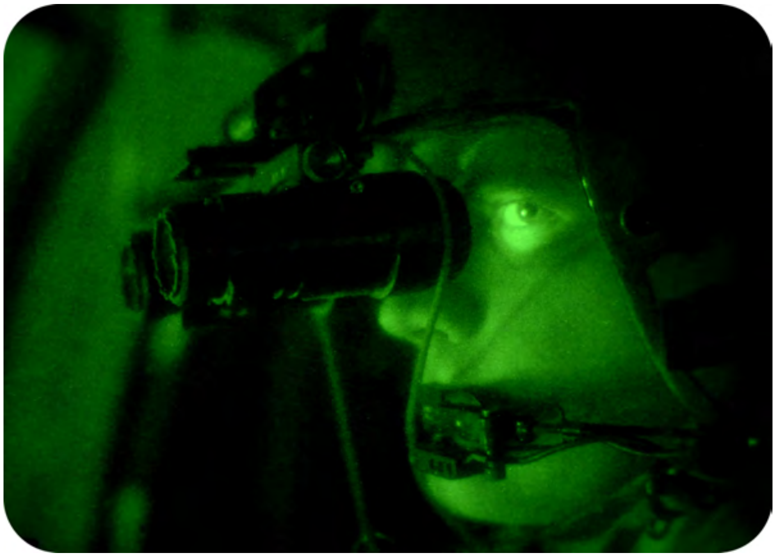


FIGURE 6.5

Night vision goggles.

Uses of Actinides

The actinides are valuable primarily because they are radioactive. These elements can be used as energy sources for applications as varied as cardiac pacemakers and generation of electrical energy for instruments on the moon. Uranium and plutonium have been employed in nuclear weapons and in nuclear power plants.

Summary

- Lanthanides and actinides are elements with unfilled *f* orbitals.
- Lanthanides are all metals with reactivity similar to group 2 elements.
- Actinides are all radioactive elements.
- Lanthanides are used in optical devices (night vision goggles), petroleum refining, and alloys.
- Actinides are found primarily in applications where their radioactivity can be used to power devices such as cardiac pacemakers.

Practice

Use the link below to answer the following questions:

http://chemistry.about.com/od/elementgroups/a/lanthanides.htm

1. List three physical characteristics of the lanthanides
2. What do lanthanides produce when they react with water?

Review

1. What electron sublevel is being filled in the lanthanides?
2. What electron sublevel is being filled in the actinides?
3. What sublevel is filled just prior to the filling of this sublevel?

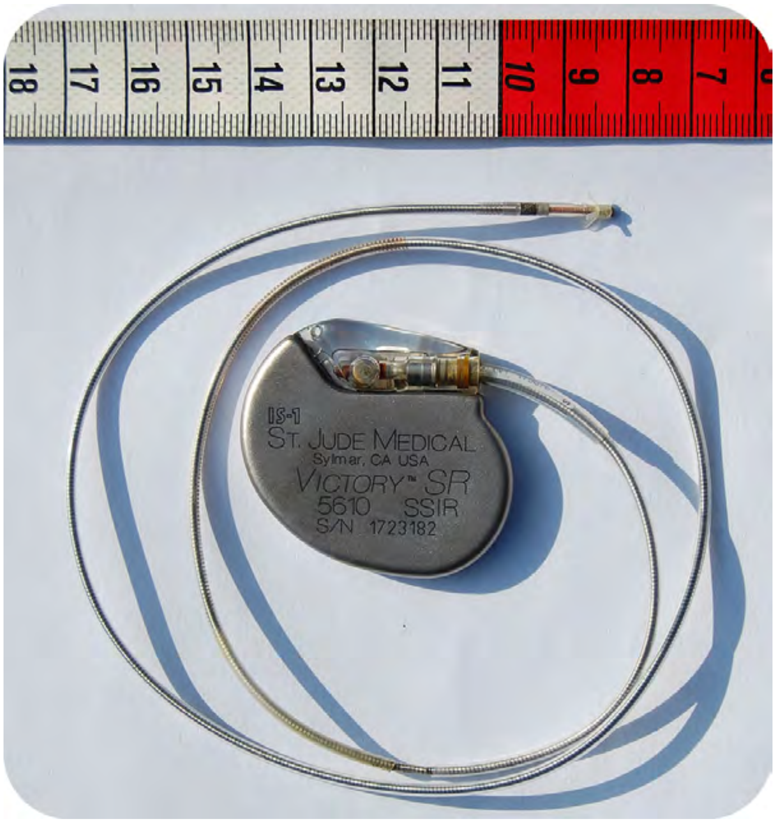


FIGURE 6.6
Pacemaker.

4. Which actinides are found naturally on earth?
5. List some uses for lanthanides.
6. List some uses for actinides.

- **lanthanide:** The lanthanides are the 14 elements from cerium (atomic number 58) to lutetium (atomic number 71). The word comes from the Greek "lanthanein" meaning "to be hidden."
- **actinide:** The actinides are the 14 elements from thorium (atomic number 90) to lawrencium (atomic number 103). The $5f$ sublevel is in the process of being filled. The actinides are all radioactive elements and only the first four have been found naturally on Earth.
- **f-block:** In the periodic table, any element that has atoms or ions who have valence electrons in f-orbitals.

6.15 Periodic Trends: Atomic Radius

- Define atomic radius.
- Describe how the atomic changes within a period.
- Describe how the atomic radius changes within a group.

Events draw large numbers of people to them. Evan an outdoor event can fill up so that there is no room for more people. The crowd capacity depends on the amount of space in the venue, and the amount of space depends on the size of the objects filling it. We can get more people into a given space than we can elephants, because the elephants are larger than people. We can get more squirrels into that same space than we can people for the same reason. Knowing the sizes of objects we are dealing with can be important in deciding how much space is needed.

Atomic Radius

The size of atoms is important when trying to explain the behavior of atoms or compounds. One of the ways we can express the size of atoms is with the **atomic radius**. This data helps us understand why some molecules fit together and why other molecules have parts that get too crowded under certain conditions.

The size of an atom is defined by the edge of its orbital. However, orbital boundaries are fuzzy and in fact are variable under different conditions. In order to standardize the measurement of atomic radii, the distance between the nuclei of two identical atoms bonded together is measured. The atomic radius is defined as one-half the distance between the nuclei of identical atoms that are bonded together.

Atomic radii have been measured for elements. The units for atomic radii are picometers, equal to 10^{-12} meters. As an example, the internuclear distance between the two hydrogen atoms in an H_2 molecule is measured to be 74 pm. Therefore, the atomic radius of a hydrogen atom is $\frac{74}{2} = 37$ pm.

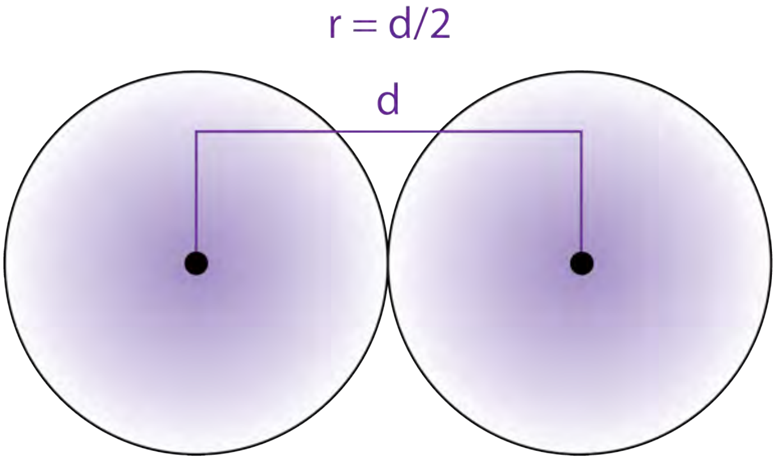


FIGURE 6.7

The atomic radius (r) of an atom can be defined as one half the distance (d) between two nuclei in a diatomic molecule.

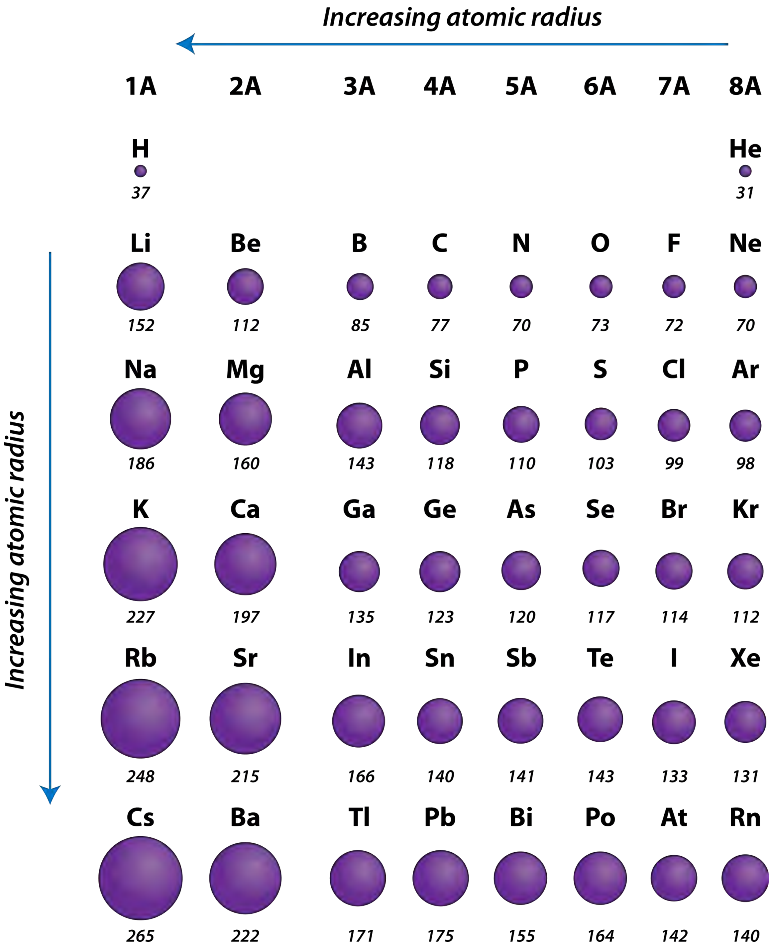


FIGURE 6.8

Atomic radii of the representative elements measured in picometers.

Periodic Trend

The atomic radius of atoms generally decreases from left to right across a period. There are some small exceptions, such as the oxygen radius being slightly greater than the nitrogen radius. Within a period, protons are added to the nucleus as electrons are being added to the same principal energy level. These electrons are gradually pulled closer to the nucleus because of its increased positive charge. Since the force of attraction between nuclei and electrons increases, the size of the atoms decreases. The effect lessens as one moves further to the right in a period because of electron-electron repulsions that would otherwise cause the atom's size to increase.

Group Trend

The atomic radius of atoms generally increases from top to bottom within a group. As the atomic number increases down a group, there is again an increase in the positive nuclear charge. However, there is also an increase in the number of occupied principle energy levels. Higher principal energy levels consist of orbitals which are larger in size than the orbitals from lower energy levels. The effect of the greater number of principal energy levels outweighs the increase in nuclear charge and so atomic radius increases down a group.

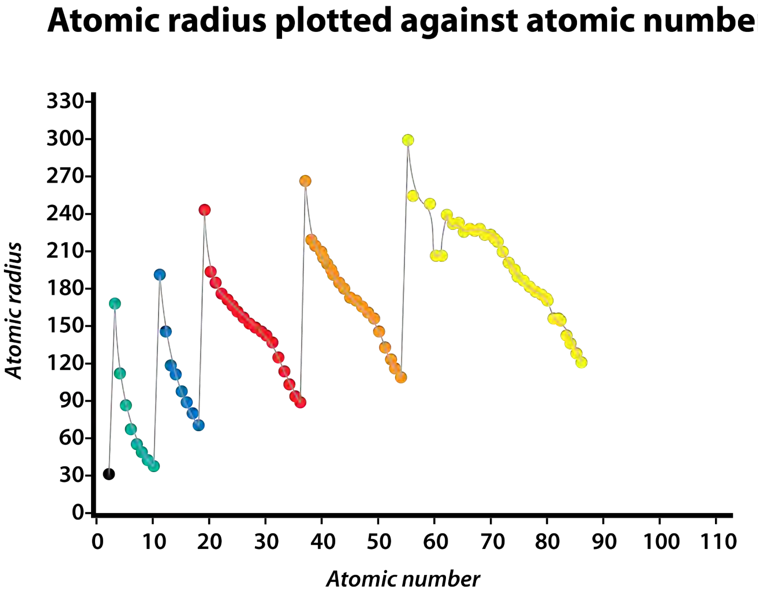


FIGURE 6.9

A graph of atomic radius plotted versus atomic number. Each successive period is shown in a different color. As the atomic number increases within a period, the atomic radius decreases.

Summary

- Atomic radius is determined as the distance between the nuclei of two identical atoms bonded together.
- The atomic radius of atoms generally decreases from left to right across a period.
- The atomic radius of atoms generally increases from top to bottom within a group.

Practice

Use the link below to answer the following questions:

http://chemwiki.ucdavis.edu/Inorganic_Chemistry/Descriptive_Chemistry/Periodic_Table_of_the_Elements/Atomic_Radi

1. What influences the atomic size of an atom?
2. What is a covalent radius?
3. What is an ionic radius?

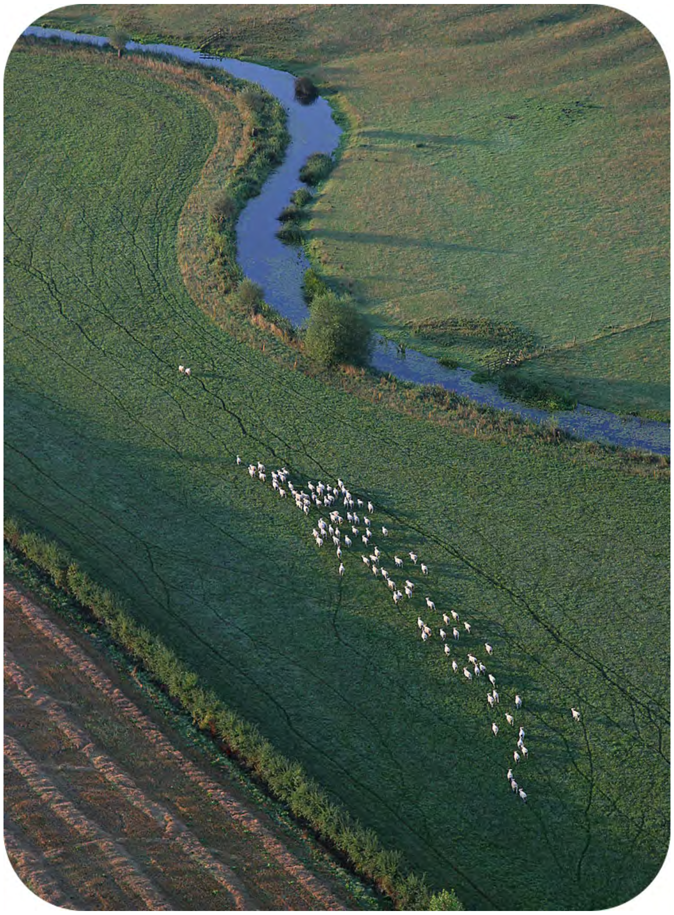
Review

1. Define “atomic radius.”
2. What are the units for measurement of atomic radius?
3. How does the atomic radius change across a period?
4. How does atomic radius change from top to bottom within a group?
5. Explain why the atomic radius of hydrogen is so much smaller that the atomic radius for potassium.

- **atomic radius:** The atomic radius is defined as one-half the distance between the nuclei of identical atoms that are bonded together.

6.16 Periodic Trends: Ionization Energy

- Define ionization energy.
- Describe factors affecting ionization energy.
- Describe how ionization energy changes across a period.
- Describe how ionization energy changes down a group.



Like many other animals, sheep travel in herds. The tendency is for each individual sheep to stay with the herd. However, a sheep may sometimes wander off, depending on how strong the attraction is for a particular food or water supply. At other times, a sheep may become frightened and run off. Whether a sheep chooses to stay with the herd or go its own way depends on the balance between attraction to the herd and attraction to the outside influence.

There is an on-going tension between the electrons and protons in an atom. Reactivity of the atom depends in part on how easily the electrons can be removed from the atom. We can measure this quantity and use it to make predictions about the behaviors of atoms.

Ionization Energy

Ionization energy is 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. The ionization energies associated with some elements are described below.

For any given atom, the outermost valence electrons will have lower ionization energies than the inner-shell kernel electrons. As more electrons are added to a nucleus, the outer electrons become shielded from the nucleus by the inner shell electrons. This is called **electron shielding**.

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

If we plot the first ionization energies vs. atomic number for the main group elements, we would have the following trend

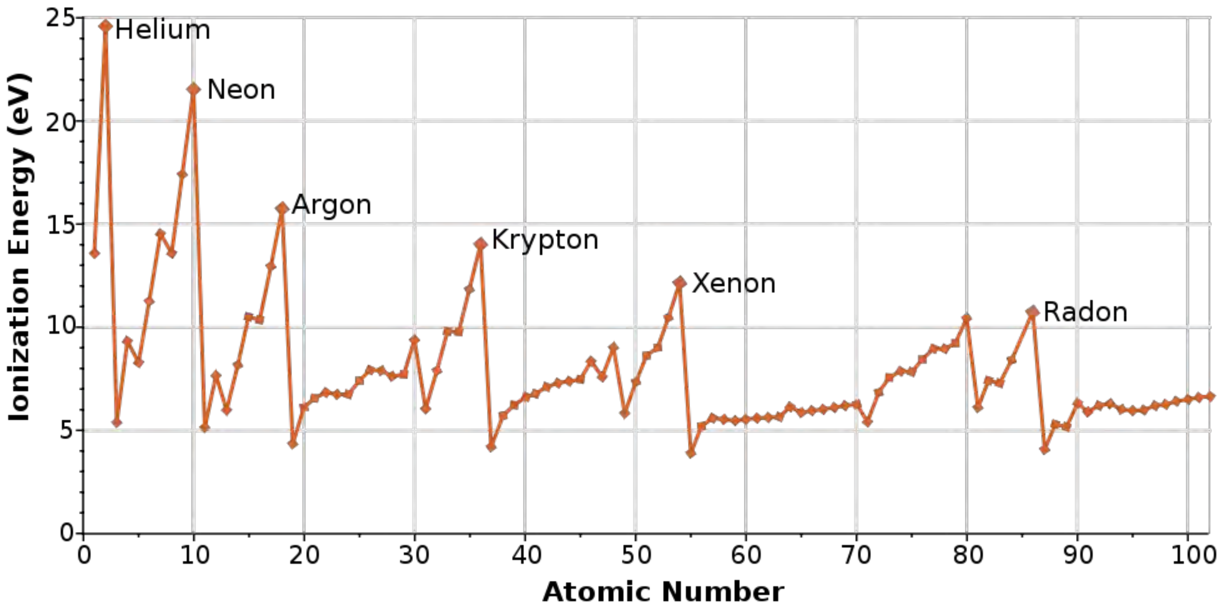


FIGURE 6.10

Ionization energy and atomic number.

Moving from left to right across the periodic table, the ionization energy for an atom increases. We can explain this by considering the nuclear charge of the atom. The more protons in the nucleus, the stronger the attraction of the nucleus to electrons. This stronger attraction makes it more difficult to remove electrons.

Within a group, the ionization energy decreases as the size of the atom gets larger. On the graph, we see that the ionization energy increases as we go up the group to smaller atoms. In this situation, the first electron removed is farther from the nucleus as the atomic number (number of protons) increases. Being farther away from the positive attraction makes it easier for that electron to be pulled off.

Summary

- Ionization energy refers to the amount of energy needed to remove an electron from an atom.
- Ionization energy decreases as we go down a group.
- Ionization energy increases from left to right across the periodic table.

Practice

Use the following link to answer the questions below:

http://dl.clackamas.cc.or.us/ch104-07/ionization_energy.htm

1. What is a "gaseous atom?"
2. Why would the ionization energy for O be somewhat less than that for N?
3. Why is a third-level electron easier to remove than a first-level one?

Review

1. Define "ionization energy."
2. Do valence electrons have larger or smaller ionization energies that the inner-shell kernel electrons?
3. What is electron shielding?
4. Describe the trends in ionization energy from left to right across the periodic table.
5. Describe the trends in ionization energy from top to bottom of a group in the periodic table.
6. Why is the second ionization energy for lithium so much larger than the first ionization energy?

- **electron shielding:** As more electrons are added to a nucleus, the outer electrons become shielded from the nucleus by the inner shell electrons

- **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.

6.17 Electron Shielding

- Define electron shielding.
- Explain sublevel shielding.

Roller derby is a popular sport, although it is unfamiliar to many people. The basic purpose is to set one team member (the "jammer") past the opposing team to score points. Other members of the team serve as blockers to prevent the opposing team from stopping the jammer. Blockers interfere with the interaction between the jammer and the opponents by getting between the jammer and the skaters trying to stop her.

The attraction between an electron and the nucleus of the atom is not a simple issue. Only with hydrogen is there a one-to-one relationship that can be discussed in terms of direct charge attraction. As the size of the atom increases, the number of protons and electrons also increase. These changes influence how the nucleus attracts electrons.

Electron Shielding

In general, the ionization energy of an atom will increase as we move from left to right across the periodic table. There are several exceptions to the general increase in ionization energy across a period. The elements of Group 13 (B, Al, etc.) have lower ionization energies than the elements of Group 2 (Be, Mg, etc.). This is an illustration of a concept called "**electron shielding**." Outer electrons are partially shielded from the attractive force of the protons in the nucleus by inner electrons.

To explain how shielding works, consider a lithium atom. It has three protons and three electrons – two in the first principal energy level and its valence electron 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 becomes easier because of the shielding effect.

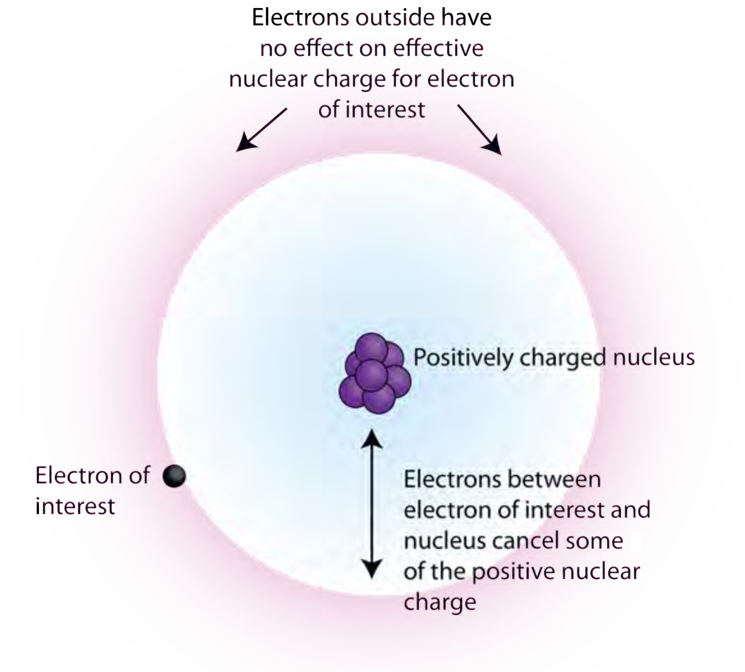


FIGURE 6.11

The shielding effect is shown by the interior electron cloud (light blue) shielding the outer electron of interest from the full attractive force of the nucleus. A larger shielding effect results in a decrease in ionization energy.

There is also a shielding effect that occurs between sublevels within the same principal energy level. Specifically, an electron in the "*s*" sublevel is capable of shielding electrons in the "*p*" sublevel of the same principal energy level. This is because of the spherical shape of the "*s*" orbital. The reverse is not true – electrons in "*p*" orbitals do not shield electrons in "*s*" orbitals.

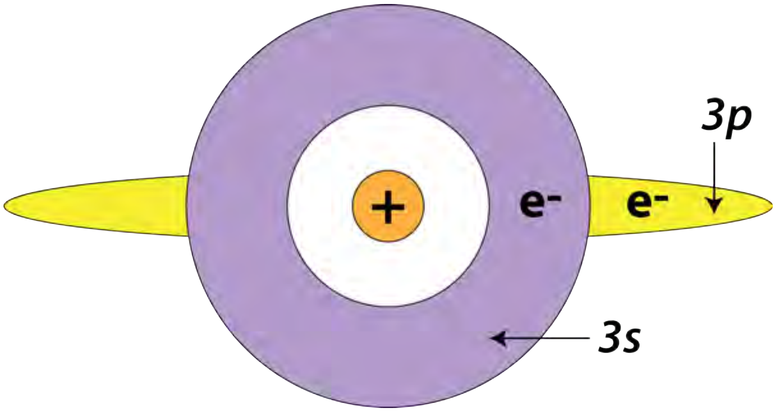


FIGURE 6.12

The spherical 3*s* orbital exhibits a shielding effect on the dumbbell shaped 3*p* orbital that is of slightly higher energy. This reduces the ionization energy of a 3*p* electron compared to a 3*s* electron.

The electron being removed from an Al atom is a 3*p* electron, which is shielded by the two 3*s* electrons as well as all the **inner core electrons**. The electron being removed from a Mg atom is a 3*s* electron, which is only shielded by the inner core electrons. Since there is a greater degree of electron shielding in the Al atom, it is slightly easier to remove the valence electron and its ionization energy is less than that of Mg. This is despite the fact that the nucleus of the Al atom contains one more proton than the nucleus of the Mg atom.

There is another anomaly between Groups 15 and 16. Atoms of Group 16 (O, S, etc.) have lower ionization energies than atoms of Group 15 (N, P, etc.). Hund's rule is behind the explanation. In a nitrogen atom, there are three electrons in the 2*p* sublevel and each is unpaired. In an oxygen atom, there are four electrons in the 2*p* sublevel, so one orbital contains a pair of electrons. It is that second electron in the orbital that is removed in the ionization of an oxygen atom. Since electrons repel each other, it is slightly easier to remove the electron from the paired set in the oxygen atom than it is to remove an unpaired electron from the nitrogen atom.

Summary

- Electron shielding refers to the blocking of valence shell electron attraction by the nucleus due to the presence of inner-shell electrons.
- Electrons in an *s* orbital can shield *p* electrons at the same energy level because of the spherical shape of the *s* orbital.
- Electrons in paired spin configurations are slightly easier to remove than unpaired electrons.

Practice

Use the link below to answer the following questions:

http://www.wisegeek.com/what-is-the-shielding-effect.htm

1. Why are electrons highly attracted to the nucleus?
2. What happens when additional electrons are present in different orbits?
3. What electrons are mainly influenced by electron shielding?

Review

1. Define “electron shielding."
2. Why do group 13 elements have lower ionization energies than group 2 elements?
3. What influence does a larger shielding effect have on ionization energy?
4. How do *s* orbit electrons affect the ionization energy of a *p* electron in the same shell?
5. Why do group 16 atoms have lower ionization energies than the corresponding group 15 atoms?

- **electron shielding:** As more electrons are added to a nucleus, the outer electrons become shielded from the nucleus by the inner shell electrons.
- **inner core electrons:** Electrons that prevent attraction between valence electrons and protons.

6.18 Electron Affinity

- Define electron affinity.
- Describe trends in electron affinity in the periodic table.

Packing for a trip can be very challenging. What do you take with you? Where will you be going and what will you need? We usually pack too much (like the suitcase above) and then find it hard to close the suitcase. When the suitcase is over-full, there is stress on the system and forces pushing the suitcase open. When electrons are added to a nucleus, the increased negative charge puts stress on the electrons already there, causing energy to be released.

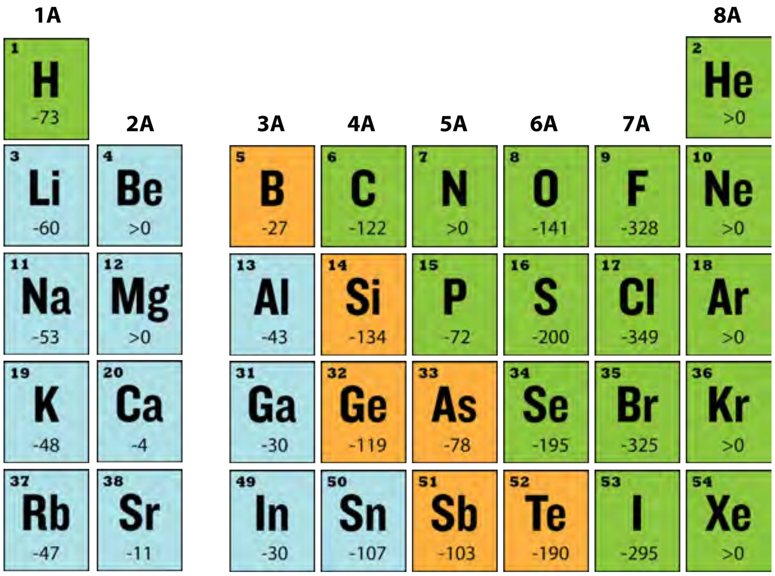
When electrons are removed from an atom, that process requires energy to pull the electron away from the nucleus. Addition of an electron produces energy from the process.

Electron Affinity

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 the chloride ion formation below:

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

The energy change that occurs when a neutral atom gains an electron is called its **electron affinity**. When energy is released in a chemical reaction or process, that energy is expressed as a negative number. The figure below shows electron affinities in kJ/mole for the representative elements. Electron affinities are measured on atoms in the gaseous state and are very difficult to measure accurately.



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 6.13

Electron affinities (in kJ/mol) of the first five periods of the representative elements. Electron affinities are negative numbers because energy is 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 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, owing in part to inherent difficulties in accurately measuring electron affinities.

Summary

- Electron affinity is a measure of the energy released when an extra electron is added to an atom.
- Electron affinities are measured in the gaseous state.
- In general, electron affinities become more negative as we move from left to right on the periodic table.
- In general, electron affinities become less negative from top to bottom of a group.

Practice

Use the link below to answer the following questions:

http://www.chemguide.co.uk/atoms/properties/eas.html

1. Which groups (using the old Roman numeral system) of elements are primarily involved with issues of electron affinity?
2. What does a negative energy imply?

3. Why is the electron affinity value for fluorine less than that of chlorine?

Review

1. Define “electron affinity."
2. Does addition of an electron to a neutral atom require energy or release energy?
3. Describe the general trend for electron affinity values moving from left to right on the periodic table.
4. Describe the general trend for electron affinity values moving from top to bottom in a group on the periodic table.
5. Why is more energy released in the formation of a halide ion than with other elements?

- **electron affinity:** The energy change that occurs when a neutral atom gains an electron.

6.19 Ionic Radii

- Define ionic radius.
- Explain how ionic radii are measured.
- Describes trends in ionic radius in the periodic table.

Peanuts can be sold two ways. The bare peanut without the shell (brown inner portion of peanut) can be purchased in jars and packages for casual munching or for cooking. The size of the peanut in the situation is smaller than the peanut plus shell since the outer portion is missing. If we add the shell to the peanut, we have a larger size for the combination.

Electrons and protons are strongly attracted to one another. The strength of that attraction and the relative numbers of the two particles in a given atom or ion have a significant influence on the size of that species. When an atom loses one or more electrons, the resulting ion becomes smaller. If electrons are added to the atom, the ion becomes larger.

Ionic Radius

The **ionic radius** for an atom is measured in a **crystal lattice**, requiring a solid form for the compound. These radii will differ somewhat depending upon the technique used. Usually X-ray crystallography is employed to determine the radius for an ion.

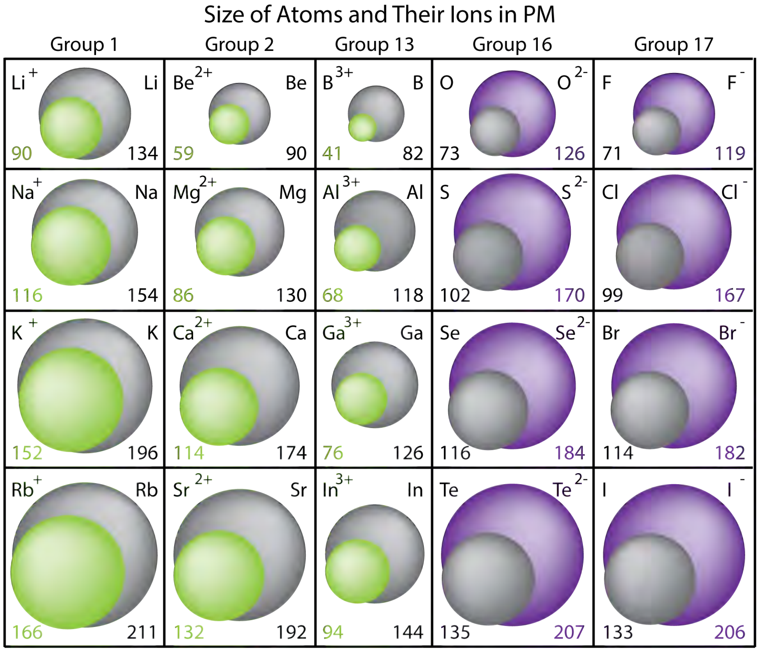


FIGURE 6.14

Comparison of ion sizes to atom sizes for Groups 1, 2, 13, 16 and 17. The atoms are shown in gray. Groups 1, 2, and 13 are metals and form cations, shown in red. Groups 16 and 17 are nonmetals and form anions, shown in blue.

The removal of electrons always results in a cation that is considerably smaller than the parent atom. When the valence electron(s) are removed, the resulting ion has one fewer occupied principal energy level, so the electron cloud that remains is smaller. Another reason is that the remaining electrons are drawn closer to the nucleus because the protons now outnumber the electrons. One other factor is the number of electrons removed. The potassium atom has one electron removed to for the corresponding ion, while calcium loses two electrons.

The addition of electrons always results in an anion that is larger than the parent atom. When the electrons outnumber the protons, the overall attractive force that the protons have for the electrons is decreased. The electron cloud also spreads out because more electrons results in greater electron-electron repulsions. Notice that the group 16 ions are larger than the group 17 ions. The group 16 elements each add two electrons while the group 17 elements add one electron per atom for form the anions.

Summary

- Ionic radius is determined by measuring the atom in a crystal lattice.
- Removal of electrons results in an ion that is smaller than the parent element.
- Addition of electrons results in an ion that is larger than the parent atom.

Practice

Use the link below to answer the following questions:

http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch7/size.html

1. What was the first compound used for determination of ionic radii?
2. What assumptions were made in doing these measurements?
3. Why is it important to know ionic radii?

Review

1. How are ionic radii measured?
2. Explain why the radius of the rubidium ion is smaller than the radius of the rubidium atom.
3. Explain why the radius of the tellurium ion is larger than the radius of the tellurium atom.
4. Why is the oxygen anion larger than the fluoride anion?
5. Why is the sodium cation larger than the magnesium cation?

- **ionic radius:** Determined by measuring the atom in a crystal lattice.
- **crystal lattice:** Inside a crystal, it's the three-dimensional symmetrical arrangement of atoms.

6.20 Periodic Trends: Electronegativity

- Define electronegativity.
- Describe trends in electronegativity in the periodic table.

Have you ever noticed how some people attract others to them? Whether it is their personality, attractiveness, or athletic skills – something pulls people toward them, while others have a smaller group of friends and acquaintances. Atoms do the same thing. One atom may pull electrons strongly to it, while a second type of atom has much less "pulling power."

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 the electrons when the atom is part of a compound. Electronegativity differs from electron affinity because electron affinity is the actual energy released when an atom gains an electron. Electronegativity is not measured in energy units, but is rather a relative scale. All elements are compared to one another, with the most electronegative element, fluorine, being assigned an electronegativity value of 3.98. Fluorine attracts electrons better than any other element. The table below shows the electronegativity values for 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.

Trends

Electronegativities generally increase from left to right across a period. This is due to an increase in nuclear charge. Alkali metals have the lowest electronegativities, while halogens have the highest. Because most noble gases do not form compounds, they do not have electronegativities. 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.

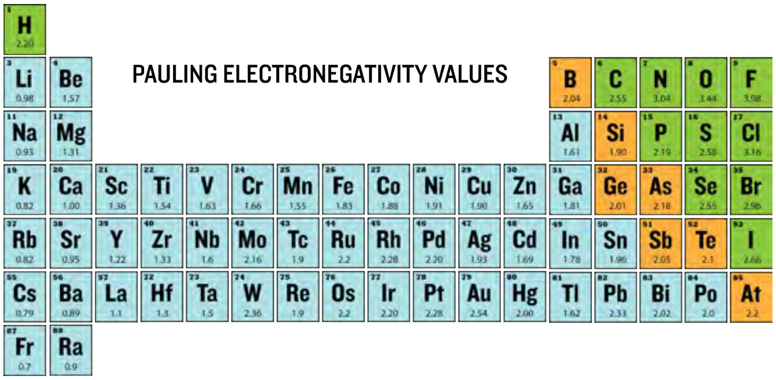
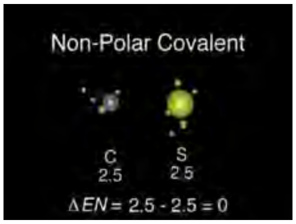


FIGURE 6.15

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 electronegativities measurements are on a relative scale.

Of the main group elements, fluorine has the highest electronegativity (EN = 4.0) and cesium the lowest (EN = 0.79). This indicates that fluorine has a high tendency to gain electrons from other elements with lower electronegativities. We can use these values to predict what happens when certain elements combine. The following video shows this.

http://www.youtube.com/watch?v=Kj3o0XvhVqQ



MEDIA

Click image to the left for more content.

When the difference between electronegativities is greater than 1.7, then a complete exchange of electrons occurs. Typically this exchange is between a metal and a nonmetal. For instance, sodium and chlorine will typically combine to form a new compound and each ion becomes isoelectric with its nearest noble gas. When we compare the EN values, we see that the electronegativity for Na is 0.93 and the value for Cl is 3.2. The absolute difference between ENs is |0.93 - 3.2| = 2.27. This value is greater than 1.7, and therefore indicates a complete electron exchange occurs.

Summary

- Electronegativity is a measure of the ability of an atom to attract the electrons when the atom is part of a compound.
- Electronegativity values generally increase from left to right across the periodic table.
- Electronegativities generally decrease from top to bottom of a group.
- The highest electronegativity value is for fluorine.

Practice

Use the link below to answer the following questions:

http://www.chemguide.co.uk/atoms/bonding/electroneg.html

1. What are the least electronegative elements?
2. What is a polar bond?
3. What happens if atom A in a bond has much more electronegativity that atom B?

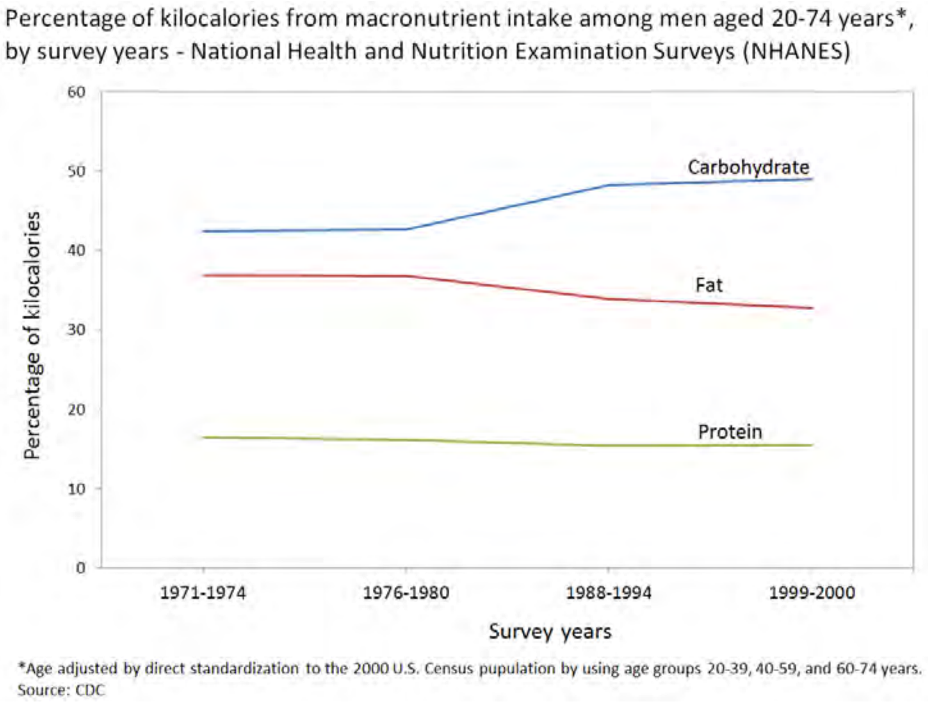
Review

1. Define “electronegativity.”
2. How does electronegativity differ from electron affinity?
3. Why are the electronegativity values of metals generally low?
4. Describe the trend in electronegativities across the periodic table.
5. Describe the trends in electronegativities in a group of the periodic table.

- **electronegativity:** A measure of the ability of an atom to attract the electrons when the atom is part of a compound.

6.21 Metallic and Nonmetallic Character

- Define metallic character.
- Define non-metallic character.
- Describe trends in metallic character in the periodic table.
- Describe trends in non-metallic character in the periodic table.



What are we eating as a nation?

The graph above indicates some trends in our diet for a thirty-year period. This graph has health implications as professionals work to help us lower weight and have less health problems. By knowing the direction our eating habits are going, we can take steps to help control bad habits and decrease such problems as high blood pressure and heart attacks.

Development of the periodic table has helped organize chemical information in many ways. We can now see trends among properties of different atoms and make predictions about the behavior of specific materials.

Metallic and Nonmetallic Character

Metallic character refers to the level of reactivity of a metal. Metals tend to lose electrons in chemical reactions, as indicated by their low ionization energies. Within a compound, metal atoms have relatively low attraction for electrons, as indicated by their low ionization energies. By following the trend summary in the figure below, you can see that the most reactive metals would reside in the lower left portion of the periodic table. The most reactive metal is cesium, which is not found in nature 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 is so rare that most of its properties have never been observed.

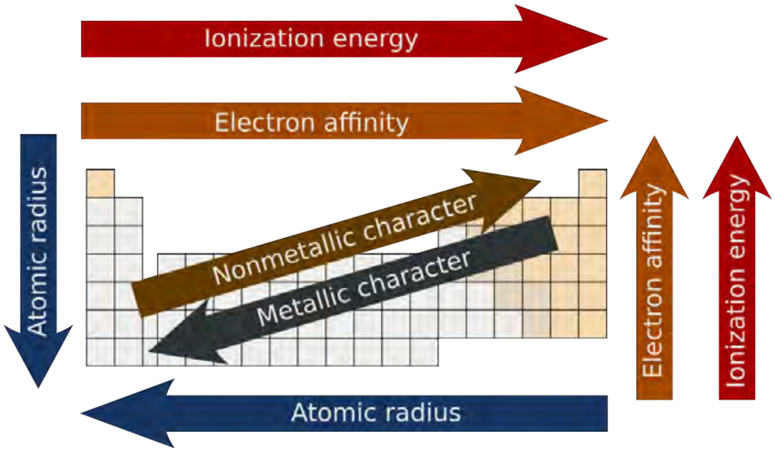


FIGURE 6.16

Trends in behaviors of elements.

Reactivity of metals is based on processes such as the formation of halide compounds with halogens and how easily they displace hydrogen from dilute acids.

The metallic character increases as you go down a group. Since the electron affinity decreases going down a group (or increases going up a group), the increased ability for metals lower in a group to lose electrons makes them more reactive. In addition, the atomic radius increases going down a group, placing the outer electrons further away from the nucleus and making that electron less attracted by the nucleus.

Nonmetals tend to gain electrons in chemical reactions and have a high attraction for electrons within a compound. The most reactive nonmetals reside in the upper right portion of the periodic table. Since the noble gases are a special group because of their lack of reactivity, the element fluorine is the most reactive nonmetal. It is 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.

Note that there is no clear division between metallic and **non-metallic** character. As we move across the periodic table, there is an increasing tendency to accept electrons (non-metallic) and a decrease in the possibility that an atom would give up one or more electrons.

Summary

- Metallic character refers to the level of reactivity of a metal.
- Non-metallic character relates to the tendency to accept electrons during chemical reactions.
- Metallic tendency increases going down a group.
- Non-metallic tendency increases going from left to right across the periodic table.

Practice

Use the link below to answer the following questions:

http://www.chem.tamu.edu/class/majors/tutorialnotefiles/metals.htm

1. List three characteristics of metals.
2. List three characteristics of non-metals.
3. Give two differences between metals and non-metals that would affect metallic and non-metallic properties.

Review

1. Define “metallic character.”
2. Define “non-metallic character.”
3. Describe the trend in metallic character going down a group.
4. Describe the trend in non-metallic character going across the periodic table.
5. Why does the metallic character increase as you go down a group?

- **metallic:** Refers to the level of reactivity of a metal.
- **nonmetallic:** Relates to the tendency to accept electrons during chemical reactions.

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CHAPTER 7

Chemical Nomenclature

Chapter Outline

7.1 Molecular Formula

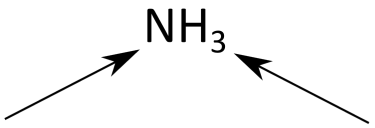
- Define molecule.
- Define molecular formula.
- Describe how to write molecular formulas.

There are many "universal languages" in the world. Musicians of every culture recognize the music embodied in a series of notes on a staff.

This passage from a Bach cello suite could be played by any trained musician from any country, because there is agreement as to what the symbols on the page mean. In the same way, molecules are represented using symbols that all chemists agree upon.

Molecular Formula

A **molecule** is two or more atoms that have been chemically combined. A **molecular formula** is a chemical formula of a molecular compound that shows the kinds and numbers of atoms present in a molecule of the compound. Ammonia is a compound of nitrogen and hydrogen as shown below:



The lack of a subscript on the N symbol indicates that there is 1 atom of nitrogen in a molecule of ammonia.

The subscript below the H symbol indicates that there are 3 hydrogen atoms in a molecule of ammonia.

Note from the example that there are some standard rules to follow in writing molecular formulas. The arrangements of the elements depend on the particular structure, so we will not concern ourselves with that point right now. The number of atoms of each kind is indicated by a subscript following the atom. If there is only one atom, no number is written. If there is more than one atom of a specific kind, the number is written as a subscript following the atom. We would not write N_3H for ammonia, because that would mean that there are three nitrogen atoms and one hydrogen atom in the molecule, which is incorrect.

The molecular formula does not tell us anything about the shape of the molecule or where the different atoms are. The molecular formula for sucrose (table sugar) is $C_{12}H_{22}O_{11}$. This simply tells us the number of carbon, hydrogen, and oxygen atoms in the molecule. There is nothing said about where the individual atoms are located. We need a much more complicated formula (shown below) to communicate that information.

Summary

- A molecular formula tells us what atoms and how many of each type of atom are present in a molecule.
- If only one atom of a specific type is present, no subscript is used.
- For atoms that have two or more present, a subscript is written after the symbol for that atom.
- Molecular formulas do not indicate how the atoms are arranged in the molecule.

Practice

Use the link below to answer the following questions:

http://www.iun.edu/ cpanhd/C101webnotes/composition/formmolcmpds.html

1. How many carbon atoms and how many hydrogen atoms are in the benzene molecule?
2. How many oxygen atoms are in one molecule of water?
3. How many oxygen atoms are in one molecule of acetic acid?

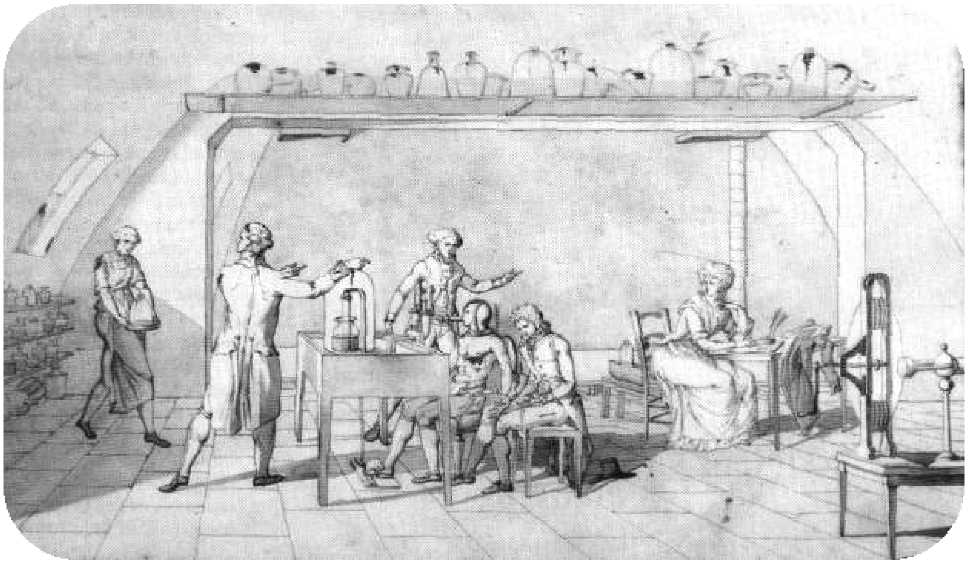
Review

1. What does a molecular formula tell us?
2. What does a molecular formula not tell us?
3. What do the subscripts mean in a molecular formula?
4. If I wrote $C_6H_{11}O_5C_6H_{11}O_6$ as the molecular formula for sucrose, would that be correct? Explain your answer.
5. Sometimes the formula for acetic acid is written CH_3COOH. Is this a true molecular formula?

- **molecule:** Two or more atoms that have been chemically combined.
- **molecular formula:** A chemical formula of a molecular compound that shows the kinds and numbers of atoms present in a molecule of the compound.

7.2 Empirical Formula

- Define empirical formula.
- Describe how to determine the empirical formula for a compound.



When the French scientist Antoine Lavoisier conducted his experiments, he did not know what the products of reactions were going to be. He had to isolate the material (whether he was heating mercury or measuring gases from breathing) and then study its elemental composition before he could understand the processes that were occurring.

Discovering that a new compound exists is the start of a long research project. In order to make this new compound in the lab, we need to know a lot about its structure. Often, the place to start is to determine the elements in the material. Then we can find out the relative amounts of each element to continue our evaluation of this new material.

Empirical Formula

An **empirical formula** is a formula that shows the elements in a compound in their lowest whole-number ratio. Glucose is an important simple sugar that cells use as their primary source of energy. Its molecular formula is $C_6H_{12}O_6$. Since each of the subscripts is divisible by 6, the empirical formula for glucose is CH_2O. When chemists analyze an unknown compound, often the first step is to determine its empirical formula. There are a great many compounds whose molecular and empirical formulas are the same. If the molecular formula cannot be simplified into a smaller whole-number ratio, as in the case of H_2O or P_2O_5, then the empirical formula is also the molecular formula.

How would we determine an empirical formula for a compound? Let's take a compound composed of carbon, hydrogen, and oxygen. We can analyze the relative amounts of each element in the compound. When we get a percent figure for each element, we now know how many grams of each are in 100 grams of the original material. This allows us to determine the number of moles for each element. The ratios can then be reduced to small whole numbers to give the empirical formula. If we wanted a molecular formula, we would need to determine the molecular weight of the compound.

Summary

- The empirical formula tells the lowest whole-number ratio of elements in a compound.
- The empirical formula does not show the actual number of atoms.

Practice

Use the link below to answer the following questions:

http://pages.towson.edu/ladon/empiric.html

1. How is an empirical formula calculated?
2. How is the number of moles determined from the percent composition?

Review

1. Define "empirical formula."
2. Why is $C_6H_{12}O_6$ not considered to be an empirical formula for glucose?
3. Can the empirical formula for a compound be the same as the molecular formula?
4. What do we need to know in order to determine a molecular formula from an empirical formula?
5. Give three examples of compounds whose empirical formulas are the same as their molecular formulas.

- **empirical formula:** A formula that shows the elements in a compound in their lowest whole-number ratio.

7.3 Cations

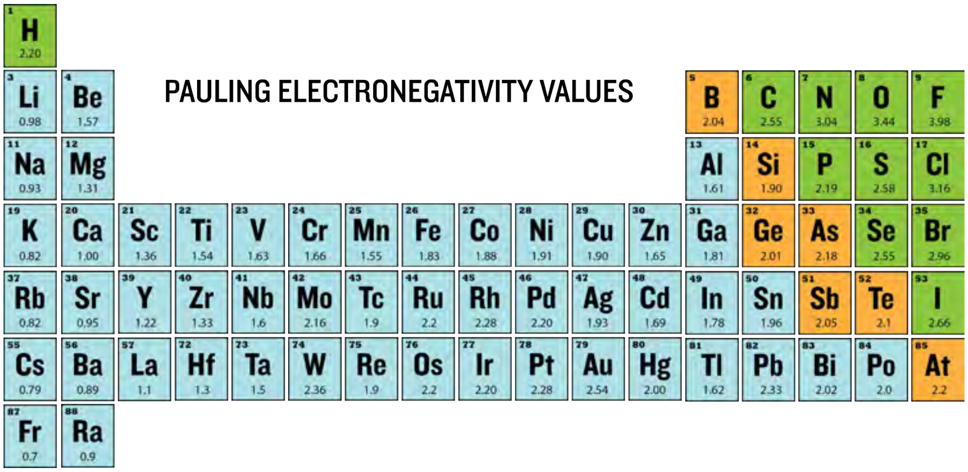
- Define cation.
- Explain how cations are formed.
- Describe the naming of cations.
- Describe how cations are designated.

When the prospectors during the California Gold Rush (1848-1855) searched for gold nuggets in the earth, they could find these nuggets because gold is an unreactive material that exists in its elemental state in many places. Not everyone was fortunate enough to find large nuggets such as those shown above, but a number of these miners did become very wealthy (of course, a large number of others went back home broke).

Many of the elements we know about do not exist in their native form. They are so reactive that they are found only in compounds. These non-elemental forms are known as ions. Their properties are very different from those of the elements they come from. The term comes from a Greek word meaning "move" and was first coined by Michael Faraday, who studied the movement of materials in an electrical field.

Cations

Some elements lose one or more electrons in forming ions. These ions are known as "**cations**" because they are positively charged and migrate toward the negative electrode (**cathode**) in an electrical field. Looking at the periodic table below, we know that the group 1 elements are all characterized by having one *s* electron in the outer orbit and group 2 elements have two *s* electrons in the outer orbit. These electrons are loosely attached to the atom and can easily be removed, leaving more protons in the atom that there are electrons, so the resulting ion has a positive charge. Cations can also be formed from electron loss to many of the transition elements.



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															

The cations are designated by the symbol for the parent element and a plus charge as a superscript after the element symbol - the potassium cation would be indicated as K^+. Note that the charge is placed after the symbol and not before it. The potassium ion is **monovalent**, meaning that it has lost one electron and has a +1 charge. The symbol for the magnesium cation would be Mg^{2+} or Mg^{++} to indicate that it has lost two electrons and has a +2 charge, so the magnesium cation would be referred to as a **divalent** cation.

The cations are simply named as the parent element. The sodium cation is still called "sodium." Often, the charge would be attached for clarity, so the sodium cation might be referred to as "sodium one plus."

Applications of Cations

Cations play important roles in our daily lives. Sodium, potassium, and magnesium ions are essential for such processes as blood pressure regulation and muscle contraction. Calcium ion is an important part of bone structure. Sodium ions can used in water softeners to remove other harmful elements. We put sodium chloride (table salt) on our food and use it as a preservative.

Summary

- Cations are formed by the loss of one or two electrons from an element.
- Groups 1 and 2 elements form cations.
- Cations are named according to the parent element.
- Cation charges are indicated with a superscript following the chemical symbol.

Practice

Use the link below to answer the following questions:

http://dl.clackamas.edu/ch104-07/cations.htm

1. How many electrons are there in the outer shell of Group IA elements?
2. What is the charge of Group IA ions?
3. How many electrons are there in the outer shell of Group IIA elements?
4. What is the charge of Group IIA ions?

Review

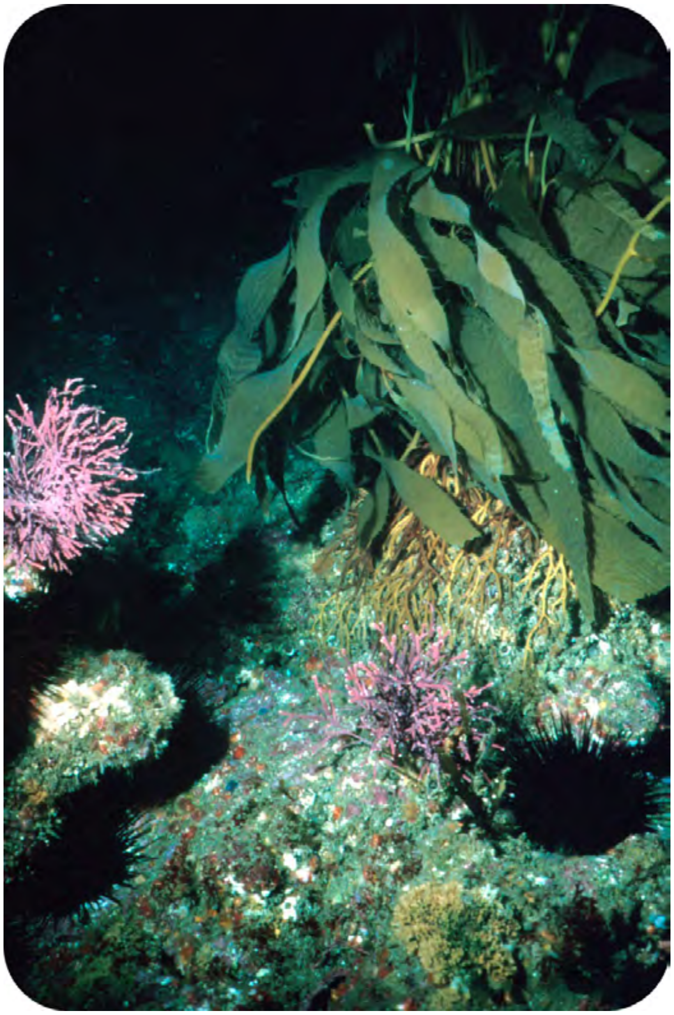
1. What is an ion?

2. What is the cathode?
3. Write the symbol for the barium cation.
4. Write the symbol for the cesium cation.
5. List three ways cations are useful.

- **cation:** Ions known as cations are because they are positively charged and migrate toward the negative electrode (cathode) in an electrical field.
- **monovalent:** Has a +1 charge.
- **divalent:** Has a +2 charge.
- **cathode:** Negative electrode.

7.4 Anions

- Define anion.
- Explain how anions are formed.
- Describe anion nomenclature.
- List uses for anions.

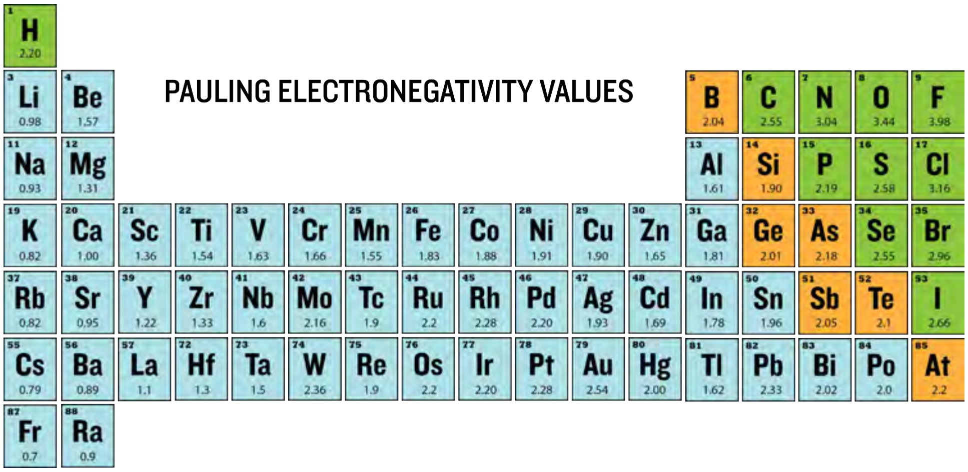


Before iodized salt was developed, some people experienced a number of developmental difficulties, including problems with thyroid gland function and mental retardation. In the 1920s, we learned that these conditions could usually be treated easily with the addition of iodide anion to the diet. One easy way to increase iodide intake was to add the anion to table salt. This simple step greatly enhanced health and development. Large amounts of iodide ion are also found in seaweed such as kelp (see picture above) and saltwater fish.

When a metal loses an electron, energy is needed to remove that electron. The other part of this process involves the addition of the electron to another element. The electron adds to the outer shell of the new element. Just as the loss of the electron from the metal produces a full shell, when the electron or electrons are added to the new element, it also results in a full shell.

Anions

Anions are negative ions that are formed when a **nonmetal** atom gains one or more electrons. Anions are so named because they are attracted to the **anode** (positive field) in an electric field. Atoms typically gain electrons so that they will have the electron configuration of a noble gas. All the elements in Group 17 have seven valence electrons due to the outer ns^2np^5 configuration. Therefore, each of these elements would gain one electron and become an anion with a 1− charge. Likewise, Group 16 elements form ions with a 2− charge, and the Group 15 nonmetals form ions with a 3− charge.



Naming anions is slightly different than naming cations. The ending of the element's name is dropped and replaced with the *–ide* suffix. For example, F^- is the fluoride ion, while O^{2-} is the oxide ion. As is the case with cations, the charge on the anion is indicated by a superscript following the symbol. Common anions are listed in the **Table** 7.1**:**

TABLE 7.1:

Anion Name	Symbol and Charge
fluoride	F^-
chloride	Cl_-
bromide	Br^-
iodide	I^-
oxide	O^{2-}
sulfide	S^{2-}
nitride	N^{3-}

Uses for Anions

Fluoride ion is widely used in water supplies to help prevent tooth decay. Chloride is an important component in ion balance in blood. Iodide ion is needed by the thyroid gland to make the hormone thyroxine.

Summary

- Anions are formed by the addition of one or more electrons to the outer shell of an atom.
- Group 17 elements add one electron to the outer shell, group 16 elements add two electrons, and group 15 elements add three electrons.
- Anions are named by dropping the ending of the element's name and adding *-ide.*

Practice

Use the link below to answer the following questions:

http://preparatorychemistry.com/bishop_anion_names_formulas_help.htm

1. Why do elements form anions?
2. Why do group 17 elements form anions more readily than group 1 elements?

Review

1. What is an anion?
2. How are anions formed?
3. Why do anions form?
4. How are anions named?
5. List three examples of anions with names, charges, and chemical symbols.
6. List three ways anions are used.

- **anion:** Negative ions that are formed when a nonmetal atom gains one or more electrons.
- **anode:** Positively charged electrode, when electric current runs through a cathode ray tube.
- **nonmetal:** Lacking the chemical and physical properties of metals.

7.5 Transition Metal Ions

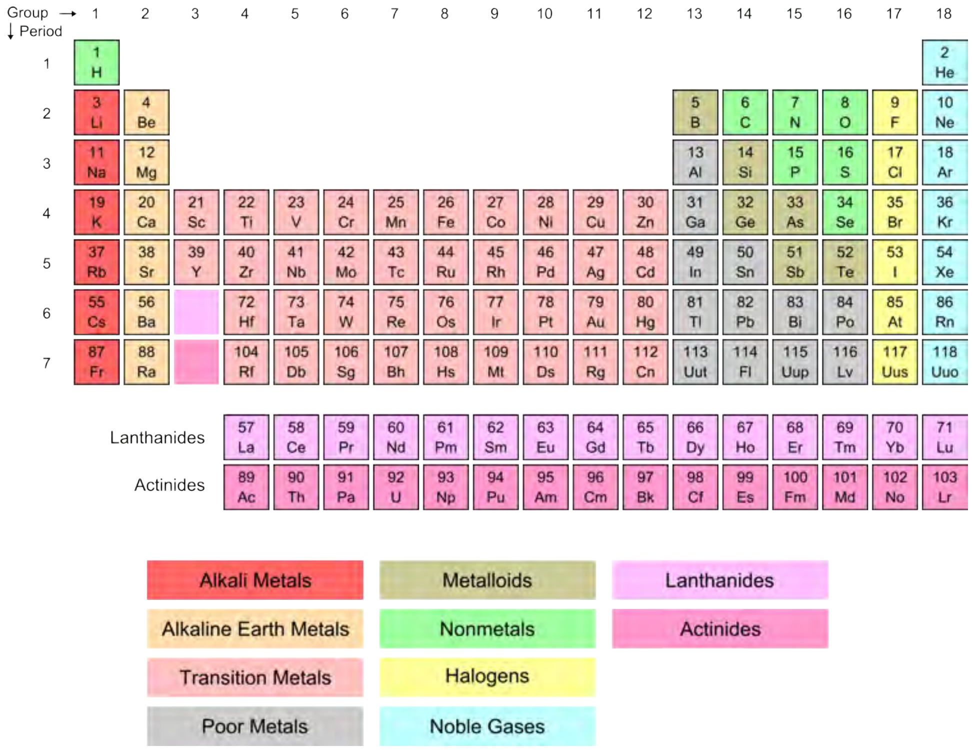
- Describe the electron configuration of the transition metals.
- Explain how transition metals form ions.
- List uses for transition metal ions.

Most of us are familiar with the common coins: penny, nickel, quarter. In some areas (such as Las Vegas), you might see large amounts of silver dollars (these get a little heavy in your pocket). But most of us have probably never seen a platiunum eagle – a eagle coin, but one that is held primarily by collectors. If you were to take a one-ounce platinum eagle into a store and try to buy one hundred dollars worth of items, the store owner most likely would not believe you when you told them the coin was worth one hudred dollars. It would also be awkward and annoying if you lost one of these coins out of your pocket. Platinum is just one of several transition metals that is worth a lot of money (gold is another one).

The group 1 and 2 elements form cations through a simple process than involves the loss of one or more outer shell electrons. These electrons come from the *s* orbital and are removed very readily.

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 cation with different ionic charges. As an example, iron commonly forms two different ions. It can sometimes lose two electrons to form the Fe^{2+} ion, while at other times it loses three electrons to form the Fe^{3+} ion. Tin and lead, though members of the *p* block rather than the ***d* block**, also are capable of forming multiple ions.



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

Ionic formation for transition metals is complicated by the fact that these elements have unfilled inner *d* shells. Although the next higher *s* orbitals are actually at a lower energy level than the *d* level, these *s* electrons are the ones that are removed during ionization.

The table below lists the names and formulas of some of the 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+}
mercury(I), $Hg_2{}^{2+}$	cobalt(II), Co^{2+}	gold(III), Au^{3+}	
silver, Ag^{+}	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+}		

Uses for Transition Metals

Because there are so many metals in this group, there are a wide variety of uses. Many of the metals are used in electronics, while others (such as gold and silver) are used in monetary systems. Iron is a versatile structural material. Cobalt, nickel, platinum, and other metals are employed as catalysts in a number of chemical reactions. Zinc is a significant component of batteries.

Summary

- Transtion metals have unfilled inner *d* electron shells.
- Ions form primarily through loss of *s* electrons.
- Many transition metals can form more than one ion.
- Transition metals have a wide variety of applications.

Practice

Use the links below to answer the following questions:

http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch12/trans.php

1. List some similarities between transition metals and main-group metals.
2. List some differences between transition metals and main-group metals.
3. Describe the electron configurations of the cobalt ions.

Review

1. What is unique about the electron configurations of transition metals?
2. Which electrons of transition metal elements are most likely to be lost duing ion formation?
3. How many ions can iron form?
4. Which transition metal forms only one ion?
5. List several uses for transition metals.

- **transition metal:** Can come from more than on ion and have unfilled inner *d* electron shells.
- *d* **block:** Capable of forming multiple ions.

7.6 Naming Binary Ionic Compounds

- Describe rules for naming binary ionic compounds.
- Describe how to name compounds in which the metal can have more than one ionic form.

Proper naming is important for identification purposes. Medicine names must be precise so that the correct drug is given, one that will help the patient and not harm them. Biological classification of species requires accurate naming for proper categorization. The insect above has been properly categorized by genus and species, so it is uniquely identified. Names must be correct for the tracing family trees in genealogical studies. Compounds used in chemical reactions must be correctly specified in order for the reaction to occur.

Binary Ionic Compounds

A **binary** ionic compound is a compound composed of a **monatomic** metal **cation** and a monatomic nonmetal **anion**.

Naming Binary Ionic Compounds

When examining the formula of a compound in order to name it, you must first decide what kind of compound it is. For a binary ionic compound, a metal will always be the first element in the formula, while a nonmetal will always be the second. The metal cation is named first, followed by the nonmetal cation. Subscripts in the formula do not affect the name. The table below shows three examples:

TABLE 7.3: Naming Binary Ionic Compounds

Formula	Name
KF	potassium fluoride
Na_3N	sodium nitride
Ca_3P_2	calcium phosphide

Notice that in each of the formulas above, the overall charge of the compound is zero. Potassium ion is K^+, while fluoride ion is F^-. Since the magnitude of the charges is equal, the formula contains one of each ion. This would also be the case for a compound such as MgS, in which the ions are Mg^{2+} and S^{2-}. For sodium nitride, the sodium ion is Na^+, while the nitride ion is N^{3-}. In order to make a neutral compound, three of the 1+ sodium ions are required in order to balance out the single 3− nitride ion. So the Na is given a subscript of 3. For calcium phosphide, the calcium ion is Ca^{2+}, while the phosphide ion is P^{3-}. The least common multiple of 2 and 3 is 6. To make the compound neutral, three calcium ions have a total charge of 6+, while two phosphide ions have a total charge of 6−. The Ca is given a subscript of 3, while the P is given a subscript of 2.

For transition metal compounds, an additional step must be taken. Since many of the transition metals can have more than one ionic form, it becomes necessary to specify which form exists in a specific compound. If a metal can have a +2 and a +3 form, the +2 form is indicated by *–ous* and the +3 form by *ic*. For example, in $FeCl_2$ the charge on the iron ion is +2 to balance the two -1 charges of the chloride. So this compound would be named ferrous chloride (the ferr- comes from the Latin word for iron, *ferrum*). In the same way, $FeCl_3$ would be ferric chloride since the iron ion in this compound has a +3 charge. For copper, the possible ion charges are +1 and +2, making CuCl cuprous chloride and $CuCl_2$ and cupric chloride (from the Latin *cuprum* for copper).

Summary

- A binary ionic compound is a compound composed of a monatomic metal cation and a monatomic nonmetal anion.
- The metal part of the compound is named as the element.
- The non-metallic part of the compound is named by dropping the end of the element and adding *–ide.*
- For binary compounds, it is not necessary to indicate the number of ions in the compound.
- Transition metal ions can have an *–ous* form and an –ic form.

Practice

Use the link below to answer the following questions:

http://library.thinkquest.org/19957/nomen/binarybody.html

1. What is the stem for compounds using the oxygen anion.
2. How would you name AlN?
3. How would you name NaCl?

Review

1. What is a binary compound?
2. Which of the following is not a binary compound?
   (a) NaCl
   (b) KH_2PO_4
   (c) KBr

3. Name the following compounds:
    (a) NaBr
    (b) $MgCl_2$
    (c) LiI
    (d) CaO
    (e) $CuBr_2$
    (f) FeO

- **binary:** A compound composed of a monatomic metal cation and a monatomic nonmetal anion.
- **monatomic:** Has one atom.
- **cation:** Ions known as cations are because they are positively charged and migrate toward the negative electrode (cathode) in an electrical field.
- **anion:** Negative ions that are formed when a nonmetal atom gains one or more electrons.

7.7 Stock System Naming

- Define the Stock system for naming ionic compounds.
- Name compounds using the Stock system.
- Write formulas of compounds when given the Stock name.

When we buy many items, it's not enough to say what car or what computer we have. We (at least, the guys do) talk about how much horsepower is "under the hood" for a car or how fast the chip is for our computer. Even a simple device like an mp3 player has more than one size. We can get an 8 MB player, or a 16 MB player. Designation of the item often is incomplete without other information as to its capabilities.

Transition metals have more than one possibility for ion formation. In order to name these compounds correctly, we need to be able to indicate which ion is involved in any given compound.

Naming Compounds Using the Stock System

Naming compounds that involve transition metal cations necessitates the use of the **Stock system**. Consider the binary ionic compound $FeCl_3$. To simply name this compound iron chloride would be incomplete because iron is capable of forming two ions with different charges. The name of any iron-containing compound must reflect which iron ion is in the compound. In this case, the subscript in the formula indicates that there are three chloride ions, each with a 1− charge. Therefore, the charge of the single iron ion must be 3+. The correct name of $FeCl_3$ is iron(III) chloride, with the cation charge written as the Roman numeral. Here are several other examples.

TABLE 7.4:

Formula	Name
Cu_2O	copper(I) oxide
CuO	copper(II) oxide
SnO_2	tin(IV) oxide

The first two are both oxides of copper (shown in the figure below). The ratio of copper ions to oxide ions determines the name. Since the oxide ion is O_2, the charges of the copper ion must be 1+ in the first formula and 2+ in the second formula. In the third formula, there is one tin ion for every two oxide ions. This means that the tin must carry a 4+ charge, making the name tin(IV) oxide.

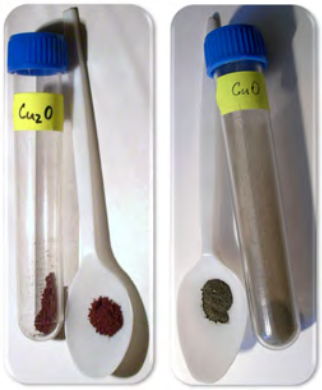


FIGURE 7.1

Copper(I) oxide, a red solid, and copper(II) oxide, a black solid, are different compounds because of the charge of the copper ion.

Summary

- The Stock system allows the specification of transition metal ionic charge when naming ionic compounds.
- Roman numerals are used to indicate the amount of positive charge on the cation.

Practice

Practice naming compounds at the following web site:

http://www.chemteam.info/Nomenclature/Binary-Stock-FormulatoName.html

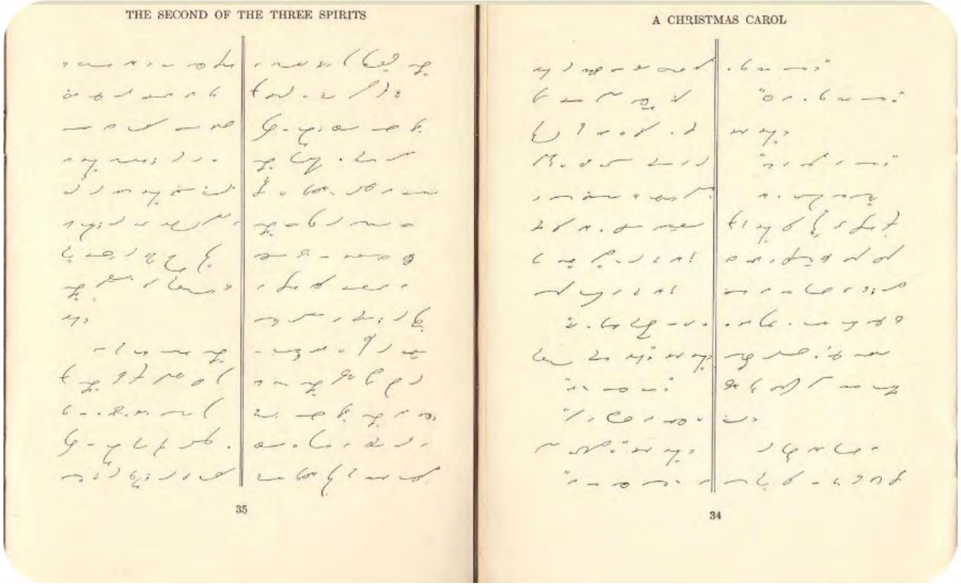
Review

- What is the Stock system?
- For which group of metal ions would we use the Stock system?
- What does the Roman numeral stand for?
- Assign a Roman numeral to each of the following cations:
  - Sn^{4+}
  - Fe^{3+}
  - Co^{2+}
  - Pb^{4+}

- **Stock system:** Allows the specification of transition metal ionic charge when naming ionic compounds.

7.8 Formulas for Binary Ionic Compounds

- Be able to write formulas for binary ionic compounds when given the name.
- Be able to name the binary ionic compound when given the formula.



Shorthand was a very popular way of recording speech, especially in dictating letters and in court testimony. Instead of trying to write out all the words, the person taking the dictation would use a set of symbols that represented syllables or words. The pages above show a shorthand version of "A Christmas Carol" written by Charles Dickens. Unless you know shorthand, the passage is meaningless. But knowing shorthand allows you to read this classic story.

Different professions also use a type of shorthand in communication to save time. Chemists use chemical symbols in combination to indicate specific compounds. There are two advantages to this approach:

1. The compound under discussion is clearly described so there can be no confusion about its identity.
2. Chemical symbols represent a universal language that all chemists can understand, no matter what their native language is.

Writing Formulas for Binary Ionic Compounds

If you know the name of a binary ionic compound, you can write its **chemical formula**. Start by writing the metal ion with its charge, followed by the nonmetal ion with its charge. Because the overall compound must be electrically neutral, decide how many of each ion is needed in order for the positive and negative charge to cancel each other out. Consider the compound aluminum nitride. The ions are:

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

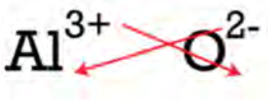
Since the ions have charges that are equal in magnitude, one of each will be the lowest ratio of ions in the formula. The formula of aluminum nitride is AlN.

The ions for the compound lithium oxide are:

Li^+ O^{2-}

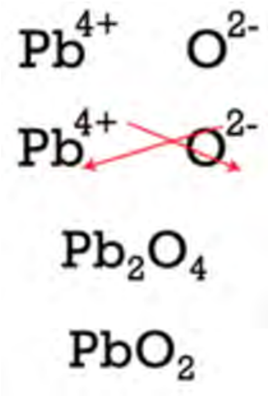
In this case, two lithium ions are required to balance out the charge of one oxide ion. The formula of lithium oxide is Li_2O.

An alternative way to writing a correct formula for an ionic compound is to use the crisscross method. In this method, the numerical value of each of the ion charges is crossed over to become the subscript of the other ion. Signs of the charges are dropped. Shown below is the crisscross method for aluminum oxide.



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

Be aware that ionic compounds are empirical formulas and so must be written as the lowest 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. It must be reduced to AlN. Following the crisscross method to write the formula for lead(IV) oxide would involve the following steps:



The crisscross first yields Pb_2O_4 for the formula, but that must be reduced to the lower ratio and PbO_2 is the correct formula.

Summary

- Formulas for binary compounds begin with the metal followed by the non-metal.
- Positive and negative charges must cancel each other out.
- Ionic compound formulas are written using the lowest ratio of ions.

Practice

Use the link below to answer the following questions:

http://www.chemteam.info/Nomenclature/Binary-Comm-NametoFormula.html

1. How did Lavoisier improve chemical nomenclature?
2. Practice writing formulas using some of the examples given here.

Review

1. Write formulas for the binary ionic compounds formed between the following pairs of elements:
   (a) cesium and fluorine
   (b) calcium and sulfur
   (c) aluminum and chlorine
   (d) zinc and nitrogen
2. Write the formula and give the name for the compound formed by the following ions:
   (a) Fe^{3+} and O^{2-}
   (b) Ni^{2+} and S^{2-}
   (c) Au^{+} and Cl^{-}
   (d) Sn^{4+} and I^{-}
3. Give names for the following compounds:
   (a) Ag_2S
   (b) PdO
   (c) $PtCl_4$
   (d) V_2O_5

- **chemical formula:** Use of chemical symbols in combination to indicate specific compounds.

7.9 Polyatomic Ions

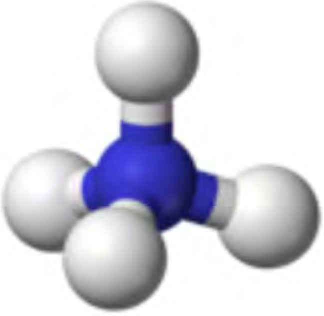
- Be able to write structures for polyatomic ions when given the name.
- Be able to name polyatomic ions when given the structures.

Shakespeare once wrote, “A rose by any other name would smell as sweet,” part of the romantic balcony scene between Romeo and Juliet in the play of that name. The two families were bitter rivals, but Juliet was saying she loved Romeo no matter what his name was. Some names are simple – we know Romeo mainly as Romeo. Most have us have a first name, middle name (often not used), and last name. In some cultures, names will be much more complex. The full name of the famous 20^{th} century artist Pablo Picasso is Pablo Diego José Francisco de Paula Juan Nepomuceno María de los Remedios Cipriano de la Santísima Trinidad Martyr Patricio Clito Ruíz y Picass.

Many materials exist as simple binary compounds composed of a metal cation and a non-metal anion, with each ion consisting of only one type of atom. Other combinations of atoms also exist, either larger ionic complexes or complete molecules. Some of the most useful materials we work with contain polyatomic ions.

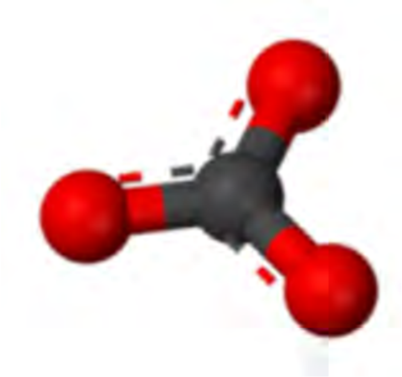
Polyatomic Ions

A **polyatomic** ion is an ion composed of more than one atom. The ammonium ion consists of one nitrogen atom and four oxygen 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 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 and so the entire ion behaves as a single unit. The figures below show several models.



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.

The table below lists a number of polyatomic ions by name and by structure. The heading for each column indicates the charge on the polyatomic ions in that group. Note that the vast majority of the ions listed are anions – there are very few polyatomic cations.

TABLE 7.5: **Common Polyatomic Ions**

1-	2-	3-	1+	2+
acetate, CH_3COO^- bromate, BrO_3^- chlorate, $ClO3^-$	carbonate, CO_3^{2-} chromate, CrO_4^{2-} dichromate, $Cr_2O_7^{2-}$	arsenate, AsO_3^{3-} phosphite, PO_3^{3-} phosphate, PO_4^{3-}	ammonium, NH_4^+	dimercury, Hg_2^{2+}

TABLE 7.5: (continued)

chlorite, ClO_2^-	hydrogen phosphate, HPO_4^{2-}
cyanide, CN^-	oxalate, $C_2O_4^{2-}$
dihydrogen phosphate, $H_2PO_4^-$	peroxide, O_2^{2-}
hydrogen carbonate, HCO_3^-	silicate, SiO_3^{2-}
hydrogen sulfate, HSO_4^-	sulfate, SO_4^{2-}
hydrogen sulfide, HS^-	sulfite, SO_3^{2-}
hydroxide, OH^-	
hypochlorite, ClO^-	
nitrate, NO_3^-	
nitrite, NO_2^-	
perchlorate, ClO_4^-	
permanganate, MnO_4^-	

The vast majority of polyatomic ions are anions, many of which end in *–ate* or *–ite*. Notice that in some cases such as nitrate (NO_3^-) and nitrite (NO_2^-), there are multiple anions that consist of the same two elements. In these cases, the difference between the ions is in the number of oxygen atoms present, while the overall charge is the same. As a class, these are called oxoanions. When there are two oxoanions for a particular element, the one with the greater number of oxygen atoms gets the *–ate* suffix, while the one with the fewer number of oxygen atoms gets the *–ite* suffix. The four oxoanions of chlorine are shown below.

- ClO^-, hypochlorite
- ClO_2^-, chlorite
- ClO_3^-, chlorate
- ClO_4^-, perchlorate

In cases such as this, the ion with one more oxygen atom than the *–ate* anion is given a *per-* prefix. The ion with one fewer oxygen atom than the *–ite* anion is given a *hypo*-prefix.

Summary

- Polyatomic ions contain more than one type of atom in the ion.
- The majority of polyatomic ions are anions that are named ending in “ate” or “ite.”
- Some anions have multiple forms and are named accordingly.

Practice

Use the link below to answer the following questions:

http://www2.pvc.maricopa.edu/tutor/chem/chem130/nomenclature/polyatomicion.html

1. List the polyatomic cations.
2. How many polyatomic ions of chromium are there? Write out the formulas and names each ion.
3. How many polyatomic ions of chlorine are there? Write out the formulas and name each ion.

Review

1. Write the formulas for the following ions:
    (a) ammonium
    (b) carbonate
    (c) sulfate
    (d) phosphate?
2. Name the following ions:
    (a) $PO_3{}^{3-}$
    (b) $SiO_3{}^{2-}$
    (c) OH^-
    (d) $MnO_4{}^-$

- **polyatomic:** An ion composed of more than one atom.

7.10 Names and Formulas of Ternary Ionic Compounds

- Be able to write structures for ternary ionic compounds when given the name.
- Be able to name ternary ionic compounds when given the structures.

Most people enjoy eating pizza. When they order a pizza (either by phone, on-line, or in a restaurant), they don't just order "pizza." Even the simplest "binary" pizza will have a topping and cheese – maybe pepperoni, maybe something else. However, many pizzas quickly become more complex. One person may want pepperoni and sausage, another may wish to order Canadian bacon and pineapple, and then you have the folks that can't decide, so they order half-this and half-that. The combinations may be more complex, but the same basic ideas about pizza are valid.

Ternary Ionic Compounds

Not all ionic compounds are composed of only monatomic ions. A **ternary ionic compound** is an ionic compound composed of three or more elements. In a typical ternary ionic compound, there is still one type of cation and one type of anion involved. The cation, the anion, or both, is a polyatomic ion.

Naming Ternary Ionic Compounds

The process of naming ternary ionic compounds is the same as naming binary ionic compounds. The cation is named first, followed by the anion. Some examples are shown below:

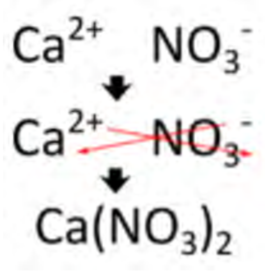
TABLE 7.6: **Examples of Ternary Ionic Compounds**

Formula	**Name**
$NaNO_3$	sodium nitrate
NH_4Cl	ammonium chloride
$Fe(OH)_3$	iron(III) hydroxide

When more than one polyatomic ion is present in a compound, the formula of the ion is placed in parentheses with a subscript outside of the parentheses that indicates how many of those ions are in the compound. In the last example above, there is one Fe^{3+} cation and three OH^- anions.

Writing Formulas for Ternary Ionic Compounds

Writing a formula for a ternary ionic compound also 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. Calcium nitrate is composed of a calcium cation and a nitrate anion.



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 in a formula, parentheses are not used. As an example, the formula for calcium carbonate is $CaCO_3$. The carbonate ion carries a 2− charge and so exactly balances the 2+ charge of the calcium ion.

There are two polyatomic ions that produce unusual formulas. The Hg_2^{2+} ion is called either the dimercury ion or, preferably, the mercury(I) ion. When bonded with an anion with a 1− charge, such as chloride, the formula is Hg_2Cl_2. Because the cation consists of two Hg atoms bonded together, this formula is not reduced to HgCl. Likewise, the peroxide ion, O_2^{2-}, is also a unit that must stay together in its formulas. For example, the formula for potassium peroxide is K_2O_2.

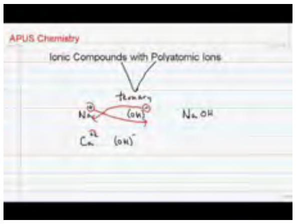
Summary

- Ternary compounds are composed of three or more elements.
- Ternary compounds are named by stating the cation first, followed by the anion.
- Positive and negative charges must balance.

Practice

Use the link below to answer the following questions:

http://www.youtube.com/watch?v=QNijl4ZBJCw



MEDIA

Click image to the left for more content.

1. What are ionic compounds containing polyatomic ions called?
2. Does the "criss-cross" method work for naming ternary compounds?

Review

1. What is a ternary compound?
2. What is the basic rule for naming ternary compounds?
3. Write the formulas for the following compounds:
    (a) mercury(II) nitrate
    (b) ammonium phosphate
    (c) calcium silicate
    (d) lead(II) chromate
4. Name the following compounds:
    (a) $KClO_3$
    (b) Rb_2SO_4
    (c) $Cd(NO_3)_2$
    (d) NaCN

- **ternary:** A compound made up of three parts.
- **ternary ionic compound:** An ionic compound composed of three or more elements.

7.11 Naming Binary Molecular Compounds

- Define molecular compound.
- Explain how molecular compounds are different from ionic compounds.
- Be able to name the compound when given the formula.

Some families name a son (usually the firstborn) after his father. So it is somewhat common to find John Smith, Jr. named after John Smith the father. A few families may take it further and name the grandson John Smith III. Countries with long histories of royalty take the naming even further. One line of kings named Henry goes up to Henry the Eighth (not the nicest guy in the world – he had six wives and two of them came to untimely ends). The use of numbering for names adds clarity to a system –we always know which Henry we are talking about.

Inorganic chemical compounds can be broadly classified into two groups: ionic compounds and molecular compounds. The structure of all ionic compounds is an extended three-dimensional array of alternating positive and negative ions. Since ionic compounds do not take the form of individual molecules, they are represented by empirical formulas. Now we will begin to examine the formulas and nomenclature of molecular compounds.

Molecular Compounds

Molecular compounds are inorganic compounds that take the form of discrete **molecules**. Examples include such familiar substance as water (H_2O) and carbon dioxide (CO_2). These compounds are very different from ionic compounds like sodium chloride (NaCl). Ionic compounds are formed when metal atoms lose one or more of their electrons to nonmetal atoms. The resulting cations and anions are electrostatically attracted to each other.

So what holds the atoms of a molecule together? Rather than forming ions, the atoms of a molecule share their **valence electrons** in such a way that a **bond** forms between pairs of atoms. In a carbon dioxide molecule, there are two of these bonds, each occurring between the carbon atom and one of the two oxygen atoms.

FIGURE 7.2

Carbon dioxide molecules consist of a central carbon atom bonded to 2 oxygen atoms.

Larger molecules can have many, many bonds that serve to keep the molecule together. In a large sample of a given molecular compound, all of the individual molecules are identical.

Naming Binary Molecular Compounds

Recall that a molecular formula shows the number of atoms of each element that a molecule contains. A molecule of water contains two hydrogen atoms and one oxygen atom, so its formula is H_2O. A molecule of octane, which is a component of gasoline, contains 8 atoms of carbon and 18 atoms of hydrogen. The molecular formula of octane is C_8H_{18}.

A binary molecular compound is a molecular compound that is composed of two elements. The elements that combine to form binary molecular compounds are both nonmetal atoms. This contrasts with ionic compounds, which were formed from a metal ion and a nonmetal ion. Therefore, binary molecular compounds are different because ionic charges cannot be used to name them or to write their formulas. Another difference is that two nonmetal atoms will frequently combine with one another in a variety of ratios. Consider the elements nitrogen and oxygen. They combine to make several compounds including NO, NO_2, and N_2O. They all can't 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. The table below shows the prefixes up to ten.

TABLE 7.7: **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-

FIGURE 7.3

Nitrogen dioxide (NO_2) is a reddish-brown toxic gas that is a prominent air pollutant produced by internal combustion engines.

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 always first in a formula and hydrogen is after nitrogen in a formula such as NH_3. The order of common nonmetals in binary compound formulas is C, P, N, H, S, I, Br, Cl, O, F.
2. When naming, the appropriate prefix is used only if there are more than one atom of that element in the formula.
3. The second element is named after the first, but with the ending of the element's name changed to *–ide*. The appropriate prefix is always used for the second element.
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 below.

TABLE 7.8:

Formula	**Name**
NO	nitrogen monoxide
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. The S_2Cl_2 emphasizes that the formulas for molecular compounds are not reduced to their lowest ratios. The *o* of mono- and the *a* of hepta- are dropped from the name when paired with oxide.

Summary

- Molecular compounds are inorganic compounds that take the form of discrete molecules.
- The atoms of these compounds are held together by covalent bonds.
- Prefixes are used to indicate the number of atoms of an element that are in the compound.

Practice

6. List the prefixes for the number of atoms of an element when there are seven atoms of that element in the compound.
7. Name the following compounds:
   (a) ClF_3
   (b) As_2O_5
   (c) B_4H_{10}

- **molecule:** Two or more atoms that have been chemically combined.
- **bond:** By sharing valence electrons, bonds hold the atoms of a molecule together.
- **valence electron:** Can form molecules by bonding with atoms.

7.12 Naming Acids

- Define acid.
- State rules for naming acids.
- Write name of acid when given formula.

A spot test for gold has been in use for decades. The sample is first treated with nitric acid. Other metals may react or dissolve in this acid, but gold will not. Then the sample is added to a mixture of nitric acid and hydrochloric acid. Gold will only dissolve in this mixture. The term "acid test" arose from the California gold rush in the late 1840s when this combination was used to test for the presence of real gold. It has since come to mean, "tested and approved" in a number of fields.

Acids

An **acid** can be defined in several ways. The most straightforward definition is that an acid is a molecular compound that contains one or more hydrogen atoms and produces hydrogen ions (H^+) when dissolved in water.

This is a different type of compound than the others we have seen so far. Acids are molecular, which means that in their pure state they are individual molecules and do not adopt the extended three-dimensional structures of ionic compounds like NaCl. However, when these molecules are dissolved in water, the chemical bond between the

FIGURE 7.4

(A) Vinegar comes in a variety of types, but all contain acetic acid. (B) Citrus fruits like grapefruit contain citric and ascorbic acids.

hydrogen atom and the rest of the molecule breaks, leaving a positively-charged hydrogen ion and an anion. This can be symbolized in a chemical equation:

$$HCl \rightarrow H^+ + Cl^-$$

Since acids produce H^+ cations upon dissolving in water, the H of an acid is written first in the formula of an inorganic acid. The remainder of the acid (other than the H) is the anion after the acid dissolves. Organic acids are also an important class of compounds, but will not be discussed here. A **binary acid** is an acid that consists of hydrogen and one other element. The most common binary acids contain a halogen. An **oxoacid** is an acid that consists of hydrogen, oxygen, and a third element. The third element is usually a nonmetal.

Naming Acids

Since all acids contain hydrogen, the name of an acid is based on the anion that goes with it. These anions can either be monatomic or polyatomic. The name of all monatomic ions ends in *–ide.* The majority of polyatomic ions end in either *–ate* or *–ite*, though there are a few exceptions such as the cyanide ion (CN^-). It is this suffix of the anion that determines how the acid is named as displayed in the table and rules below.

TABLE 7.9: **Naming System for Acids**

Anion Suffix	Example	Name of Acid	Example
-ide	chloride (Cl^-)	hydro_____ic acid	hydrochloric acid (HCl)
-ate	sulfate ($SO_4{}^{2-}$)	_____ic acid	sulfuric acid (H_2SO_4)
-ite	nitrite ($NO_2{}^-$)	_____ous acid	nitrous acid (HNO_2)

The three different suffixes that are possible for the anions lead to the three rules below.

1. When the anion ends in *–ide,* the acid name begins with the prefix *hydro-*. The root of the anion name goes in the blank (*chlor* for chloride), followed by the suffix *–ic*. HCl is hydrochloric acid because Cl^- is the chloride ion. HCN is hydrocyanic acid because CN^- is the cyanide ion.
2. When the anion ends in *–ate,* the name of the acid is the root of the anion followed by the suffix *–ic*. There is no prefix. H_2SO_4 is sulfuric acid (not sulfic) because $SO_4{}^{2-}$ is the sulfate ion.
3. When the anion ends in *–ite,* the name of the acid is the root of the anion followed by the suffix *–ous*. Again, there is no prefix. HNO_2 is nitrous acid because $NO_2{}^-$ is the nitrite ion.

Note how the root for a sulfur-containing oxoacid is *sulfur-* instead of just *sulf-*. The same is true for a phosphorus-containing oxoacid. The root is *phosphor-* instead of simply *phosph-*.

Many foods and beverages contain citric acid. Vinegar is a dilute solution of acetic acid. Car batteries contain sulfuric acid that helps in the release of electrons to create electricity.

Watch a video on naming acids:

http://www.kentchemistry.com/links/naming/acids.htm

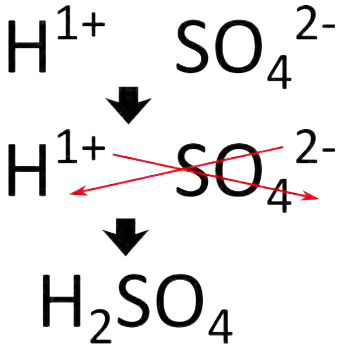


FIGURE 7.5
Criss-cross approach to writing formula for sulfuric acid.

Summary

- Acids are molecular compounds that release hydrogen ions.
- A binary acid consists of hydrogen and one other element.
- Oxoacids contain hydrogen, oxygen, and one other element.
- The name of the acid is based on the anion attached to the hydrogen.
- Writing formulas for acids follows the same rules as for binary ionic compounds.

Practice

Use the link below to answer the following questions:

http://www.kentchemistry.com/links/naming/acids.htm

1. When naming acids, is the hydrogen named?
2. What prefix is added to the anion root?
3. What suffix is added to the anion root?
4. How are oxo acids named?

Review

1. Define "acid."
2. What is a binary acid?
3. What is an oxoacid?
4. Name the following acids:
    (a) H_2SO_4
    (b) HCN
    (c) HCl
    (d) H_3PO_4
5. Write formulas for the following acids:
    (a) hydrobromic acid
    (b) perchloric acid
    (c) nitrous acid

- **acid:** An acid is a molecular compound that contains one or more hydrogen atoms and produces hydrogen ions (H+) when dissolved in water.
- **binary acid:** An acid that consists of hydrogen and one other element.

- **oxoacid:** An acid that consists of hydrogen, oxygen, and a third element. The third element is usually a nonmetal.

7.13 Names and Formulas of Bases

- Define base.
- State rules for naming bases.
- Write the name of a base when given the chemical formula.
- Write the chemical formula for a base when given the name.

Soap making has a long history. Until recently, soap was made using animal fats and lye from wood ashes. The lye served as a base to break down the fats and help form the soap. Needless to say, unless the soap was washed to remove the lye, it was very harsh on the skin. Many families would make their own soap by boiling the lye and fat in a large kettle over an open fire, a long and hot task.

Bases

The simplest way to define a **base** is an ionic compound that produces **hydroxide ions** when dissolved in water. One of the most commonly used bases is sodium hydroxide, illustrated below.

Names and Formulas of Bases

There is no special system for naming bases. Since they all contain the OH^- anion, names of bases end in hydroxide. The cation is simply named first. Some examples of names and formulas for bases are shown below.

TABLE 7.10:

Formula	Name

TABLE 7.10: (continued)

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

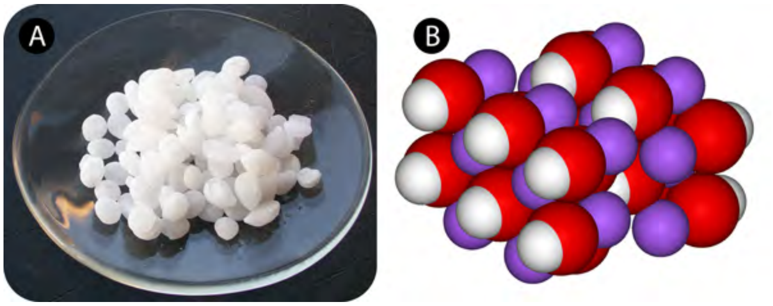


FIGURE 7.6

(A) Sodium hydroxide, a base, is a solid that is typically produced as small white pellets. (B) The structure of sodium hydroxide is an extended three-dimensional network. The purple spheres are the sodium ions (Na^+). The red and white spheres are oxygen and hydrogen atoms respectively, which are bonded together to form hydroxide ions (OH^-).

Notice that because bases are ionic compounds, the number of hydroxides in the formula does not affect the name. The compound must be neutral, so the charges of the ions are balanced just as for other ionic compounds. Sodium ion (Na^+) requires one OH^- ion to balance the charge, so the formula is NaOH. Calcium ion (Ca^{2+}) requires two OH^- ions to balance the charge, so the formula is $Ca(OH)_2$. Hydroxide ion is a polyatomic ion and must be put in parentheses when there are more than on in a formula.

Summary

- Bases are ionic compounds that produce hydroxide ions when dissolved in water.
- The cation is named first followed by "hydroxide."

Practice

Use the link below to practice naming bases and writing formulas for bases:

http://www.chem.uiuc.edu/webfunchem/bases/nombaseIndex.htm

Review

1. What is a base?
2. What is the charge on the hydroxide anion?
3. Name the following bases:
   (a) LiOH
   (b) $Mg(OH)_2$
   (c) $Fe(OH)_3$
4. Write the formulas for the following bases:
   (a) nickel (II) hydroxide
   (b) aluminum hydroxide
   (c) silver hydroxide

- **base:** An ionic compound that produces hydroxide ions when dissolved in water.
- **hydroxide ion:** Has one hydrogen atom and one oxygen atom.

7.14 References

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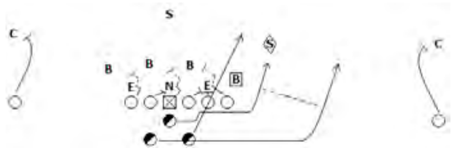
CHAPTER 8 Ionic and Metallic Bonding

Chapter Outline

8.1 Electron Dot Diagrams

- Describe the electron dot diagram system of representing structure.
- Draw electron dot diagrams for elements.



How do we show electrons in atoms?

Diagrams contain a lot of useful information in a compact format. What does the diagram above tell us? The football play diagrammed above describes the lineup of each player on the team and describes how they will move when the ball is snapped. Diagrams of electrons give similar information about where certain electrons are. We can mark these electrons and indicate what happens to them when an element reacts.

Electron Dot Diagrams

Recall that the valence electrons of an atom are the electrons that are in the highest occupied principal energy level. Valence electrons are primarily responsible for the chemical properties of elements. The number of valence electrons can be easily determined from the electron configuration. Several examples from the second period elements are shown below.

TABLE 8.1:

lithium	$1s^22s^1$	1 valence electron
beryllium	$1s^22s^2$	2 valence electrons
nitrogen	$1s^22s^22p^3$	5 valence electrons
neon	$1s^22s^22p^6$	8 valence electrons

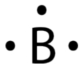
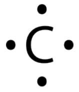
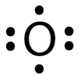
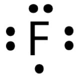
In each case, valence electrons are those in the second principal energy level. As one proceeds left to right across a period, the number of valence electrons increases by one. In the *s* block, Group 1 elements have one valence electron, while Group 2 elements have two valence electrons. In the *p* block, the number of valence electrons is equal to the group number minus ten. Group 13 has three valence electrons, Group 14 has four, up through Group 18 with eight. The eight valence electrons, a full outer *s* and *p* sublevel, give the noble gases their special stability.

When examining chemical bonding, it is necessary to keep track of the valence electrons of each atom. **Electron dot diagrams** are diagrams in which the valence electrons of an atom are shown as dots distributed around the element's symbol. A beryllium atom, with two valence electrons, would have the electron dot diagram below.

• Be •

Since electrons repel each other, the dots for a given atom are distributed evenly around the symbol before they are paired. **Table** 8.2 shows the electron dot diagrams for the entire second period.

TABLE 8.2: **Electron Dot Diagrams for the Second Period Elements**

Group Number	Electron Dot Diagram
1	
2	
13	
14	
15	
16	
17	
18	

Electron dot diagrams would be the same for each element in the representative element groups. Most transition elements have two valence electrons, though some that have unusual electron configurations have only one.

Summary

- Electron dot diagrams show the valence electrons for an atom.
- The dot diagrams are the same for each element in the representative element groups.

Practice

Use the link below to answer the following questions:

http://en.wikibooks.org/wiki/High_School_Chemistry/Lewis_Electron_Dot_Diagrams

1. What are valence electrons?
2. What are the valence electrons for magnesium?
3. Why are both 3*s* and 3*p* electrons included as valence electrons for chlorine?
4. Why do oxygen and sulfur have the same electron dot structures?

Review

1. What are valence electrons primarily responsible for?
2. Calcium would have the same electron dot structure as which element pictured in the table?
3. What is the symbol for an element that would have the same electron dot structure as carbon?
4. Would you expect the group 18 elements to have the same electron dot diagram as neon?

- **electron dot diagram:** A diagram in which the valence electrons of an atom are shown as dots distributed around the element's symbol.

8.2 Octet Rule

- State the octet rule.
- Use the octet rule to predict outcomes of chemical reactions.

How are electrons organized in atoms?

Graduations are exciting times. The processional, the ceremonies, even the speeches can be handled because this marks the end of a stage of life and the beginning of another one. The ceremony itself is challenging for those organizing it. There are just enough seats on the stage for the graduates. How do you avoid getting too many people in a row and not enough in the next row? Someone is stationed at the end of the row to count the students as they enter. Only so many are allowed to go into a row, and then you begin to fill the next row. Electrons in atoms behave the same way. There are rules that determine where electrons go in compounds.

Octet Rule

The noble gases are unreactive because of their electron configurations. The noble gas neon has the electron configuration of $1s^2 2s^2 2p^6$. It has a full outer shell and cannot incorporate any more electrons into the valence shell. The other noble gases have the same outer shell electron configuration even though they have different numbers of inner-shell electrons.

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 atoms tend to form compounds in ways that give them eight valence electrons and thus the electron configuration of a noble gas. An exception to an octet of electrons is in the case of the first noble gas, helium, which only has two valence electrons. This primarily affects the element hydrogen, which forms stable compounds by achieving 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. The second way is by transferring valence electrons from one atom to another. Atoms of metals

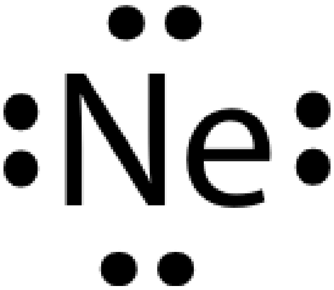


FIGURE 8.1

Electron configuration of neon atom.

tend to lose all of their valence electrons, which leaves them with an octet from the next lowest principal energy level. Atoms of nonmetals tend to gain electrons in order to fill their outermost principal energy level with an octet.

Summary

- Atoms form compounds in ways that give them eight valence electrons.
- Metals tend to lose electrons to achieve this configuration.
- Nonmetals tend to gain electrons to achieve this configuration.

Practice

Use the link below to answer the following questions:

http://www.mikeblaber.org/oldwine/chm1045/notes/Bonding/Except/Bond08.htm

1. Do most elements follow the octet rule?
2. How does hydrogen violate the octet rule?
3. Does sulfur always follow the octet rule?
4. What are free radicals?

Review

1. What is the electron configuration of a noble gas?
2. Why is this configuration important?
3. How do metals change to obey the octet rule?
4. How do nonmetals change to obey the octet rule?

- **octet rule:** Atoms tend to form compounds in ways that give them eight valence electrons and thus the electron configuration of a noble gas.

8.3 Cation Formation

- Define cation.
- Describe how cations are formed.
- Write equations to illustrate cation formation.

How are cations formed?

In many parts of the country, the water contains high concentrations of minerals that stain clothes, build up deposits on bathtubs and water heaters, and create problems with soap foaming properly. This problem is caused by what is called "hard water." The water contains excessive amounts of cations such as iron and calcium. These ions create a lot of problems in the water. Ion exchange resins (seen above) will remove these minerals and clean up the water.

Cation Formation

Cations are the positive ions formed by the loss of one or more electrons. The most commonly formed cations of the representative elements are those that involve the loss of all of the valence electrons. Consider the alkali metal sodium (Na). It has one valence electron in the third principal energy level. Upon losing that electron, the sodium ion now has an octet of electrons from the second principal energy level. The equation below illustrates this process.

$$\begin{array}{lllll} \text{Na} & \rightarrow & \text{Na}^{+} & + & \text{e}^{-} \\ 1s^2 2s^2 2p^6 3s^1 & & 1s^2 2s^2 2p^6 \text{ (octet)} & & \end{array}$$

The electron configuration of the sodium ion is now the same as that of the noble gas neon. The term **isoelectronic** refers to an atom and an ion of a different atom (or two different ions) that have the same electron configuration. The sodium ion is isoelectronic with the neon atom. Consider a similar process with magnesium and with aluminum:

$$\begin{array}{lllll} \text{Mg} & \rightarrow & \text{Mg}^{2+} & + & 2\text{e}^{-} \\ 1s^2 2s^2 2p^6 3s^2 & & 1s^2 2s^2 2p^6 \text{ (octet)} & & \\ \text{Al} & \rightarrow & \text{Al}^{3+} & + & 3\text{e}^{-} \\ 1s^2 2s^2 2p^6 3s^2 3p^1 & & 1s^2 2s^2 2p^6 \text{ (octet)} & & \end{array}$$

In this case, the magnesium atom loses its two valence electrons in order to achieve the same noble-gas configuration. The aluminum atom loses its three valence electrons. The Mg^{2+} ion, the Al^{3+} ion, the Na^{+} ion, and the

Ne atom are all isoelectronic. For representative elements under typical conditions, three electrons is the maximum number that will be lost.

We can also show the loss of valence electron(s) with an electron dot diagram.

$$\mathrm{Na}\cdot \rightarrow \mathrm{Na}^{+} + \mathrm{e}^{-}$$
$$\cdot\mathrm{Mg}\cdot \rightarrow \mathrm{Mg}^{2+} + 2\mathrm{e}^{-}$$

Summary

- Cations form when an atom loses one or more electrons.
- The resulting cation has the electron configuration of the noble gas atom in the row above it in the periodic table.

Practice

Use the link below to answer the following questions:

http://www.wisegeek.org/what-is-deionized-water.htm

1. What are some of the cations removed from deionized water?
2. How is deionized water made?
3. What is not removed from deionized water?
4. Does deionized water slow aging and prevent disease?

Review

1. What is a cation?
2. How many valence electrons does the sodium atom have?
3. Which atom is the sodium ion isoelectronic with?
4. How many electrons does magnesium lose to form the magnesium ion?

- **isoelectronic:** An atom and an ion of a different atom, or two different ions, that have the same electron configuration.

8.4 Anion Formation

- Define anion.
- Describe electron configurations of common anions.

FIGURE 8.2

A pressed glass open salt dish made in the early 1830s.

How do you make chlorine safe to eat?

How do you transform a deadly gas into something you can sprinkle on your eggs and eat for breakfast? Chlorine in its free form is very dangerous if you breathe the fume or come in contact with the gas. However, after reaction with sodium, we have sodium chloride formed as the sodium atom gives up an electron to chlorine which accepts the electron to for the chloride anion.

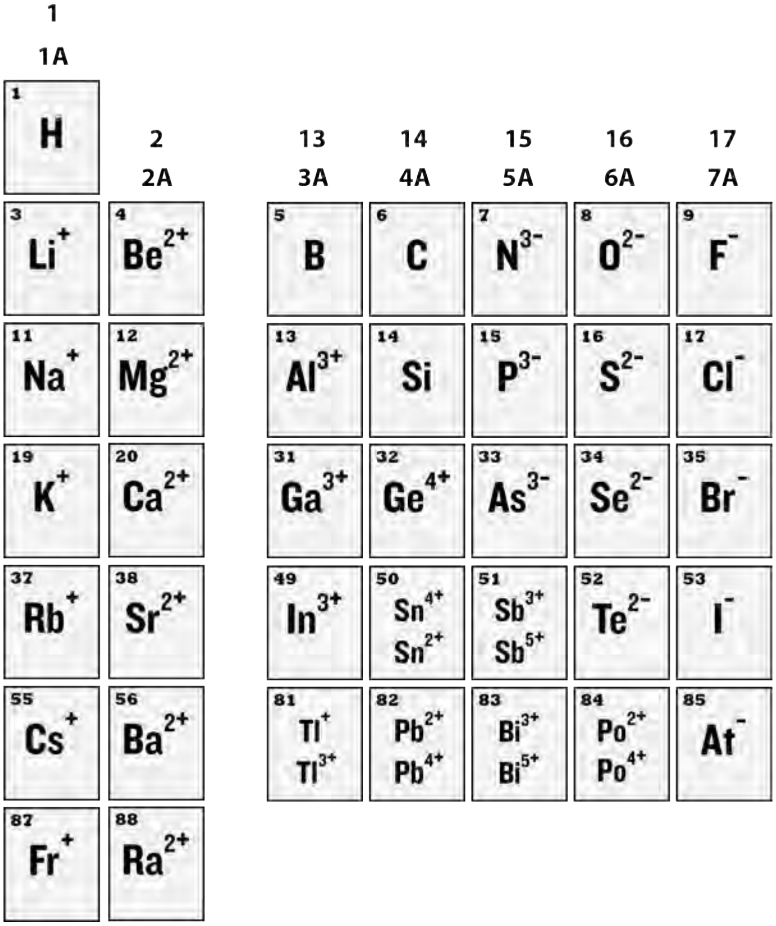
Anions

Anions are the negative ions formed from the gain of one or more electrons. When nonmetal atoms gain electrons, they often do so until their outermost principal energy level achieves an octet. This process is illustrated below for the elements fluorine, oxygen, and nitrogen.

$$\begin{array}{llll}
\mathrm{F} & + \mathrm{e}^- & \rightarrow & \mathrm{F}^- \\
1s^2 2s^2 2p^5 & & & 1s^2 2s^2 2p^6 \text{ (octet)} \\
\mathrm{O} & + 2\mathrm{e}^- & \rightarrow & \mathrm{O}^{2-} \\
1s^2 2s^2 2p^4 & & & 1s^2 2s^2 2p^6 \text{ (octet)} \\
\mathrm{N} & + 3\mathrm{e}^- & \rightarrow & \mathrm{N}^{3-} \\
1s^2 2s^2 2p^3 & & & 1s^2 2s^2 2p^6 \text{ (octet)}
\end{array}$$

All of these anions are isoelectronic with each other and with neon. They are also isoelectronic with the three cations from the previous section. Under typical conditions, three electrons is the maximum that will be gained in the formation of anions.

Outer electron configurations are constant within a group, so this pattern of ion formation repeats itself for Periods 3, 4, and following (see **Figure** 8.3).



1 1A	2 2A	13 3A	14 4A	15 5A	16 6A	17 7A
1 H						
3 Li^+	4 Be^{2+}	5 B	6 C	7 N^{3-}	8 O^{2-}	9 F^-
11 Na^+	12 Mg^{2+}	13 Al^{3+}	14 Si	15 P^{3-}	16 S^{2-}	17 Cl^-
19 K^+	20 Ca^{2+}	31 Ga^{3+}	32 Ge^{4+}	33 As^{3-}	34 Se^{2-}	35 Br^-
37 Rb^+	38 Sr^{2+}	49 In^{3+}	50 Sn^{4+} Sn^{2+}	51 Sb^{3+} Sb^{5+}	52 Te^{2-}	53 I^-
55 Cs^+	56 Ba^{2+}	81 Tl^+ Tl^{3+}	82 Pb^{2+} Pb^{4+}	83 Bi^{3+} Bi^{5+}	84 Po^{2+} Po^{4+}	85 At^-
87 Fr^+	88 Ra^{2+}					

FIGURE 8.3

Ion charges.

It is important not to misinterpret the concept of being isoelectronic. A sodium ion is very different from a neon atom because the nuclei of the two contain different numbers of protons. One is an essential ion that is a part of table salt, while the other is an unreactive gas that is a very small part of the atmosphere. Likewise, sodium ions are very different than magnesium ions, fluoride ions, and all the other members of this isoelectronic series (N^{3-}, O^{2-}, F^-, Ne, Na^+, Mg^{2+}, Al^{3+}).

Kevin DooleySummary

- Anions are negative ions formed by accepting electrons.
- The outermost principal energy level usually is an octet.

Practice

Use the link below to answer the following questions:

http://preparatorychemistry.com/bishop_anion_names_formulas_help.htm

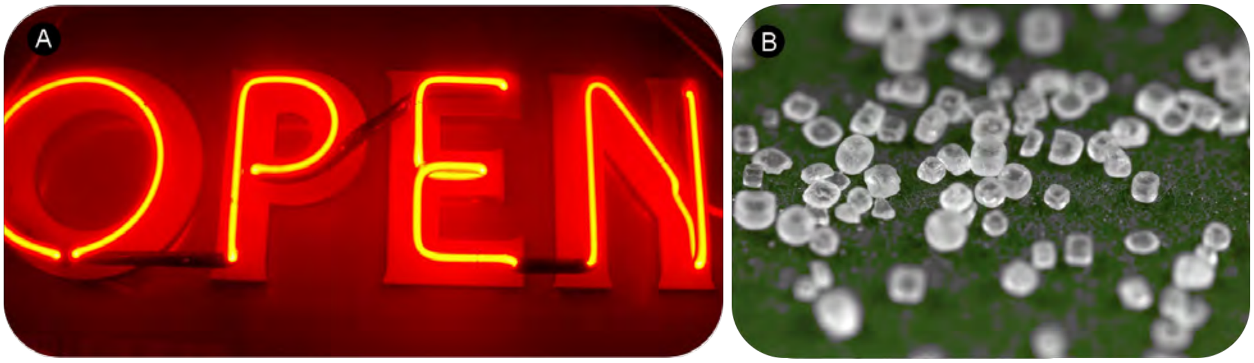


FIGURE 8.4

Neon gas (A) and sodium chloride crystals (B). Neon atoms and sodium ions are isoelectronic. Neon is a colorless and unreactive gas that glows a distinctive red-orange color in a gas discharge tube. Sodium ions are most commonly found in crystals of sodium chloride, ordinary table salt.

1. What do nonmetals tend to do?
2. What noble gas is Se^{2-} isoelectronic with?
3. What -3 anion is isoelectronic with Ar?
4. What is a polyatomic anion?

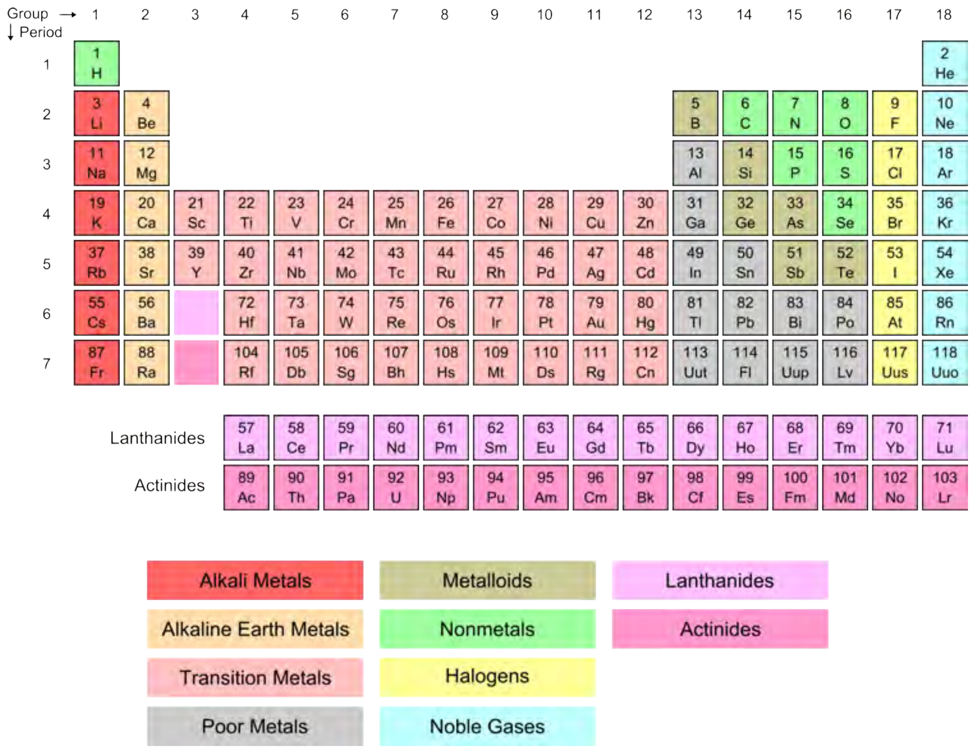
Review

1. What is an anion?
2. Write the electronic configurations for the chlorine atom and the chloride anion.
3. What does isoelectronic mean?

- **anion:** The negative ions formed from the gain of one or more electrons.

8.5 Transition Metal Ion Formation

- Describe the formation of transition metal ions.



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

How do transition metals form ions?

The transition metals are an interesting and challenging group of elements. They have perplexing patterns of electron distribution that don't always follow the electron filling rules. Predicting how they will form ions is also not always obvious.

Transition Metal Ions

Transition metals belong to the *d* block, meaning that the *d* sublevel of electrons is in the process of being filled with up to ten electrons. Many transition metals cannot lose enough electrons to attain a noble-gas electron configuration. In addition, the majority of transition metals are capable of adopting ions with different charges. Iron, which forms either the Fe^{2+} or Fe^{3+} ions, loses electrons as shown below.

$$\begin{array}{llll}
\text{Fe} & \rightarrow & \text{Fe}^{2+} & + \quad 2\text{e}^- \\
[\text{Ar}]3d^6 4s^2 & & [\text{Ar}]3d^6 & \\
\text{Fe} & \rightarrow & \text{Fe}^{3+} & + \quad 3\text{e}^- \\
[\text{Ar}]3d^6 4s^2 & & [\text{Ar}]3d^5 &
\end{array}$$

According to the Aufbau process, the electrons fill the 4*s* sublevel before beginning to fill the 3*d* sublevel. However, the outermost *s* electrons are always the first to be removed in the process of forming transition metal cations. Because most transition metals have two valence electrons, the charge of 2+ is a very common one for their ions. This is the case for iron above. A half-filled *d* sublevel (d^5) is particularly stable, which is the result of an iron atom losing a third electron.

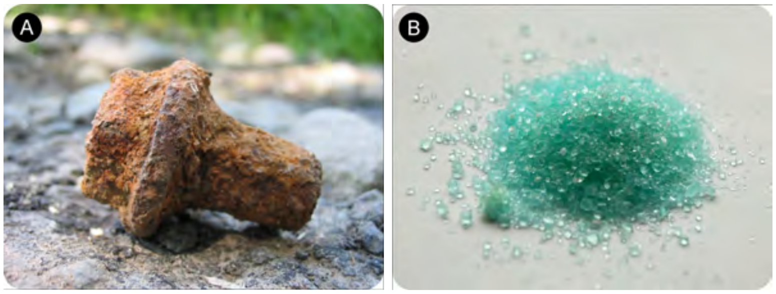


FIGURE 8.5
A. Rust is a complex combination of oxides of iron(III), among them iron(III) oxide, Fe_2O_3. B. Iron(II) sulfate, $FeSO_4$, has been known since ancient times as green vitriol and was used for centuries in the manufacture of inks.

Some transition metals that have relatively few *d* electrons may attain a noble-gas electron configuration. Scandium is an example.

$$\begin{array}{llll} \text{Sc} & \rightarrow & \text{Sc}^{3+} & + \quad 3\text{e}^- \\ [\text{Ar}]3d^1 4s^2 & & [\text{Ar}] & \end{array}$$

Others may attain configurations with a full *d* sublevel, such as zinc and copper.

$$\begin{array}{llll} \text{Zn} & \rightarrow & \text{Zn}^{2+} & + \quad 2\text{e}^- \\ [\text{Ar}]3d^{10} 4s^2 & & [\text{Ar}]3d^{10} & \\ \text{Cu} & \rightarrow & \text{Cu}^{+} & + \quad \text{e}^- \\ [\text{Ar}]3d^{10} 4s^1 & & [\text{Ar}]3d^{10} & \end{array}$$

The resulting configuration above, with 18 electrons in the outermost principal energy level, is referred to as a **pseudo noble-gas electron configuration**. It gives particular stability to the Zn^{2+} and Cu^+ ions.

Summary

- Transition metal ion formation is more complex than simple cation formation.
- Transition metal ions often involve rearrangements of both *d* and *s* electrons.

Practice

Answer the question on the link below:

http://www.dynamicscience.com.au/tester/solutions/chemistry/atomic%20structure/transitionmetalsionformation.htm

Review

1. What block do the transition metals fall in?
2. Which sublevel is filled first?
3. Which sublevel loses electrons first?

4. What is the pseudo noble-gas electron configuration?

- **pseudo noble-gas electron configuration:** 18 electrons in the outermost principal energy level.
- **transition metal:** Metals whose *d* sublevels are in the process of filling to ten electrons.

8.6 Ionic Bonding

- Define ionic compound.
- Define ionic bond.
- Use electron dot diagrams to illustrate electron transfer and ionic bond formation.

Does the sea really have salt in it?

We can get common table salt from several sources. It can be mined in the solid form in salt mines or found as a solid in deposits. We can also get salt from the ocean, but it really does not exist as salt when in solution. The sodium ions and chloride ions are dissolved, but not combined into a structure until all the water is removed.

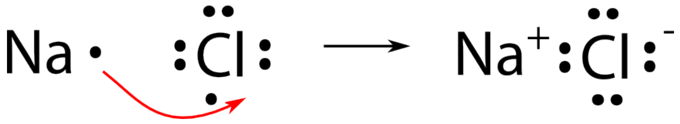
Most of the rocks and minerals that make up the Earth's crust are composed of positive and negative ions held together by ionic bonding. An ionic compound is an electrically neutral compound consisting of positive and negative ions. You are very familiar with some ionic compounds such as sodium chloride (NaCl). A sodium chloride crystal consists of equal numbers of positive sodium ions (Na^+) and negative chloride ions (Cl^-).

Ionic Bonds

Oppositely charged particles attract each other. This attractive force is often referred to as an **electrostatic force**. An **ionic bond** is the electrostatic force that holds ions together in an **ionic compound**. The strength of the ionic bond is directly dependent upon the quantity of the charges and inversely dependent on the distance between the charged particles. A cation with a 2+ charge will make a stronger ionic bond than a cation with a 1+ charge. A larger ion makes a weaker ionic bond because of the greater distance between its electrons and the nucleus of the oppositely charged ion.

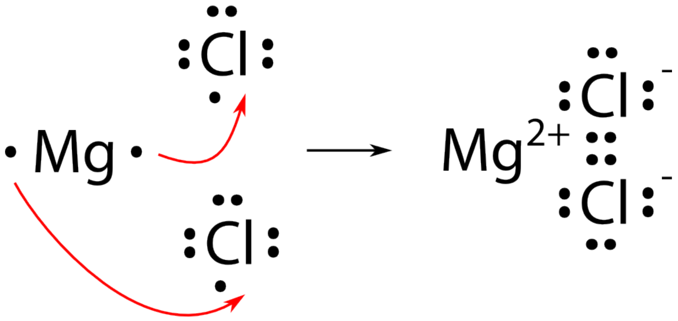
Electron Dot Diagrams

We will use sodium chloride as an example to demonstrate the nature of the ionic bond and how it forms. As you know, sodium is a metal and loses its one valence electron to become a cation. Chlorine is a nonmetal and gains one electron in becoming an anion. Both achieve a noble-gas electron configuration. However, electrons cannot be simply "lost" to nowhere in particular. A more accurate way to describe what is happening is that a single electron is transferred from the sodium atom to the chlorine atom as shown below.



The ionic bond is the attraction of the Na^+ ion for the Cl^- ion. It is conventional to show the cation without dots around the symbol to emphasize that the original energy level that contained the valence electron is now empty. The anion is now shown with a complete octet of electrons.

For a compound such as magnesium chloride, it is not quite as simple. Because magnesium has two valence electrons, it needs to lose both to achieve the noble-gas configuration. Therefore, two chlorine atoms will be needed.



The final formula for magnesium chloride is $MgCl_2$.

Summary

- An ionic compound contains positive and negative ions.
- An ionic bond is electrostatic in nature.
- Electron dot diagrams can be used to illustrate electron movements and ion formation.

Practice

Use the link below to answer the following questions:

http://chemed.chem.wisc.edu/chempaths/GenChem-Textbook/Ionic-Bonding-565.html

1. What do cations and anions form?
2. What influences attraction for electrons?
3. What metals generally form ionic bonds?

Review

1. What is an ionic compound?

2. What is an ionic bond?
3. Which cation (Na^+ or Ca^{2+}) would form a stronger ionic bond with Cl^-

- **electrostatic force:** Attraction of oppositely charged particles toward one another.
- **ionic bond:** The electrostatic force that holds ions together in an ionic compound.
- **ionic compound:** An electrically neutral compound consisting of positive and negative ions.

8.7 Ionic Crystal Structure

- Describe the lattice structure of ionic compounds.

Why are crystals appealing?

Crystals are found everywhere there are chemical deposits. The ruby crystal shown above is extremely valuable, both because of its beauty and its utility in such equipment as lasers. For some people, crystals are said to have magical qualities. For others, the "magic" is in the regular structure of the crystal as the cations and anions line up in a regular fashion.

Ionic Crystal Structure

Electron dot diagrams show the nature of the electron transfer that takes place between metal and nonmetal atoms. However, ionic compounds do not exist as discrete molecules, as the dot diagrams may suggest. In order to minimize the potential energy of the system, ionic compounds take on the form of an extended three-dimensional array of alternating cations and anions. This maximizes the attractive forces between the oppositely charges ions. The figure below shows two different ways of representing the ionic crystal lattice. A ball and stick model makes it

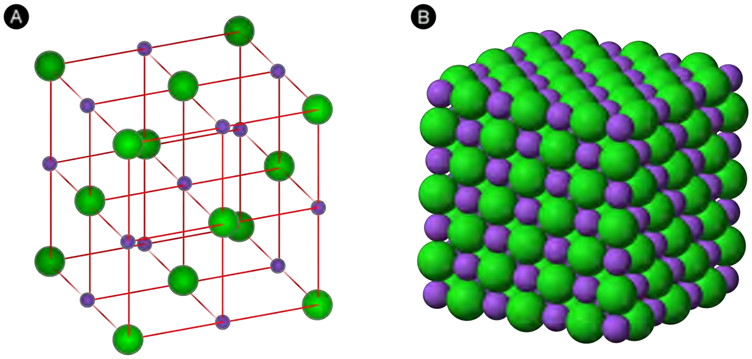


FIGURE 8.6

Two models of a sodium chloride crystal are shown. The purple spheres represent the Na^+ ions, while the green spheres represent the Cl^- ions. (A) In an expanded view, the distances between ions are exaggerated, more easily showing the coordination numbers of each ion. (B) In a space filling model, the electron clouds of the ions are in contact with each other.

easier to see how individual ions are oriented with respect to one another. A space filling diagram is a more accurate representation of how the ions pack together in the **crystal**.

Naturally occurring sodium chloride **(halite)** does not look at first glance like the neat diagrams shown above. It is only when we use modern techniques to analyze the crystal structure at the atomic level that we can see the true regularity of the organized ions.

FIGURE 8.7

Halite crystals.

Summary

- Ionic compounds take on the form of extended three-dimensional arrays of cations and anions.
- The arrangement maximizes the attractive force between oppositely-charged ions.

Practice

Use the link below to answer the following questions:

http://www.chemguide.co.uk/atoms/structures/ionicstruct.html

1. How many chloride ions are touched by a sodium ion?
2. How many sodium ions are touched by a chloride ion?
3. What contributes to the stability of an ionic compound?
4. Why do CsCl and NaCl have different structures?

Review

1. Do ionic compounds exist as discrete molecules?
2. What does this three-dimensional array do?
3. What gives the most accurate rendition of how the ions arrange themselves?

- **crystal:** A solid material whose constituent atoms, molecules, or ions are arranged in an ordered pattern extending in three-dimensional space.
- **halite:** Naturally occurring form of sodium chloride.

8.8 Coordination Number

- Define coordination number.
- Determine coordination number when given the lattice structure of the crystal.

What makes the colors different?

The two cobalt salts pictured above both contain Co^{2+} cations. The difference in color is due to the species surrounding the cobalt ion. The presence of water molecules in the coordination sphere around the central cobalt ion changes the distances among species and the color of the material.

Coordination Number

The **coordination number** is the number of ions that immediately surround an ion of the opposite charge within a crystal lattice. If you examine the figure below, you will see that there are six chloride ions immediately surrounding a single sodium ion. The coordination number of sodium is 6. Likewise, six sodium ions immediately surround each chloride ions, making the coordination number of chloride also equal to 6. Because the formula unit of sodium chloride displays a 1:1 ratio between the ions, the coordination numbers must be the same.

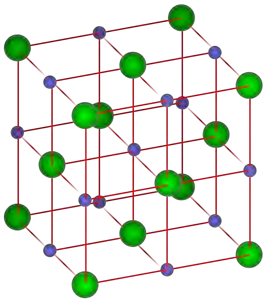


FIGURE 8.8

Lattice structure for sodium chloride. The blue balls represent the sodium ions and the green balls represent the chloride ions

The formula unit for cesium chloride is CsCl, also a 1:1 ratio. However, as shown in the figure below, the coordination numbers are not 6 as in NaCl. The center ion is the Cs^{+} ion and is surrounded by the eight Cl^{-} ions at the corners of the cube. Each Cl^{-} ion is also surrounded by eight Cs^{+} ions. The coordination numbers in this type of crystal are both 8. CsCl and NaCl do not adopt identical crystal packing arrangements because the Cs^+ ion is considerably larger than the Na^+ ion.

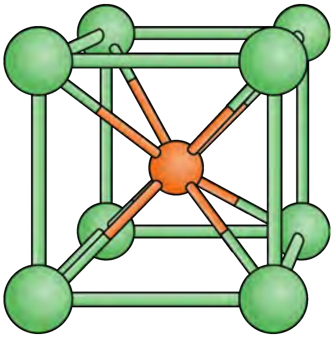


FIGURE 8.9

In a cesium chloride crystal, the cesium ion (orange) occupies the center, while the chloride ions (green) occupy each corner of the cube. The coordination number for both ions is 8.

Another type of crystal is illustrated by titanium(IV) oxide, TiO_2, which is commonly known as rutile. The rutile crystal is shown below.

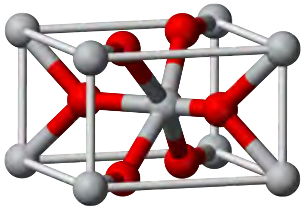


FIGURE 8.10

Titanium(IV) oxide forms tetragonal crystals. The coordination number of the Ti^{4+} ions (gray) is 6, while the coordination number of the ${O_2}^-$ ions (red) is 3.

The gray Ti^{4+} ions are surrounded by six red O^{2-} ions. The O^{2-} ions are surrounded by three Ti^{4+} ions. The coordination of the titanium(IV) cation is 6, which is twice the coordination number of the oxide anion, which is 3. This fits with the formula unit of TiO_2, since there are twice as many O^{2-} ions as Ti^{4+} ions.

The crystal structure of all ionic compounds must reflect the formula unit. In a crystal of iron(III) chloride, $FeCl_3$, there are three times as many chloride ions as iron(III) ions.

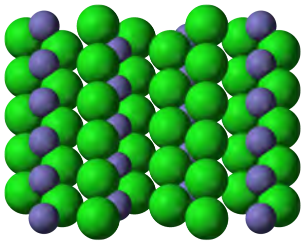


FIGURE 8.11

Iron(III) chloride. The bluish-gray Fe^{3+} ions are surrounded by green Cl^- ions.

Summary

- The coordination number of a compound is determined by the type and number of ions or other species surrounding a central ion.

- Often the color of a compound is affected by the specific materials coordinated to that central ion.

Practice

Use the link below to answer the following questions:

http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch12/complex.php

1. What are the ions or molecules that bind to transition metal ions called?
2. How many complexes of $CoCl_3$ can be isolated?
3. What is a monodentate ligand?
4. What are the most common coordination numbers?

Review

1. What is the coordination number for Na^+ in NaCl?
2. What is the coordination number for Cs^+?
3. Why are the packing arrangements for Na^+ and Cs^+ different?

- **coordination number:** The number of ions that immediately surround an ion of the opposite charge within a crystal lattice.

8.9 Physical Properties of Ionic Compounds

- List and describe the physical properties of ionic compounds.

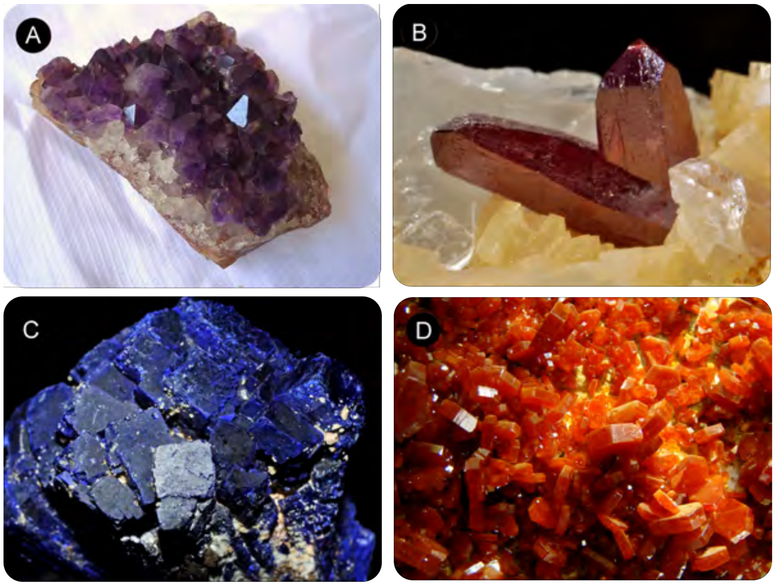


FIGURE 8.12
In nature, the ordered arrangement of ionic solids gives rise to beautiful crystals. (A) Amethyst – a form of quartz, SiO_2, whose purple color comes from iron ions. (B) Cinnabar – the primary ore of mercury is mercury(II) sulfide, HgS. (C) Azurite – a copper mineral, $Cu_3(CO_3)_2(OH)_2$. D) Vanadinite – the primary ore of vanadium, $Pb_5(VO_4)_3Cl$.

What produces colored crystals?

The figure above shows just a few examples of the color and brilliance of naturally occurring ionic crystals. The regular and orderly arrangement of ions in the crystal lattice is responsible for the various shapes of these crystals, while transition metal ions give rise to the colors.

Physical Properties of Ionic Compounds

Melting Points

Because of the many simultaneous attractions between cations and anions that occur, ionic crystal lattices are very strong. The process of melting an ionic compound requires the addition of large amounts of energy in order to break all of the ionic bonds in the crystal. For example, sodium chloride has a melting temperature of about 800°C.

Shattering

Ionic compounds are generally hard, but **brittle.** Why? It takes a large amount of mechanical force, such as striking a crystal with a hammer, to force one layer of ions to shift relative to its neighbor. However, when that happens, it brings ions of the same charge next to each other (see **Figure** 8.13). The repulsive forces between like-charged ions cause the crystal to shatter. When an ionic crystal breaks, it tends to do so along smooth planes because of the regular arrangement of the ions.

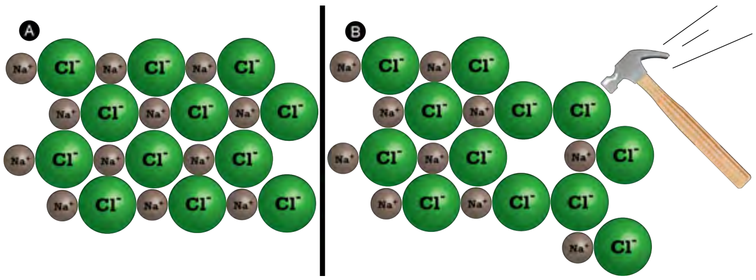


FIGURE 8.13

(A) The sodium chloride crystal is shown in two dimensions. (B) When struck by a hammer, the negatively-charged chloride ions are forced near each other and the repulsive force causes the crystal to shatter.

Conductivity

Another characteristic property of ionic compounds is their **electrical conductivity.** The figure below shows three experiments in which two electrodes that are connected to a light bulb are placed in beakers containing three different substances.

In the first beaker, distilled water does not conduct a current because water is a molecular compound. In the second beaker, solid sodium chloride also does not conduct a current. Despite being ionic and thus composed of charges particles, the solid crystal lattice does not allow the ions to move between the electrodes. Mobile charged particles are required for the circuit to be complete and the light bulb to light up. In the third beaker, the NaCl has been dissolved into the distilled water. Now the crystal lattice has been broken apart and the individual positive and negative ions can move. Cations move to one electrode, while anions move to the other, allowing electricity to flow (see **Figure** 8.15). Melting an ionic compound also frees the ions to conduct a current. Ionic compounds conduct an electric current when melted or dissolved in water.

Summary

- Ionic compounds have high melting points.
- Ionic compounds are hard and brittle.
- Solutions of ionic compounds and melted ionic compounds conduct electricity, but solid materials do not.

Practice

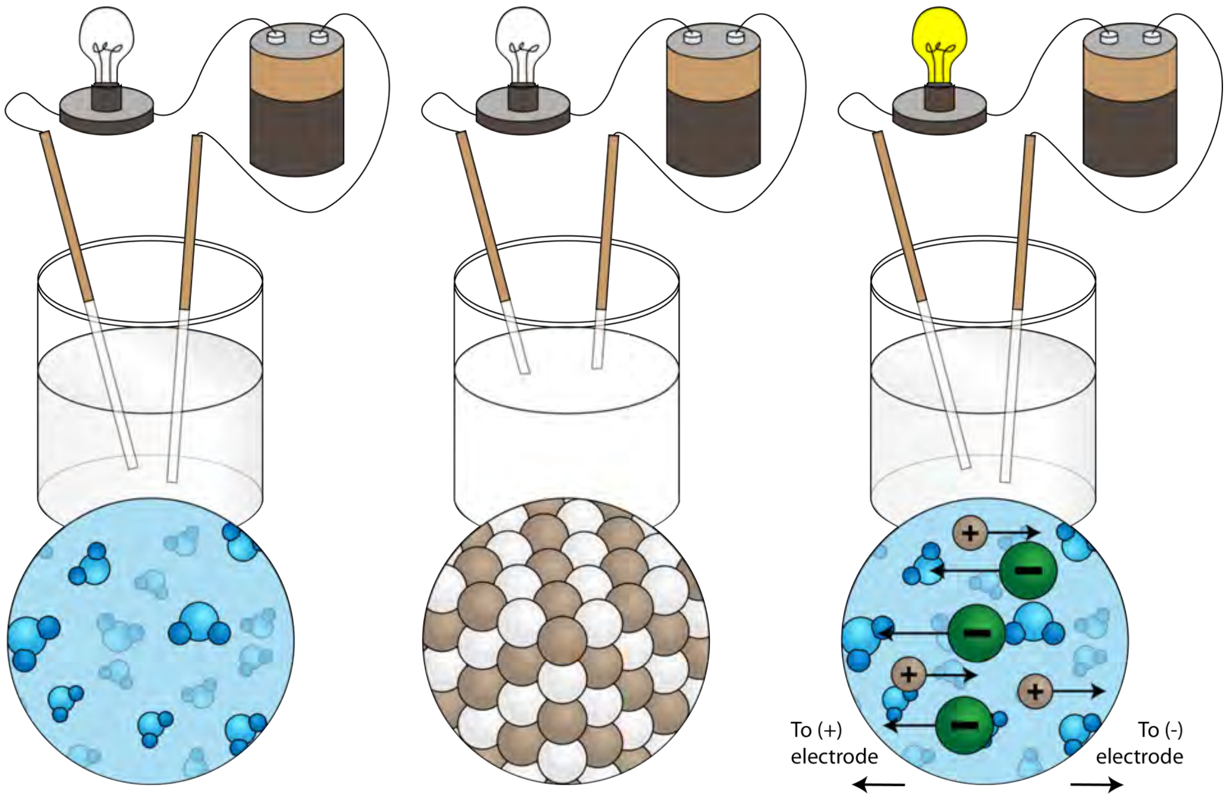
Watch the video at the link below and answer the following questions:

http://www.youtube.com/watch?v=buWrSgs_ZHk

MEDIA

Click image to the left for more content.

1. Do all ionic compounds form crystals?
2. Will melted ionic compounds conduct electricity?
3. What are the melting and boiling points of KI?



A Distilled water does not conduct a current.

B Positive and negative ions fixed in a solid do not conduct a current.

C In solution, positive and negative ions move and conduct a current.

FIGURE 8.14

(A) Distilled water does not conduct electricity. (B) A solid ionic compound also does not conduct. (C) A water solution of an ionic compound conducts electricity well.

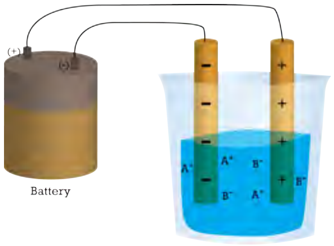


FIGURE 8.15

In an ionic solution, the A^+ ions migrate toward the negative electrode, while the B^- ions migrate toward the positive electrode.

Review

1. Why are ionic compounds brittle?
2. Why are melting points high for ionic compounds?
3. What happens when an electric current is passed through a solution of an ionic compound?

- **brittle:** Easily broken, cracked, or snapped.
- **electrical conductivity:** The ability to conduct an electric current.

8.10 Metallic Bonding

- Define metallic bond.
- Describe properties of metals.

Why do metals behave the way they do?

The image above is of a copper plate that was made in 1893. The utensil has a great deal of elaborate decoration and the item is very useful. What would have happened if we decided that copper chloride was just as good a material (well, it does have copper in it). The CuCl would end up as a powder when we pounded on it to shape it. Metals behave in unique ways. The bonding that occurs in a metal is responsible for its distinctive properties: luster, malleability, ductility, and excellent conductivity.

The Metallic Bond

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. Electrons which are capable of moving freely throughout the empty orbitals of the metallic crystal are called **delocalized electrons** (see **Figure** 8.16). A **metallic bond** is the attraction of the stationary metal cations to the surrounding mobile electrons.

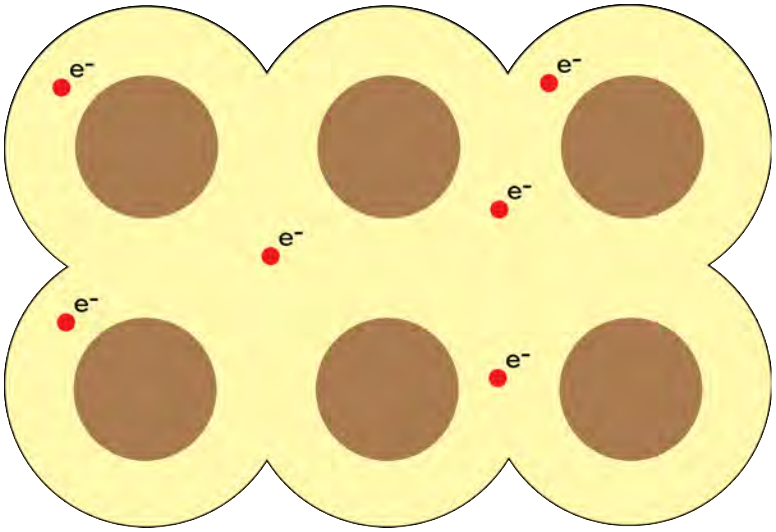


FIGURE 8.16

In a metal, the stationary metal cations are surrounded by a sea of mobile valence electrons that are not associated with any one cation.

Properties of Metals

The metallic bonding model explains 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. When light is shone on to the surface of a metal, its electrons absorb small amounts of energy and become excited into one of its many empty orbitals. The electrons immediately fall back down to lower energy levels and emit light. This process is responsible for the high **luster** of metals.

FIGURE 8.17

The American Platinum Eagle is the official platinum bullion coin of the United States and was first minted in 1997. The luster of a metal is due to its metallic bonds.

Recall that ionic compounds are very brittle. Application of a force results in like-charged ions in the crystal coming too close to one another, causing the crystal to shatter. When a force is applied to a metal, the free-flowing electrons can slip in between the stationary cations and prevent them from coming in contact. Imagine ball bearings that have been coated with oil sliding past one another. As a result, metals are very **malleable** and **ductile**. They can be hammered into shapes, rolled into thin sheets, or pulled into thin wires.

Summary

- The metallic bond is responsible for the properties of metals.
- Metals conduct electricity and heat well.
- Metals are ductile and malleable.
- Metals have luster.

Practice

Use the link below to answer the following questions:

http://www.chemguide.co.uk/atoms/bonding/metallic.html

1. What happens to valence electrons in metals?
2. What holds the atoms of a metal together?
3. What happens to the metallic bond when a metal is melted?
4. What happens to the metallic bond when a metal boils?

Review

1. What is a delocalized electron?
2. Why do metals conduct electricity and heat well?
3. Why do metals have luster?

- **delocalized electrons:** Electrons which are capable of moving freely throughout the empty orbitals of the metallic crystal.
- **ductile:** Able to be drawn out into a thin wire.
- **luster:** A gentle sheen or soft glow, especially that of a partly reflective surface.
- **malleable:** Able to be hammered or pressed permanently out of shape without breaking or cracking.
- **metallic bond:** The attraction of the stationary metal cations to the surrounding mobile electrons.

8.11 Crystal Structures of Metals

- Define closest packing.
- Describe closest packing arrangements in metals.


Civil War Cannon

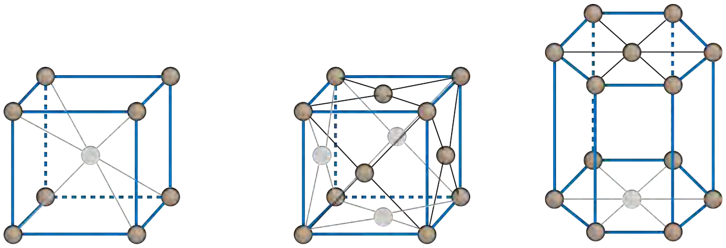

Cannonballs

How would you stack cannon balls?

Before modern artillery with explosive shells, cannons were used to fire cannon balls at the enemy. The soldiers operating the cannon needed to be able to get to the cannon balls quickly and efficiently. An arrangement such as the pyramid worked well for the purpose.

Crystal Structures of Metals

When identical spheres are stacked, each successive layer fits into the small spaces where different spheres come together. This orderly and regular arrangement of the metal balls minimizes the empty space between them. **Closest packing** is the most efficient arrangement of spheres. Atoms of a metal crystal are arranged in similar patterns, called close-packed structures. Pure metals adopt one of several related close-packed structures as shown below.


Cubic body centered (bcc)
Fe, V, Nb, Cr

Cubic face centered (fcc)
Al, Ni, Ag, Cu, Au

Hexagonal
Ti, Zn, Mg, Cd

FIGURE 8.18
Most pure metals naturally adopt one of these three closest packing arrangements.

On the far left is the body-centered cubic (bcc) structure. In that crystal, metal atoms occupy the eight corners of a cube along with one atom in the very center. The coordination number of each atom in the body-centered cubic structure is 8. In the face-centered cubic (fcc) structure, there are eight atoms at each corner of the cube and six atoms in the center of each face. The coordination number of each atom in the face-centered cubic structure is

12. The hexagonal close-packed (hcp) structure also has a coordination number of 12, but crystals of this type are hexagonally shaped rather than cubic.

Summary

- Atoms of a metal crystal are arranged in close-packed structures.
- This type of structure minimizes the empty space between the atoms.

Practice

Use the link below to answer the following questions:

http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch13/structure.php

1. Is simple cubic packing an efficient way to stack spheres?
2. What is the coordination number of a body-centered cubic stacking?
3. What is the most efficient way of stacking spheres?
4. How much space is filled with this structure?

Review

1. What is the most efficient arrangement of spheres?
2. What is the coordination number of a face-centered cubic structure?
3. What other structure has a coordination number of 12?

- **closest packing:** The most efficient arrangement of spheres.

8.12 Alloys

- Define alloy.
- Describe compositions and uses for common alloys.

What are the best guitar strings to use?

Many guitar players are very choosy when it comes to their strings. There is a variety to select from, depending on the type of guitar and the style of music. Electric guitars need steel strings so the magnetic pick-up will detect the string vibrations. Acoustic guitar players have several choices. Bronze strings (mixed with different amounts of cooper and zinc) have perhaps the brightest tone. There are several combinations of bronze alloys to choose from. For those with lots of money, titanium strings are available (but very expensive). Gold coating also helps string life and makes its unique contribution to tone. Alloy chemistry has contributed greatly to the strength, durability, and tonal quality of guitar strings.

Alloys

An **alloy** is a mixture composed of two or more elements, at least one of which is a metal. You are probably familiar with some alloys such as brass and bronze. **Brass** is an alloy of copper and zinc. **Bronze** is an alloy of copper and tin. Alloys are commonly used in manufactured items because the properties of these metal mixtures are often superior to a pure metal. Bronze is harder than copper and more easily cast. Brass is very malleable and its acoustic properties make it useful for musical instruments.

Steels are a very important class of alloys. The many types of steels are primarily composed of iron, with various amounts of the elements carbon, chromium, manganese, nickel, molybdenum, and boron. Steels are widely used in building construction because of their strength, hardness, and resistance to corrosion. Most large modern structures like skyscrapers and stadiums are supported by a steel skeleton (see **Figure ??**).

FIGURE 8.19

Bronze, an alloy of copper and tin, has been in use since ancient times. The Bronze Age saw the increased use of metals rather than stone for weapons, tools, and decorative objects. Brass, an alloy of copper and zinc, is widely used in musical instruments like the trumpet and trombone.

FIGURE 8.20

The Willis Tower (formerly called the Sears Tower) in Chicago was once the tallest building in the world and is still the tallest in the Western Hemisphere. The use of steel columns makes it possible to build taller, stronger, and lighter buildings.

Alloys can be one of two general types. In one type, called a **substitutional alloy,** the various atoms simply replace each other in the crystal structure. In another type, called an **interstitial alloy,** the smaller atoms such as carbon fit in between the larger atoms in the crystal packing arrangement.

Summary

- Alloys are mixtures of materials, at least one of which is a metal.
- Bronze alloys were widely used in weapons.
- Brass alloys have long been employed in musical instruments.
- Steel alloys are strong and durable.

Practice

Use the link below to answer the following questions:

http://ruthtrumpold.id.au/blogs/designtech/?p=365

1. What alloys are extensively used in the production of cars and engine parts?
2. Why are copper alloys used in electrical equipment?
3. Why are titanium alloys used in chemical, petrochemical, and biomaterial applications?

Review

1. What is brass made of?
2. What is bronze made of?
3. Why is steel widely used in construction?
4. What is a substitutional alloy?

- **alloy:** A mixture composed of two or more elements, at least one of which is a metal.
- **brass:** An alloy of copper and zinc.
- **bronze:** An alloy of copper and tin.
- **interstitial alloy:** The smaller atoms such as carbon fit in between the larger atoms in the crystal packing arrangement.
- **substitutional alloy:** The various atoms simply replace each other in the crystal structure.

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CHAPTER 9 Covalent Bonding

Chapter Outline

9.1 Energy and Covalent Bond Formation

- Define diatomic molecule.
- Draw the potential energy diagram for two atoms that are bonding.
- Define covalent molecule.

Cl—Be—Cl

Why do $BeCl_2$ and LiCl bond differently?

We have learned that halide salts of elements in group1 are typically ionic compounds. We would expect LiCl to exist as Li^+ cations and Cl^- anions (and it does). However, if we move one column to the right, lithium's neighbor beryllium forms a different type of bond altogether. This bond consists of shared electrons between the Be and Cl atoms, not electrostatic attraction among ions.

Energy and Covalent Bond Formation

Molecular compounds are those that take the form of an individual molecule. Molecular compounds are generally comprised of two or more nonmetal atoms. Familiar examples include water (H_2O), carbon dioxide (CO_2) and ammonia (NH_3). Recall that the molecular formula shows the number of each atom that occurs in a molecule of that compound. One molecule of water contains two hydrogen atoms and one oxygen atom. Hydrogen (H_2) is an example of an element that exists naturally as a diatomic molecule. A **diatomic molecule** is a molecule containing two atoms.

Most atoms attain a lower potential energy when they are bonded to other atoms than when they are separated. Consider two isolated hydrogen atoms that are separated by a distance large enough to prevent any interaction between them. At this distance, the potential energy of the system is said to be equal to zero (see **Figure ??**).

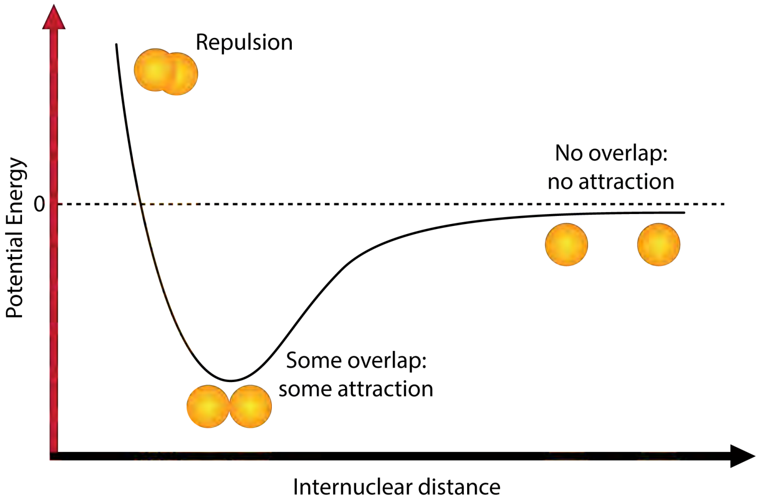


FIGURE 9.1
The graph shows how the potential energy of two hydrogen atoms changes as a function of their separation distance.

As the atoms approach one another, their electron clouds gradually begin to overlap. Now there are several interactions which begin to occur. One is that the single electrons that each hydrogen atom possesses begin to repel each other. This repulsive force would tend to make the potential energy of the system increase. However, the electron of each atom begins to be attracted to the nucleus of the other atom. This attractive force tends to make the potential energy of the system decrease.

As the atoms first begin to interact, the attractive force is stronger than the repulsive force and so the potential energy of the system decreases, as seen in the diagram. Remember that the lower potential energy increases the stability of the system. As the two hydrogen atoms move closer and closer together, the potential energy continues to decrease. Eventually, a position is reached where the potential energy is at its lowest possible point. If the hydrogen atoms move any closer together, a third interaction begins to dominate and that is the repulsive force between the two positively-charged nuclei. This repulsive force is very strong as can be seen by the sharp rise in energy at the far left of the diagram.

The point at which the potential energy reached its minimum represents the ideal distance between hydrogen atoms for a stable chemical bond to occur. This type of chemical bond is called a covalent bond. A **covalent bond** is a bond in which two atoms share one or more pairs of electrons. The single electrons from each of the two hydrogen atoms are shared when the atoms come together to form a hydrogen molecule (H_2).

Summary

- Covalent bonds are formed when atoms share electrons between them.

Practice

Use the link below to answer the following questions. Please only read the first two pages.

http://www.chem.ox.ac.uk/vrchemistry/electronsandbonds/intro1.htm

1. Why can two atoms come closer together if they form a covalent bond?
2. What role do the electrons have in attracting the two atoms?
3. Are two atoms closer together more or less stable than when they are apart?

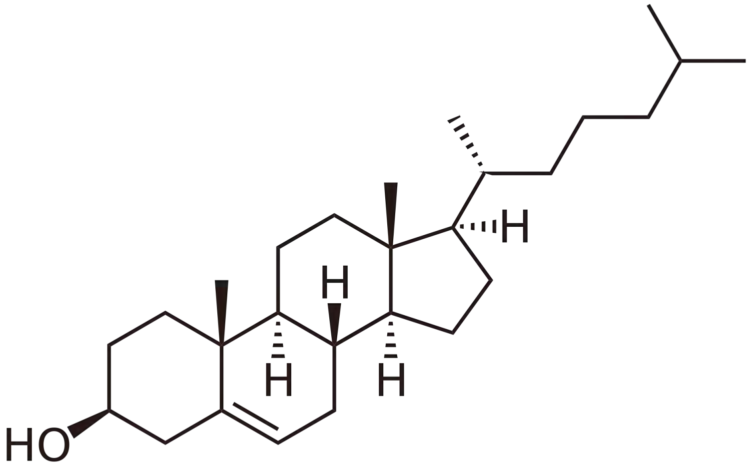
Review

1. What is a diatomic molecule?
2. What does lower potential energy do to a system?
3. What is the ideal distance for two atoms?

- **covalent bond:** A bond in which two atoms share one or more pairs of electrons.
- **diatomic molecule:** A molecule containing two atoms.

9.2 Lewis Electron-Dot Structures

- Define Lewis electron-dot structure.
- Define single covalent bond.
- Define structural formula.



What does cholesterol really look like?

We can write the structure of the cholesterol molecule a couple of different ways. The simplest approach is to just write $C_{27}H_{46}O$. This "structure" is not very useful because it does not tell us how the carbons, hydrogens, and oxygen are connected to one another. The structure in the figure above is much more helpful – we see how the different atoms are connected together to form the molecule.

Lewis Electron-Dot Structures

In a previous chapter, you learned that the valence electrons of an atom can be shown in a simple way with an electron dot diagram. A hydrogen atom is shown as H• because of its one valence electron. The structures of molecules that are held together by covalent bonds can be diagrammed by **Lewis electron-dot structures**. The hydrogen molecule is shown in the **Figure** 9.2.

The shared pair of electrons is shown as two dots in between the two H symbols (H:H). This is called a **single covalent bond**, when two atoms are joined by the sharing of one pair of electrons. The single covalent bond can also be shown by a dash in between the two symbols (H–H). A **structural formula** is a formula that shows the arrangement of atoms in a molecule and represents covalent bonds between atoms by dashes.

The Octet Rule and Covalent Bonds

When ions form, they conform to the **octet rule** by either losing or gaining electrons in order to achieve the electron configuration of the nearest noble gas. In a similar way, nonmetal atoms share electrons in the formation of a covalent in bond such a way that each of the atoms involved in the bond can attain a noble-gas electron configuration. The shared electrons are "counted" for each of the atoms involved in the sharing. For hydrogen

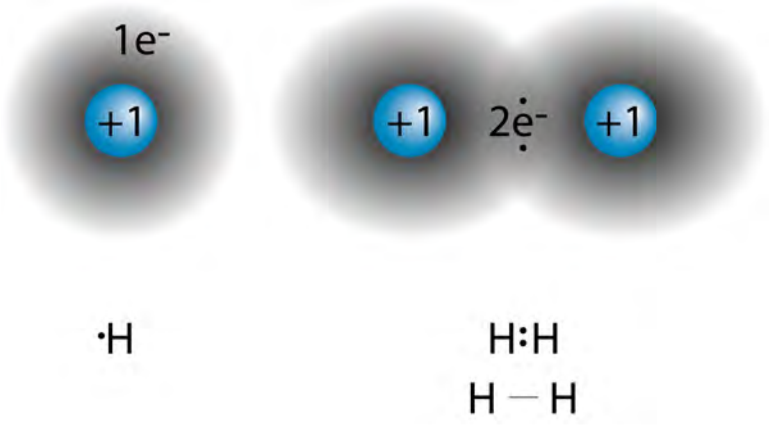


FIGURE 9.2

On the left is a single hydrogen atom with one electron. On the right is an H_2 molecule showing the electron cloud overlap.

(H_2), the shared pair of electrons means that each of the atoms is able to attain the electron configuration of helium, the noble gas with two electrons. For atoms other than hydrogen, the sharing of electrons will usually provide each of the atoms with eight valence electrons.

Summary

- Lewis electron-dot structures show the bonding in covalent molecules.
- Covalent bonds between atoms can be indicated either with dots (:) or a dash (-).

Practice

Use the link below to answer the following questions:

http://chemistry.about.com/od/generalchemistry/a/lewisstructures.htm

1. Who developed the electron-dot structure system?
2. Are lines or dots more commonly used?
3. How are unbounded electrons represented?
4. Which atom is selected as the central atom?

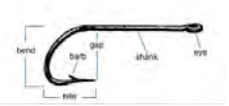
Review

1. What is a single covalent bond?
2. How can covalently-bound atoms obey the octet rule?
3. Does the hydrogen molecule obey the octet rule?

- **Lewis electron-dot structures:** A way of representing covalent bonds in molecules.
- **octet rule:** Ions form by adding or losing electrons to form an outer shell of eight.
- **single covalent bond:** When two atoms are joined by the sharing of one pair of electrons.
- **structural formula:** A formula that shows the arrangement of atoms in a molecule and represents covalent bonds between atoms by dashes.

9.3 Single Covalent Bonds

- Define a single covalent bond.
- Draw Lewis dot structures of molecules containing single covalent bonds.

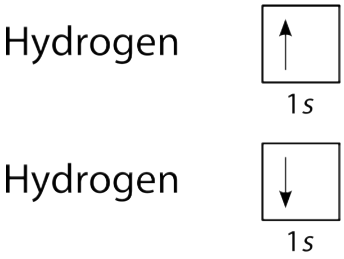


What holds molecules together?

In one form or another, the idea of atoms connecting to form larger substances has been with us for a long time. The Greek philosopher Democritus (460-370 BC) believed that atoms had hooks on them that allowed atoms to connect with one another. Today we believe that atoms are held together by bonds formed when two atoms share a set of electrons, a much more complicated picture than the simple hooks that Democritus preferred.

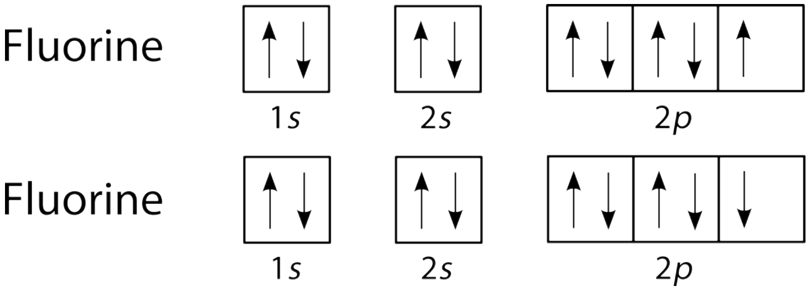
Single Covalent Bonds

A covalent bond forms when two orbitals with one electron each overlap each other. For the hydrogen molecule, this can be shown as:



Upon formation of the H_2 molecule, the shared electrons must have opposite spin, so they are shown with opposite spin in the atomic 1*s* orbital.

The halogens also form single covalent bonds in their diatomic molecules. An atom of any halogen, such as fluorine, has seven valence electrons. Its unpaired electron is located in the 2*p* orbital.



The single electrons in the third 2*p* orbital combine to form the covalent bond:

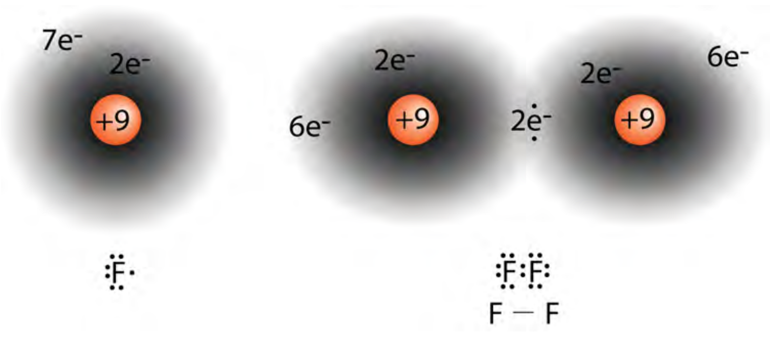


FIGURE 9.3

On the left is a fluorine atom with seven valence electrons. On the right is the F_2 molecule.

The diatomic fluorine molecule (F_2) contains a single shared pair of electrons. Each F atom also has three pair of electrons that are not shared with the other atom. A **lone pair** is a pair of electrons in a Lewis electron-dot structure that is not shared between atoms. The oxygen atom in the water molecule shown below has two lone pair sets of electrons. Each F atom has three lone pairs. Combined with the two electrons in the covalent bond, each F atom follows the octet rule.

Sample Problem 9.1: Lewis Electron Dot Structures

Draw the Lewis electron dot structure for water.

Step 1: List the known quantities and plan the problem

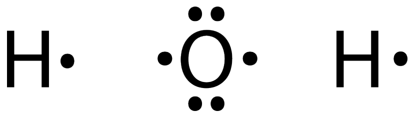
Known

- molecular formula of water = H_2O
- 1 O atom = 6 valence electrons
- 2 H atoms = $2 \times 1 = 2$ valence electrons
- total number of valence electrons = 8

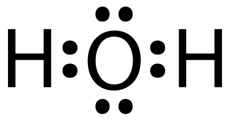
Use the periodic table to determine the number of valence electrons for each atom and the total number of valence electrons. Arrange the atoms and distribute the electrons so that each atom follows the octet rule. The oxygen atom will have 8 electrons, while the hydrogen atoms will each have 2.

Step 2: Solve

Electron dot diagrams for each atom are:



Each hydrogen atom with its single electron will form a covalent bond with the oxygen atom where it has a single electron. The resulting Lewis electron dot structure is:



Step 3: Think about your result.

The oxygen atom follows the octet rule with two pairs of bonding electrons and two lone pairs. Each hydrogen atom follows the octet rule with one bonding pair of electrons.

Summary

- Covalent bonds form when electrons in two atoms form overlapping orbitals.
- Lone pair electrons in an atom are not shared with another atom.

Practice

Read the article and practice drawing Lewis structures for some of the single covalent bond compounds listed at the end.

http://www2.fiu.edu/ landrumj/LewisStructures.pdf

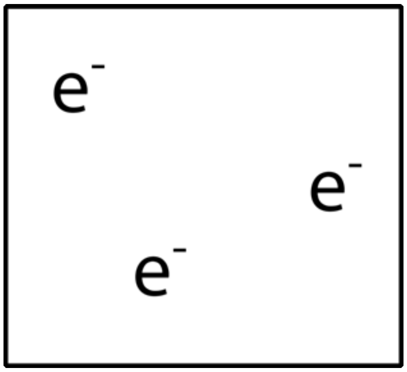
Review

- How does a covalent bond form?
- What do the spins of the shared electrons need to be?
- Do lone pair electrons form covalent bonds?

- **lone pair:** A pair of electrons in a Lewis electron-dot structure that is not shared between atoms.

9.4 Multiple Covalent Bonds

- Define double bond.
- Define triple bond.
- Draw Lewis electron dot structures for compounds containing double or triple bonds.



What do you do with the leftovers?

When working with covalent structures, it sometimes looks like you have leftover electrons. You apply the rules you learned so far and here are still some electrons hanging out there unattached. You can't just leave them there. So where do you put them?

Multiple Covalent Bonds

Some molecules are not able to satisfy the octet rule by making only single covalent bonds between the atoms. Consider the compound ethene, which has a molecular formula of C_2H_4. The carbon atoms are bonded together, with each carbon also being bonded to two hydrogen atoms.

$$\begin{aligned}&\text{two C atoms} = 2 \times 4 = 8 \text{ valence electrons}\\&\text{four H atoms} = 4 \times 1 = 4 \text{ valence electrons}\\&\text{total of 12 valence electrons in the molecule}\end{aligned}$$

If the Lewis electron dot structure was drawn with a single bond between the carbon atoms and with the octet rule followed, it would look like this:

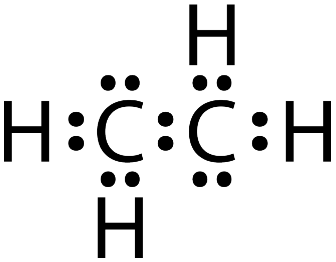


FIGURE 9.4

Incorrect dot structure of ethene.

This Lewis structure is incorrect because it contains a total of 14 electrons. However, the Lewis structure can be changed by eliminating the lone pairs on the carbon atoms and having the share two pairs instead of only one pair.

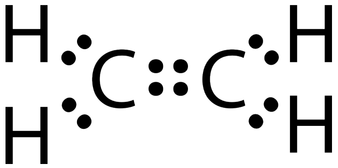


FIGURE 9.5

Correct dot structure for ethene.

A **double covalent bond** is a covalent bond formed by atoms that share two pairs of electrons. The double covalent bond that occurs between the two carbon atoms in ethane can also be represented by a structural formula and with a molecular model as shown in **Figure** 9.6.

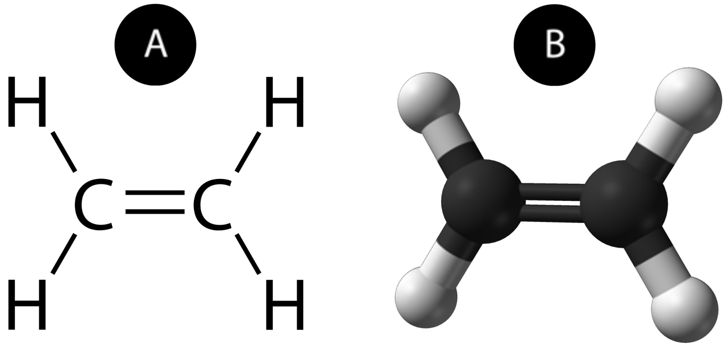


FIGURE 9.6

(A) The structural model for C_2H_4 consists of a double covalent bond between the two carbon atoms and single bonds to the hydrogen atoms. (B) Molecular model of C_2H_4.

A **triple covalent bond** is a covalent bond formed by atoms that share three pairs of electrons. The element nitrogen is a gas that composes the majority of Earth's atmosphere. A nitrogen atom has five valence electrons, which can be shown as one pair and three single electrons. When combining with another nitrogen atom to form a diatomic molecule, the three single electrons on each atom combine to form three shared pairs of electrons.

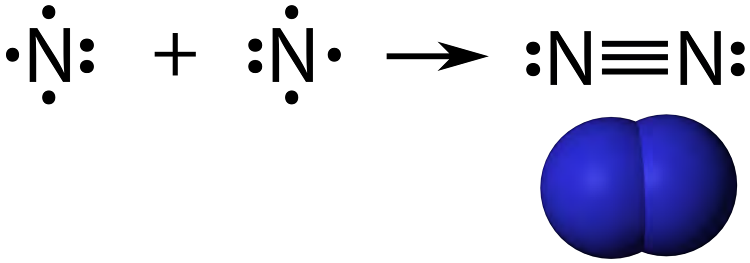


FIGURE 9.7

Triple bond in N_2.

Each nitrogen atom follows the octet rule with one lone pair of electrons and six electrons that are shared between the atoms.

Summary

- Lewis structures can be drawn for molecules that share multiple pairs of electrons.

Practice

Read the material at the link below and take the quiz (Test Bite).

http://www.bbc.co.uk/schools/gcsebitesize/science/add_aqa_pre_2011/atomic/covalentrev1.shtml

Review

1. Why is the first ethene Lewis structure incorrect?
2. What do the single electrons in nitrogen do to for a triple bond?
3. Draw the Lewis structure for ethyne C_2H_2.

- **double covalent bond:** A covalent bond formed by atoms that share two pairs of electrons.
- **triple covalent bond:** A covalent bond formed by atoms that share three pairs of electrons.

9.5 Coordinate Covalent Bond

- Define coordinate covalent bond.

Is sharing a good thing?

Remember when you were younger and were told to share your favorite toy with your brother or sister or friend? You probably didn't want to share, but did anyway. It turned out that you had more fun playing with the toy together that if you had kept it to yourself. Atoms also have to share what's theirs with another atom that has nothing to contribute to the situation. But the end result is a new structure.

Coordinate Covalent Bonds

Each of the covalent bonds that we have looked at so far has involved each of the atoms that are bonding contributing one of the electrons to the shared pair. There is an alternate type of covalent bond in which one of the atoms provided both of the electrons in a shared pair. Carbon monoxide, CO, is a toxic gas that is released as a by-product during the burning of fossil fuels. The bonding between the C atom and the O atom can be thought of as proceeding in this way.

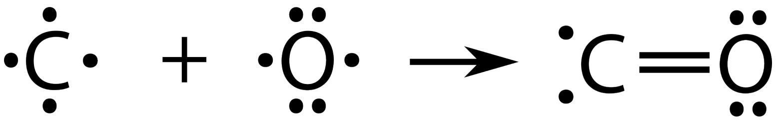


FIGURE 9.8

Formation of a CO double bond (incorrect structure).

At this point, a double bond has formed between the two atoms, with each atom providing one of the electrons to each bond. The oxygen atom now has a stable octet of electrons, but the carbon atom only has six electrons and is unstable. This situation is resolved if the oxygen atom contributes one of its lone pairs in order to make a third bond with the carbon atom.

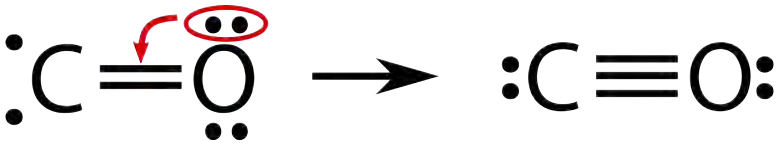


FIGURE 9.9

Correct CO structure.

The carbon monoxide molecule is correctly represented by a triple covalent bond between the carbon and oxygen atoms. One of the bonds is a **coordinate covalent bond**, a covalent bond in which one of the atoms contributes both of the electrons in the shared pair.

Once formed, a coordinate covalent bond is the same as any other covalent bond. It is not as if the two conventional bonds in the CO molecule are stronger or different in any other way than the coordinate covalent bond.

Summary

- Coordinate covalent bonds can form when one atom provides a lone pair of electrons to the bond.
- Coordinate covalent bonds are as strong as other covalent bonds.

Practice

Use the link below to answer the following questions:

http://www.chemguide.co.uk/atoms/bonding/dative.html

1. What is another name for a coordinate covalent bond?
2. In forming ammonium chloride from ammonia and HCl, what is transferred to the nitrogen?
3. Give another example of the formation of a coordinate covalent bond?
4. In the reaction between ammonia and BF_3, which molecule provides the electrons for the bond?

Review

1. Where does the third covalent bond in the CO molecule come from?
2. Why is the incorrect structure for CO above wrong?
3. Are coordinate covalent bonds stronger or weaker than regular covalent bonds?

- **coordinate covalent bond:** A covalent bond in which one of the atoms contributes both of the electrons in the shared pair.

9.6 Covalent Bonding in Polyatomic Ions

- Draw the Lewis structure of a polyatomic ion when given appropriate information.

How do we extend basic principles?

The United States Supreme Court has the unenviable task of deciding what the law is. This responsibility can be a major challenge when there is no clear principle involved or where there is a new situation not encountered before. Chemistry faces the same challenge in extending basic concept to fit a new situation. Drawing of Lewis structures for polyatomic ions uses the same approach, but tweaks the process a little to fit a somewhat different set of circumstances.

Polyatomic Ions

Recall that a **polyatomic ion** is a group of atoms that are covalently bonded together and which carry an overall electrical charge. The ammonium ion, $NH_4{}^+$, is formed when a hydrogen ion (H^+) attaches to the lone pair of an ammonia (NH_3) molecule in a coordinate covalent bond.

When drawing the Lewis structure of a polyatomic ion, the charge of the ion is reflected in the number of total valence electrons in the structure. In the case of the ammonium ion:

$$\begin{aligned}&1 \text{ N atom} = 5 \text{ valence electrons}\\&4 \text{ H atoms} = 4 \times 1 = 4 \text{ valence electrons}\\&\text{subtract 1 electron for the } 1+ \text{charge of the ion}\\&\text{total of 8 valence electrons in the ion}\end{aligned}$$

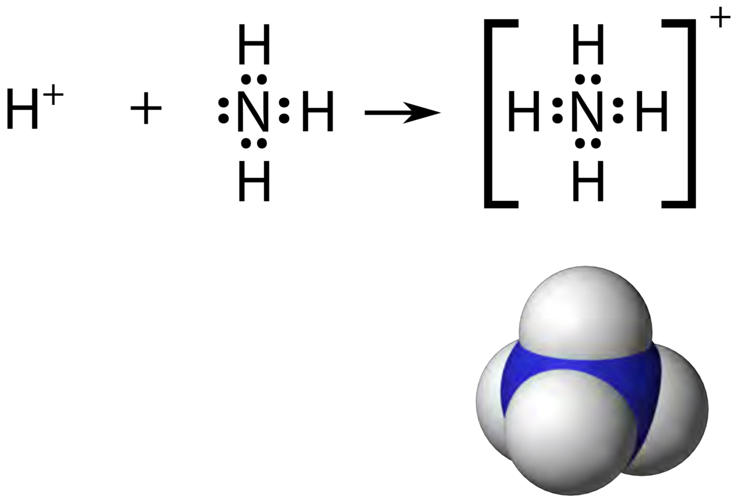


FIGURE 9.10

The ammonium ion.

It is customary to put the Lewis structure of a polyatomic ion into a large set of brackets, with the charge of the ion as a superscript outside the brackets.

Sample Problem: Lewis Electron Dot Structure of a Polyatomic Ion

Draw the Lewis electron dot structure for the sulfate ion.

Step 1: List the known quantities and plan the problem.

Known

molecular formula of sulfate ion = $SO_4{}^{2-}$
1 S atom = 6 valence electrons
4 O atoms = $4 \times 6 = 24$ valence electrons
add 2 electrons for the $2-$ charge of the ion
total of 32 valence electrons

The less electronegative sulfur atom is the central atom in the structure. Place the oxygen atoms around the sulfur atom, each with a single covalent bond. Distribute lone pairs to each oxygen atom in order to satisfy the octet rule. Count the total number of atoms. If there are too many electrons in the structure, make multiple bonds between the S and O.

Step 2: Solve.

Step 3: Think about your result.

The Lewis structure for the sulfate ion consists of a central sulfur atom with four single bonds to oxygen atoms. This yields the expected total of 32 electrons. Since the sulfur atom started with six valence electrons, two of the S-O bonds are coordinate covalent.

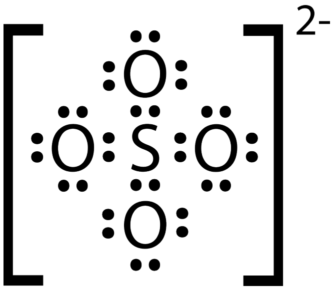


FIGURE 9.11

The sulfate ion.

Summary

- Lewis structures for polyatomic ions follow the same rules as those for other covalent compounds.

Practice

Do problem 2 on the web site below:

http://teachers.yourhomework.com/lipetz/bondingandlewisstructures.pdf

Review

1. What are two characteristics of polyatomic ions?
2. Which atom becomes the central atom in the structure?
3. Where is the charge on the ion placed?

- **polyatomic ion:** A group of atoms that are covalently bonded together and which carry an overall electrical charge.

9.7 Resonance

- Define resonance.
- Draw resonance structures of appropriate compounds.

Which image is real?

We look at the picture above and think we are looking at the image of a room as reflected in a mirror (and we probably are). But we can crop the picture in such a way as to give the impression we are looking at the real room through a door. We would see the same thing and receive the same information, but it would be from a different perspective. There are molecules that can be represented in different ways and reality becomes a matter of interpretation.

Resonance

There are some cases in which more than one viable Lewis structure can be drawn for a molecule. An example is the ozone (O_3) molecule. There are a total of 18 electrons in the structure and so the following two structures are possible.

The structure on the left can be converted to the structure on the right by a shifting of electrons without altering the positions of the atoms.

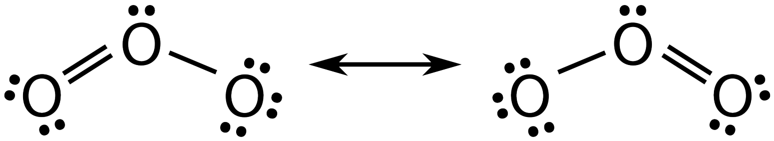


FIGURE 9.12

Resonance forms of ozone.

It was once thought that the structure of a molecule such as O_3 consisted of one single bond and one double bond which then shifted back and forth as shown above. However, further studies showed that the two bonds are identical. Any double covalent bond between two given atoms is typically shorter than a single covalent bond. Studies of the O_3 and other similar molecules showed that the bonds were identical in length. Interestingly, the length of the bond is in between the lengths expected for an O-O single bond and a double bond.

Resonance is the use of two or more Lewis structures to represent the covalent bonding in a molecule. One of the valid structures is referred to as a resonance structure. It is now understood that the true structure of a molecule which displays resonance is that of an average or a hybrid of all the resonance structures. In the case of the O_3 molecule, each of the covalent bonds between O atoms is best thought of as being "one and a half" bonds, as opposed to either a pure single bond or a pure double bond. This "half-bond" can be shown as a dotted line in both the Lewis structure and the molecular model.

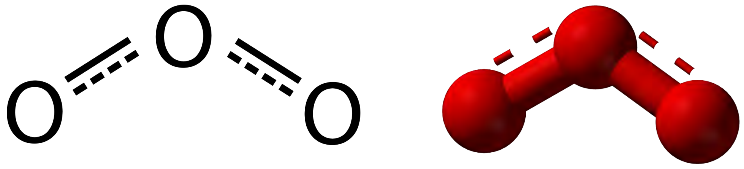


FIGURE 9.13

"Half-bond" model of ozone molecule.

Many polyatomic ions also display resonance. In some cases, the true structure may be an average of three valid resonance structures, as in the case of the nitrate ion, $NO_3{}^-$.

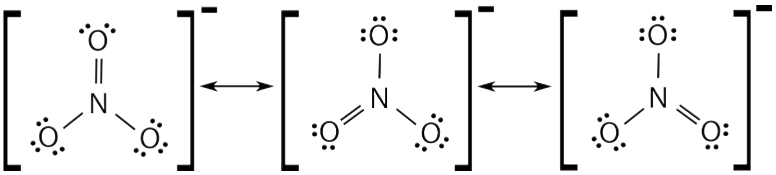


FIGURE 9.14

Resonance structure of nitrate anion.

The bond lengths between the central N atom and each O atom are identical and the bonds can be approximated as being equal to one and one-third bonds.

Summary

- Resonance structures are averages of different Lewis structure possibilities.
- Bond lengths are intermediate between covalent single bonds and covalent double bonds.

Practice

Do problem 3 on the web page below:

http://teachers.yourhomework.com/lipetz/bondingandlewisstructures.pdf

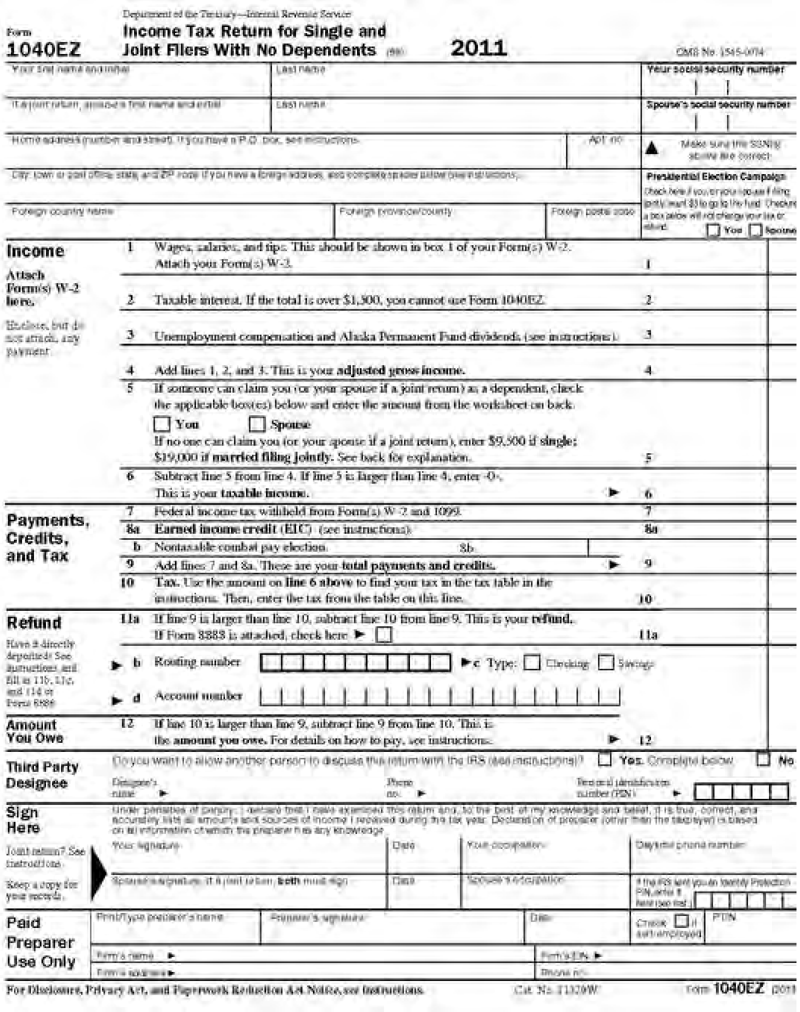
Review

1. How many electrons total are in the ozone structure?
2. What is changed in the two resonance structures of ozone?
3. How can we think of the covalent bonds in ozone?

- **resonance:** The use of two or more Lewis structures to represent the covalent bonding in a molecule.

9.8 Exceptions to the Octet Rule

- List the exceptions to the octet rule.



Department of the Treasury—Internal Revenue Service
Form **1040EZ** **Income Tax Return for Single and Joint Filers With No Dependents** **2011**

Presidential Election Campaign
☐ You ☐ Spouse

Income
Attach Form(s) W-2 here.

1 Wages, salaries, and tips. This should be shown in box 1 of your Form(s) W-2. Attach your Form(s) W-2. 1

2 Taxable interest. If the total is over $1,500, you cannot use Form 1040EZ. 2

3 Unemployment compensation and Alaska Permanent Fund dividends (see instructions). 3

4 Add lines 1, 2, and 3. This is your **adjusted gross income.** 4

5 If someone can claim you (or your spouse if a joint return) as a dependent, check the applicable box(es) below and enter the amount from the worksheet on back.
☐ You ☐ Spouse
If no one can claim you (or your spouse if a joint return), enter $9,500 if **single;** $19,000 if **married filing jointly.** See back for explanation. 5

6 Subtract line 5 from line 4. If line 5 is larger than line 4, enter -0-. This is your **taxable income.** ► 6

Payments, Credits, and Tax

7 Federal income tax withheld from Form(s) W-2 and 1099. 7

8a **Earned income credit (EIC)** (see instructions). 8a

b Nontaxable combat pay election. 8b

9 Add lines 7 and 8a. These are your **total payments and credits.** ► 9

10 **Tax.** Use the amount on **line 6 above** to find your tax in the tax table in the instructions. Then, enter the tax from the table on this line. 10

Refund

11a If line 9 is larger than line 10, subtract line 10 from line 9. This is your **refund.** If Form 8888 is attached, check here ► ☐ 11a

► b Routing number ☐☐☐☐☐☐☐☐☐ ► c Type: ☐ Checking ☐ Savings

► d Account number

Amount You Owe

12 If line 10 is larger than line 9, subtract line 9 from line 10. This is the **amount you owe.** For details on how to pay, see instructions. ► 12

Third Party Designee ☐ **Yes.** Complete below. ☐ **No**

Sign Here

Paid Preparer Use Only

For Disclosure, Privacy Act, and Paperwork Reduction Act Notice, see instructions. Form **1040EZ** (2011)

Are rules always followed?

Every spring, millions of Americans file their income tax forms. The different rules determine how much tax a person pays. There are also exceptions to the rules. You pay less tax if you are married and/or have children. There are certain limits on how much money you can make before paying taxes. The rule is that you pay taxes, but there are also exceptions based on your personal situation. The bonding rules for molecules are generally applicable, but there are some exceptions allowed.

Exceptions to the Octet Rule

As the saying goes, all rules are made to be broken. In the case of the octet rule, that is true. Exceptions to the octet rule fall into one of three categories: (1) an **incomplete octet**, (2) **odd-electron molecules**, and (3) an **expanded octet.**

Incomplete Octet

In some compounds, the number of electrons surrounding the central atom in a stable molecule is fewer than eight. Beryllium is an alkaline earth metal and so may be expected to form ionic bonds. However, its very small size and somewhat higher ionization energy compared to other metals actually lead to beryllium forming primarily molecular compounds. Since beryllium only has two valence electrons, it does not typically attain an octet through sharing of electrons. The Lewis structure of gaseous beryllium hydride (BeH_2) consists of two single covalent bonds between Be and H.

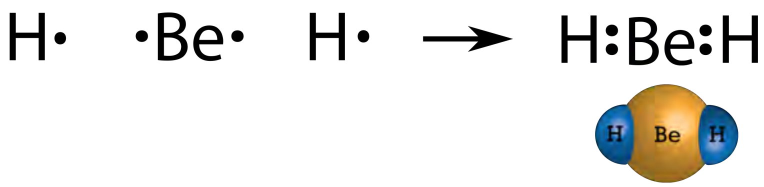


FIGURE 9.15
Beryllium hydride.

Boron and aluminum, with three valence electrons, also tend to form covalent compounds with an incomplete octet. The central boron atom in boron trichloride (BCl_3) has six valence electrons as shown below.

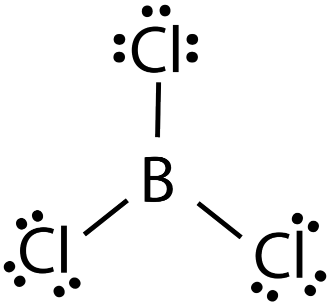


FIGURE 9.16
Boron trichloride.

Odd-Electron Molecules

There are a number of molecules whose total number of valence electrons is an odd number. It is not possible for all of the atoms in such a molecule to satisfy the octet rule. An example is nitrogen dioxide (NO_2). Each oxygen atom contributes six valence electrons and the nitrogen atom contributes five for a total of seventeen. Possible Lewis structures for NO_2 are:

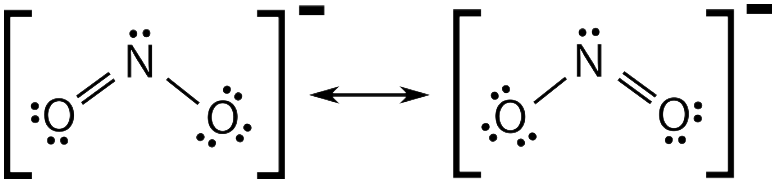


FIGURE 9.17
Lewis structures for NO_2.

Expanded Octets

Atoms of the second period cannot have more than eight valence electrons around the central atom. However, atoms of the third period and beyond are capable of exceeding the octet rule by having more than eight electrons around the central atom. Starting with the third period, the *d* sublevel becomes available, so it is possible to use these orbitals in bonding, resulting in an expanded octet.

Phosphorus and sulfur are two elements that react with halogen elements and make stable compounds with expanded octets. In phosphorus pentachloride, the central phosphorus atom makes five single bonds to chlorine atoms and as a result has ten electrons surrounding it. In sulfur hexafluoride, the central sulfur atom has twelve electrons from its six bonds to fluorine atoms.

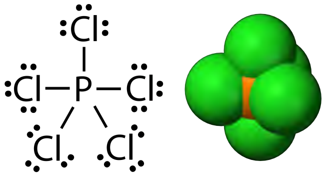


FIGURE 9.18

Phosphorus pentachloride. Left image: Lewis structure Right image: molecular model

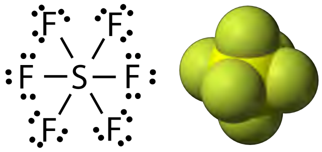


FIGURE 9.19

Sulfur hexafluoride. Left image: Lewis structure Right image: molecular model.

Summary

- Exceptions exist to the rules for covalent bonding.
- These exceptions apply to atoms whose electrons will not accommodate the normal octet rule.

Practice

Use the link below to answer the following questions:

http://chemistry.about.com/od/workedchemistryproblems/a/How-To-Draw-A-Lewis-Structure-Octet-Exception.htm

1. What is the first step in drawing the Lewis structure?
2. What is the next step?
3. Which atom will be the central atom?
4. Do you complete the octets for the non-central atoms?

Review

1. What is an incomplete octet?
2. What is an odd-electron molecule?
3. Why are there extra electrons in the expanded octet?

- **expanded octet:** Use of d sublevel in bonding as well as other sublevels.
- **incomplete octet:** The number of electrons surrounding the central atom in a stable molecule is fewer than eight.
- **odd-electron molecules:** Molecules whose total number of valence electrons is an odd number.

9.9 Bond Energy

- Define bond energy.
- Describe the relationship between reactivity and bond energy.

How does smog form?

We know that nitrogen makes up about 79% of the gases in the air and that this gas is chemically very inert. However, we also know that a major contributor to the production of smog is a mixture of nitrogen compounds collectively referred to as NO_x. Due to the high combustion temperatures in modern car engines (brought about by the need for better fuel efficiency), we make more NO_x that will react with other materials to create smog. So, our inert nitrogen gas can be converted to other compounds if enough energy is available to break the triple bonds in the N_2 molecule.

Bond Energy

The formation of a chemical bond results in a decrease in potential energy. Consequently, breaking a chemical bond requires an input of energy. **Bond energy** is the energy required to break a covalent bond between two atoms. A high bond energy means that a bond is strong and the molecule that contains that bond is likely to be stable and less reactive. More reactive compounds will contain bonds that have generally lower bond energies. Some bond energies are listed in the **Table** 9.1

TABLE 9.1: **Bond Energies**

Bond	**Bond Energy (kJ/mol)**
H–H	436
C–H	414

TABLE 9.1: (continued)

C–C	347
C=C	620
C≡C	812
F–F	157
Cl–Cl	243
Br–Br	193
I–I	151
N≡N	941

The halogen elements all exist naturally as diatomic molecules (F_2, Cl_2, Br_2, and I_2). They are generally very reactive and thus have relatively low bond energies.

As can be seen by a comparison of the bond energies for the various carbon-carbon bonds, double bonds are substantially stronger than single bonds. Likewise, triple bonds are even stronger. The triple bond that exists between the nitrogen atoms in nitrogen gas (N_2) makes it very unreactive. All plants and animals require the element nitrogen, but it cannot be obtained from the direct absorption of nitrogen gas from the atmosphere because of its strong, unreactive triple bond. Instead, bacteria convert the nitrogen to a more usable form such as ammonium and nitrate ions, which is then absorbed by plants from the soil. Animals only obtain nitrogen by eating those plants.

Summary

- Bond energy is an indication of the amount of energy needed for a chemical reaction.
- The higher the bond energy, the less reactive the bond is.

Practice

Use the link below to answer the following questions:

http://chemwiki.ucdavis.edu/Theoretical_Chemistry/Chemical_Bonding/General_Principles/Bond_Energies

1. What is needed for bonds to break or form?
2. The shorter the bond length, the ______ the bond energy.
3. A higher bond energy means what?
4. Why is the energy change positive when a bond is broken?

Review

1. What does a high bond energy mean?
2. What kind of bonds do more reactive compounds have?
3. Which will react more readily: a C-H bond or a Cl-Cl bond?

- **bond energy:** The energy required to break a covalent bond between two atoms.

9.10 VSEPR Theory

- Define the VSEPR theory.

What do I do now?

Into every scientist's life comes that moment when you realize that you were wrong. Sometimes you think about a problem and recognize where you went astray. Other times you find out when you go into the lab and the experiment doesn't work (or gets way too exciting). What has to happen then is a change in direction. The good scientist sees the problem and comes up with a new answer. Then that answer has to be tested to see how it works.

Putting atoms together to form compounds can be done on paper or in the lab. However, when the shape of the molecule made in the lab is different from the shape of the molecule drawn on paper, then we need to rethink our ideas and find better explanations.

VSEPR Theory

In 1956, British scientists R.J. Gillespie and R.S. Nyholm recognized that the current model for explaining bond angles did not work well. The theory at that time relied on hybrid orbitals to explain all aspects of bonding. The problem was that the theory gave incorrect prediction of bond angles for many compounds. They developed a new approach based on earlier work by other scientists that incorporated a consideration of electron pairs in predicting three-dimensional structure.

The **valence shell** is the outermost electron-occupied shell of an atom. The valence shell holds the electrons that are involved in bonding and are the electrons shown in a Lewis structure. The acronym VSEPR stands for the **valence-shell electron pair repulsion** model. The model states that electron pairs will repel each other such that the shape of the molecule will adjust so that the valence electron-pairs stay as far apart from each other as possible. Molecules can be systematically classified according to the number of bonding pairs of electrons as well as 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.

Summary

- VSEPR theory allows more accurate predictions of molecular shape.

Practice

Use the link below to answer the following questions:

http://www.ehow.com/about_4739704_what-vsepr-model.html

1. When was the VSEPR model first proposed?
2. What is the basic theory behind the model?
3. What is the significance of this theory?

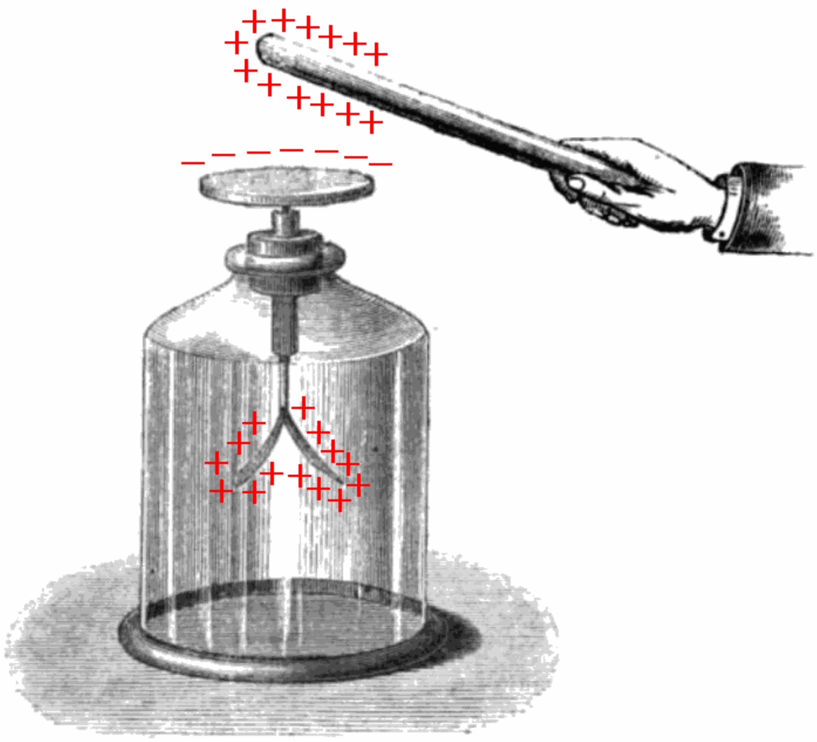
Review

1. Who did the major work in developing the VSEPR theory?
2. Where are the electrons that are involved in bonding?
3. What is the basic idea behind the VSEPR theory?

- **valence shell:** The outermost electron-occupied shell of an atom.
- **valence-shell electron pair repulsion (VSEPR):** Electron pairs will repel each other such that the shape of the molecule will adjust so that the valence electron-pairs stay as far apart from each other as possible.

9.11 Molecular Shapes: No Lone Pairs on Central Atom

- Describe molecules whose shapes are influenced by VSEPR theory.



How does an electroscope work?

An electroscope is a device used to study charge. When a charged object (the rod) touches the upper post, electrons flow into the jar and on to the two gold leaves. The leaves repel each other since both have negative charges on them. The VSEPR theory says that electron pairs will repel each other such that the shape of the molecule will adjust so that the valence electron-pairs stay as far apart from each other as possible.

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_2: Beryllium hydride (BeH_2)

Beryllium hydride consists of a central beryllium atom with two single bonds to hydrogen atoms. Recall that it violates the octet rule.

H-B-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 below in a "ball and stick" model.

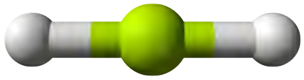


FIGURE 9.20

Beryllium hydride model.

The bond angle from H-Be-H 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 and the oxygen atoms.

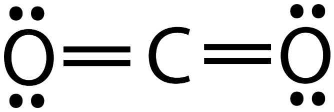


FIGURE 9.21

Carbon dioxide bonding.

The repulsion between the two groups of four electrons (two pairs) is no different than the repulsion of the two groups of two electrons (one pair) in the BeH_2 molecule. Carbon dioxide is also linear.

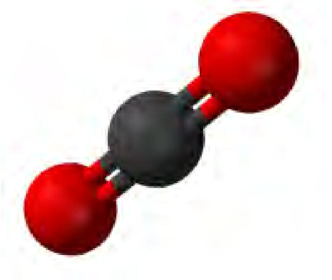


FIGURE 9.22

Carbon dioxide.

AB_3: Boron Trifluoride (BF_3)

Boron trifluoride consists of a central boron atom with three single bonds to fluorine atoms. The boron atom also has an incomplete octet.

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.

AB_4: Methane (CH_4)

Methane 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. 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

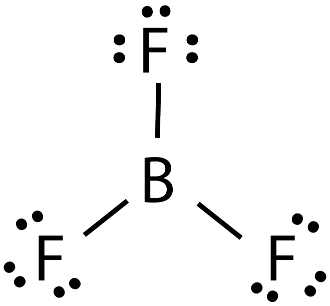


FIGURE 9.23

Boron trifluoride bonding.

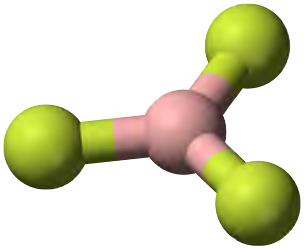


FIGURE 9.24

Boron trifluoride model.

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.

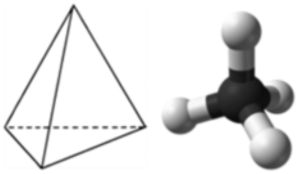


FIGURE 9.25

Tetrahedral structure of methane.

The molecular geometry of the methane molecule is 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. 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 is to be visualized as receding into the page, while the solid triangle bond is to be visualized as coming out of the page.

Summary

- Electron pairs repel each other and influence bond angles and molecular shape.

Practice

Use the link below to answer the following questions:

http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch8/vsepr.html

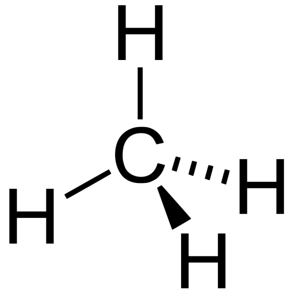


FIGURE 9.26

Methane perspective model.

1. What is the shape of PF_5?
2. What C-H bod angles would we predict for methane if the molecule were planar?
3. What molecule has the configuration of an octahedron?

Review

1. What are the bond angles in carbon dioxide?
2. What molecule has bond angles of 109.5°?
3. What is the geometry of the BF_3 molecule?

- **central atom:** The atom around which other atoms are arranged.

9.12 Molecular Shapes: Lone Pair(s) on Central Atom

- Define lone pair.
- Describe how lone pair electrons influence molecular geometry.

How does it all fit?

When we travel, we often take a lot more stuff than we need. Trying to fit it all in a suitcase can be a real challenge. We may have to repack or just squeeze it all in. Atoms often have to rearrange where the electrons are in order to create a more stable structure.

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 total number of electron pairs, both bonding pairs and lone pairs, leads to what is called the **electron domain geometry.** When one or more of the bonding pairs of electrons is replaced with a lone pair, the molecular geometry (actual shape) of the molecule is altered. In keeping with the A and B symbols established in the previous section, we will use E to represent a lone pair on the central atom (A). A subscript will be used when there is more than one lone pair. Lone pairs on the surrounding atoms (B) do not affect the geometry.

AB_3E: Ammonia, NH_3

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.

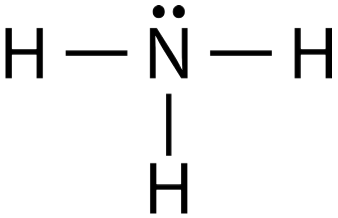


FIGURE 9.27
Lone pair electrons in ammonia.

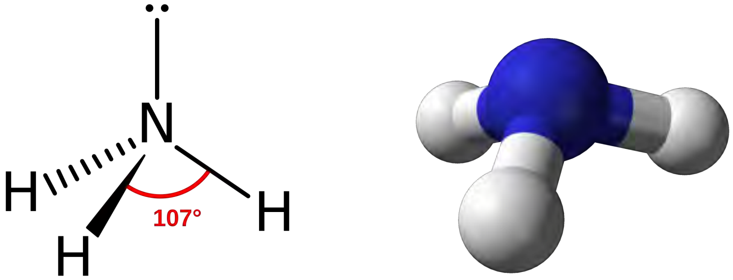


FIGURE 9.28
Ammonia molecule.

Recall that the bond angle in the tetrahedral CH_4 molecule is 109.5°. Again, the replacement of one of the bonded electron pairs with a lone pair compresses the angle slightly. The H-N-H angle is approximately 107°.

AB_2E_2: Water, H_2O

A water molecule consists of two bonding pairs and two lone pairs.

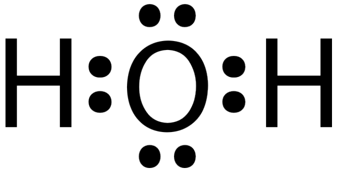


FIGURE 9.29
Lone pair electrons on water.

As for methane and ammonia, the domain geometry for a molecule with four electron pairs is tetrahedral. In the water molecule, two of the electron pairs are lone pairs rather than bonding pairs. The molecular geometry of the water molecule is bent. The H-O-H bond angle is 104.5°, which is smaller than the bond angle in NH_3.

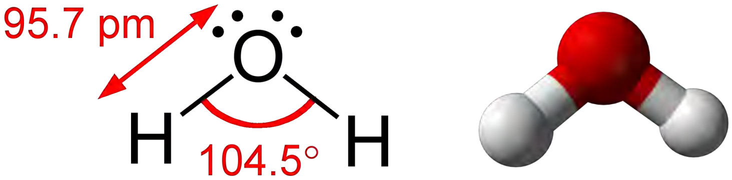


FIGURE 9.30
Water molecule.

AB_4E: Sulfur Tetrafluoride, SF_4

The Lewis structure for SF_4 contains four single bonds and a lone pair on the sulfur atom.

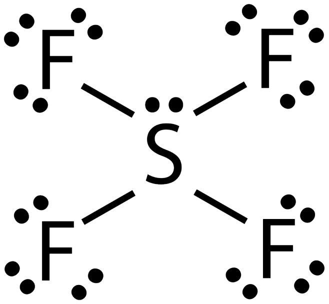


FIGURE 9.31
Lone pair electrons in SF_4.

The sulfur atom has five electron groups around it, which corresponds to the trigonal bipyramidal domain geometry, as in PCl_5. Recall that the trigonal bipyramidal geometry has three equatorial atoms and two axial atoms attached to the central atom. Because of the greater repulsion of a lone pair, it is one of the equatorial atoms that are replaced by a lone pair. The geometry of the molecule is called a distorted tetrahedron or seesaw.

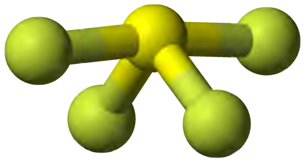


FIGURE 9.32
Ball and stick model for SF_4.

TABLE 9.2: **Geometries in Which the Central Atom Has One or More Lone Pairs**

Total Number of Electron Pairs	Number of Bonding Pairs	Number of Lone Pairs	Electron Domain Geometry	Molecular Geometry	Examples
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	distorted tetrahedron (seesaw)	SF_4
5	3	2	trigonal bipyramidal	T-shaped	CIF_3
5	2	3	trigonal bipyramidal	linear	$I_3{}^-$
6	5	1	octahedral	square pyramidal	BrF_5
6	4	2	octahedral	square planar	XeF_4

Summary

- The presence of lone pair electrons influences the three-dimensional shape of the molecule.

Practice

Use the link below to answer the following questions:

http://www.mpilkington.com/23.pdf

1. What is the general principle in dealing with molecules containing more than four electron pairs?
2. In the picture with five electron pairs around the central atom, why is the arrangement on the right preferred?
3. In the picture with six electron pairs, why is the configuration with the lone pairs at 180^o to each other more stable?

Review

1. Why does water have a bent geometry?
2. Why is ammonia not a planar molecule?
3. How would we write the configuration for xenon tetrafluoride using the ABE system?

- **electron domain geometry:** Geometry based only on the number of electron pairs around the central atom, both bonding pairs and lone pairs.

9.13 Bond Polarity

- Define electronegativity.
- Use electronegativity values to determine bond type.

What makes people share?

Have you ever spent time with someone you really didn't like? You had nothing in common with them and did not want to have anything to do with them. On the other hand, there are people you enjoy being with. You have a lot in common and like to share with them. Atoms work the same way. If there are strong differences in their attraction of electrons, one atoms gets the electrons and the other atom loses them. If they are similar, they share the electrons to form a covalent bond.

Bond Polarity

Electronegativity is defined as the ability of an atom to attract electrons when the atoms are in a compound. Electronegativities of elements are shown in the periodic table below.

The degree to which a given bond is ionic or covalent is determined by calculating the difference in electronegativity between the two atoms involved in the bond.

As an example, consider the bond that occurs between an atom of potassium and an atom of fluorine. Using the table, the difference in electronegativity is equal to 4.0 - 0.8 = 3.2. Since the difference in electronegativity is relatively large, the bond between the two atoms is ionic. Since the fluorine atom has a much larger attraction for electrons than the potassium atom does, the valence electron from the potassium atom is completely transferred to the fluorine atom. The **Figure** 9.34 shows how difference in electronegativity relates to the ionic or covalent character of a chemical bond.

Nonpolar Covalent Bonds

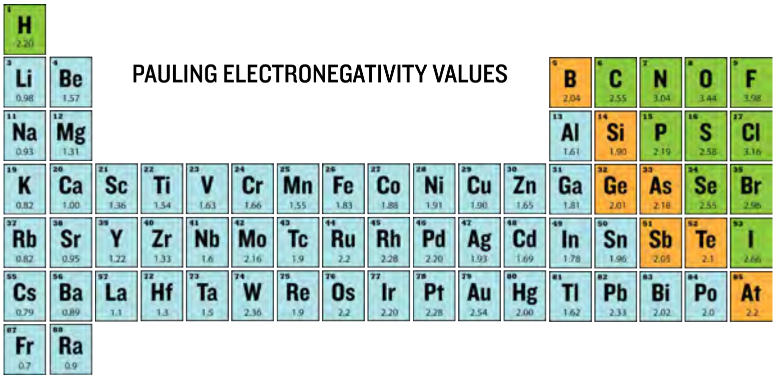


FIGURE 9.33

Electronegativities of elements.

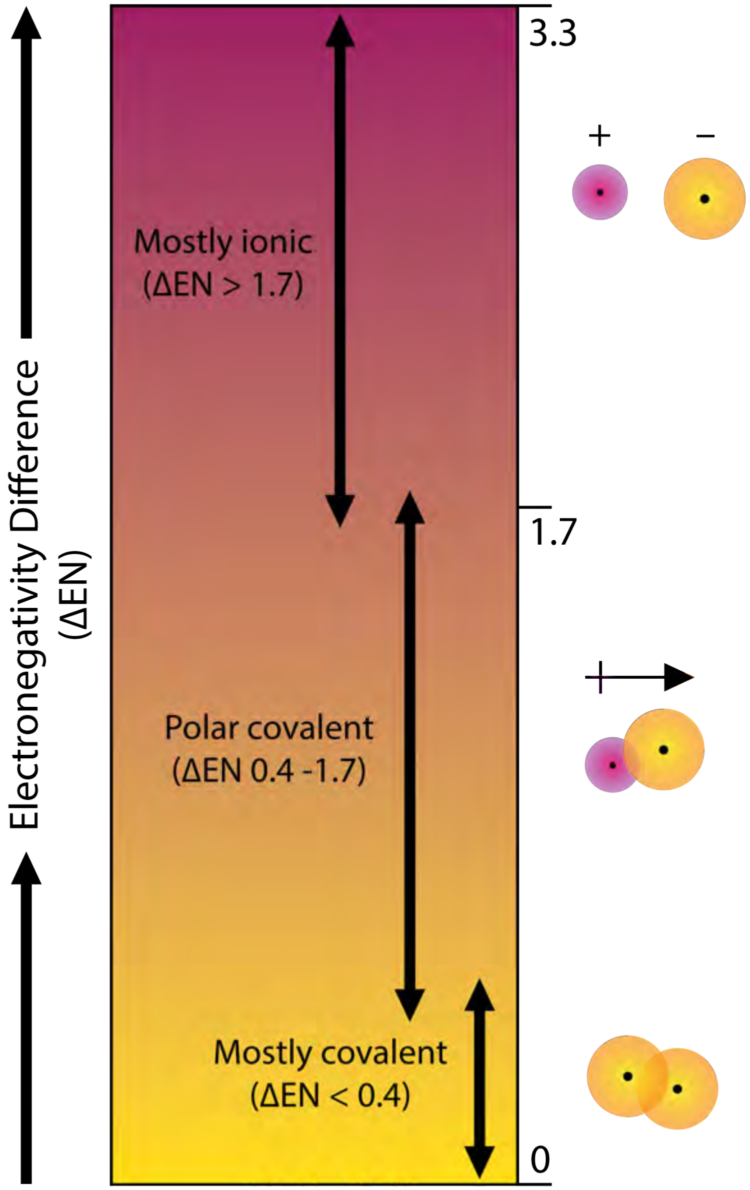


FIGURE 9.34

Bond type is predicated on the difference in electronegativity of the two elements involved in the bond.

A bond in which the electronegativity difference is less than 1.7 is considered to be mostly covalent in character. However, at this point we need to distinguish between two general types of covalent bonds. A **nonpolar covalent bond** is a covalent bond in which the bonding electrons are shared equally between the two atoms. In a nonpolar covalent bond, the distribution of electrical charge is balanced between the two atoms (see **Figure** 9.35).

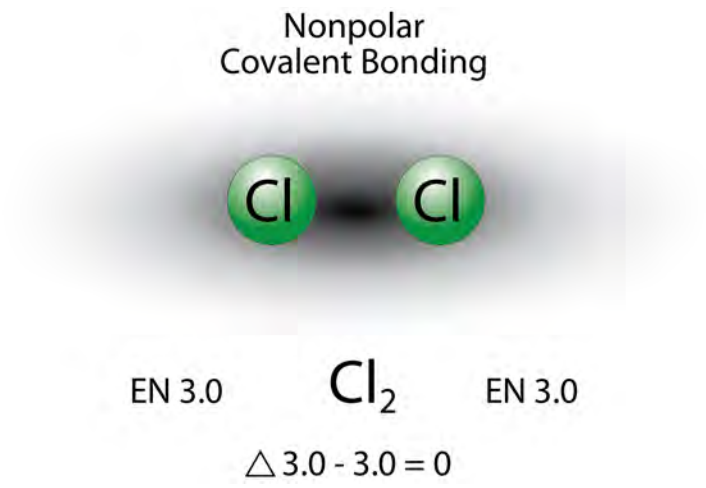


FIGURE 9.35

A nonpolar covalent bond is one in which the distribution of electron density between the two atoms is equal.

The two chlorine atoms share the pair of electrons in the single covalent bond equally, and the electron density surrounding the Cl_2 molecule is symmetrical. Also note that molecules in which the electronegativity difference is very small (<0.4) are also considered nonpolar covalent. An example would be a bond between chlorine and bromine ($\Delta EN = 3.0 - 2.8 = 0.2$).

Polar Covalent Bonds

A bond in which the electronegativity difference between the atoms is between 0.4 and 1.7 is called a polar covalent bond. A **polar covalent bond** is a covalent bond in which the atoms have an unequal attraction for electrons and so the sharing is unequal. In a polar covalent bond, sometimes simply called a polar bond, the distribution of electrons around the molecule is no longer symmetrical.

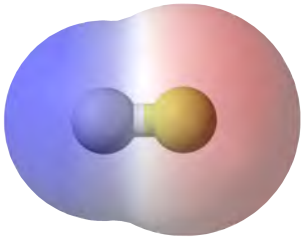


FIGURE 9.36

In the polar covalent bond of HF, the electron density is unevenly distributed. There is a higher density (red) near the fluorine atom, and a lower density (blue) near the hydrogen atom.

An easy way to illustrate the uneven electron distribution in a polar covalent bond is to use the Greek letter delta (δ).

The atom with the greater electronegativity acquires a partial negative charge, while the atom with the lesser electronegativity acquires a partial positive charge. The delta symbol is used to indicate that the quantity of charge is less than one. A crossed arrow can also be used to indicate the direction of greater electron density.

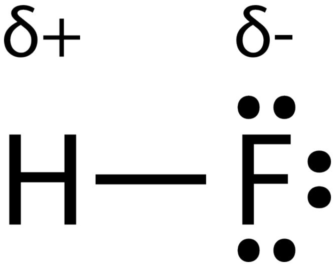


FIGURE 9.37

Use of δ to indicate partial charge.

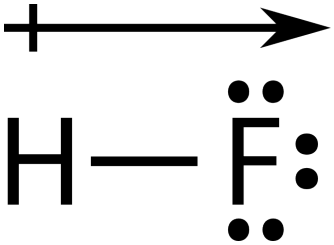


FIGURE 9.38

Use of crossed arrow to indicate polarity.

Summary

- The electronegativity of an atom determines how strongly it attracts electrons to itself.
- The polarity of a bond is affected by the electronegativity values of the two atoms involved in that bond.

Practice

Take the quiz on the right-hand side of this page:

http://www.sophia.org/determining-bond-polarity/determining-bond-polarity-tutorial

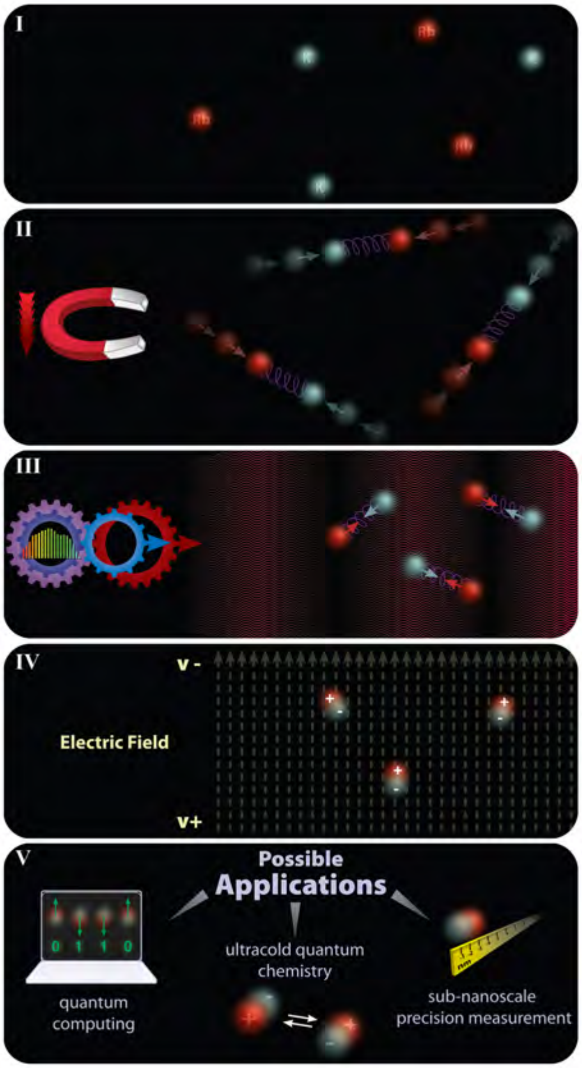
Review

1. What is the bond type of a bond with a difference of 1.9?
2. What would be he bond type for BH_2?
3. Your friend tells you that the LiF bond is covalent. What do you say?

- **electronegativity:** The ability of an atom to attract electrons when the atoms are in a compound.
- **nonpolar covalent bond:** A covalent bond in which the bonding electrons are shared equally between the two atoms.
- **polar covalent bond:** A covalent bond in which the atoms have an unequal attraction for electrons and so the sharing is unequal.

9.14 Polar Molecules

- Define polar molecule.
- Describe how to determine polarity of a molecule.



How cold are ultracold polar molecules?

Ultracold polar molecules have been created by research scientists. These "molecules" consists of Rb and K atoms excited by lasers to form a type of Rb-K compound where the Rb has a positive charge and the K has a negative charge. The material is formed at temperatures extremely close to absolute zero. The researchers believe these techniques will help them make new reactions and new materials.

Polar Molecules

A **polar molecule** is a molecule in which one end of the molecule is slightly positive, while the other end is slightly negative. A diatomic molecule that consists of a polar covalent bond, such as HF, is a polar molecule. The two electrically charged regions on either end of the molecule are called poles, similar to a magnet having a north and a south pole. A molecule with two poles is called a **dipole**. Hydrogen fluoride is a dipole.

FIGURE 9.39

A dipole is any molecule with a positive end and a negative end, resulting from unequal distribution of electron density throughout the molecule.

Polar molecules orient themselves in the presence of an electric field with the positive ends of the molecules being attracted to the negative plate while the negative ends of the molecules are attracted to the positive plate.

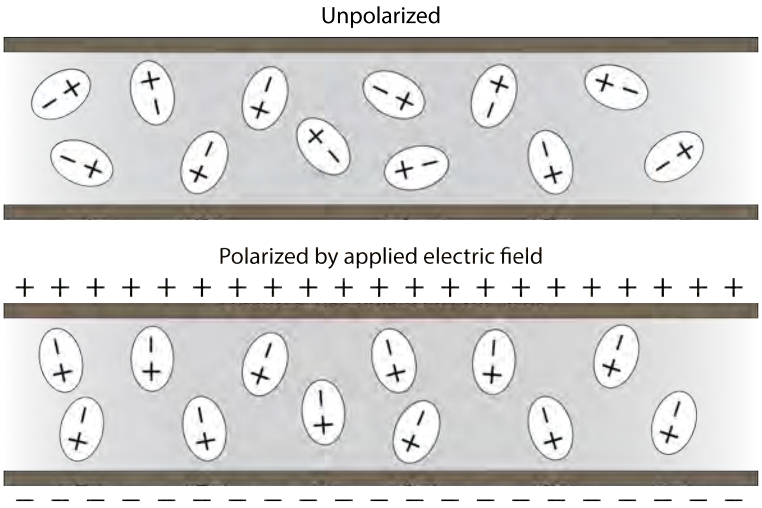


FIGURE 9.40

Polar molecules are randomly oriented in the absence of an applied electric field (top). In an electric field, the molecules orient themselves because of the attraction of opposite charges (bottom).

For molecules with more than two atoms, the molecular geometry must also be taken into account when determining if the molecule is polar or nonpolar. The **Figure** 9.41 shows a comparison between carbon dioxide and water. Carbon dioxide (CO_2) is a linear molecule. The oxygen atoms are more electronegative than the carbon atom, so there are two individual dipoles pointing outward from the C atom to each O atom. However, since the dipoles are of equal strength and are oriented in this way, they cancel each other out and the overall molecular polarity of CO_2 is zero.

Water is a bent molecule because of the two lone pairs on the central oxygen atom. The individual dipoles point from the H atoms toward the O atom. Because of the shape, the dipoles do not cancel each other out and the water molecule is polar. In the **Figure** 9.41, the net dipole is shown in blue and points upward.

Some other molecules are shown in the figure below. Notice that a tetrahedral molecule such as CH_4 is nonpolar. However, if one of the peripheral H atoms is replaced with another atom that has a different electronegativity, the molecule becomes polar. A trigonal planar molecule (BF_3) may be nonpolar if all three peripheral atoms are the same, but a trigonal pyramidal molecule (NH_3) is polar.

Summary

- Polar molecules result from differences in electronegativity of the atoms in the molecule.
- Dipoles that are directly opposite one another cancel each other out.

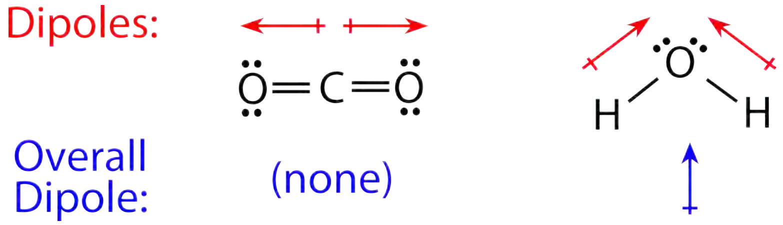


FIGURE 9.41

The molecular geometry of a molecule affects its polarity.

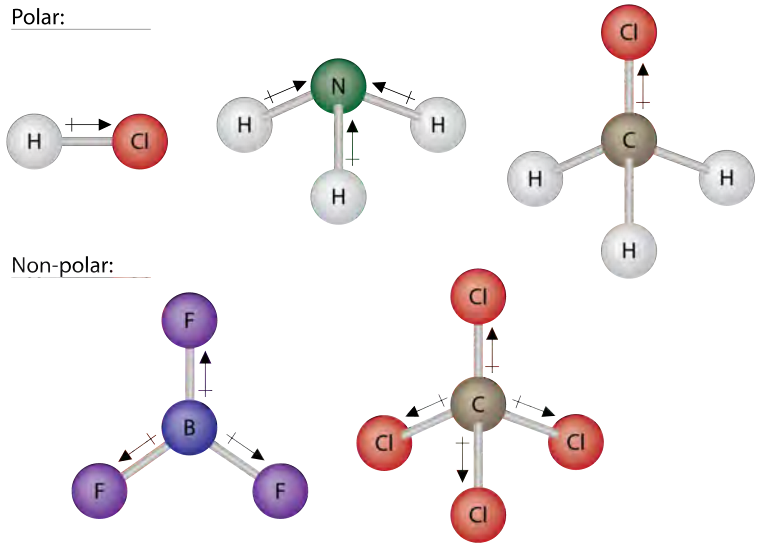


FIGURE 9.42

Some examples of polar and nonpolar molecules based on molecular geometry.

Practice

Use the link below to answer the following questions:

http://preparatorychemistry.com/bishop_molecular_polarity.htm

1. How do you identify polar bonds in a molecule?
2. What electronegativity difference would indicate a polar bond?
3. Is a molecule with symmetric polar bonds a polar molecule?

Review

1. What is a dipole?
2. How does shape affect the polarity of a molecule?
3. What is the difference between a polar bond and a polar molecule?

- **dipole:** A molecule with two poles.
- **polar molecule:** A molecule in which one end of the molecule is slightly positive, while the other end is slightly negative.

9.15 Van der Waals Forces

- Define Van der Waals forces.
- Describe dipole-dipole interactions.
- Describe London dispersion forces.

How to Keep it Cool?

Magnetic resonance imaging (NMR) devices use liquid nitrogen to cool the superconducting magnets. Nitrogen is a gas at room temperature and liquefies at -195.8°C. Its neighbor on the periodic table (oxygen) boils at -182.95°C. The interactions between nitrogen molecules (N_2) are weaker, so the boiling point is lower. Interactions between non-polar molecules depend on the degree of electron fluctuation within the molecule.

Van der Waals Forces

The first type of intermolecular force we will consider are called van der Waals forces, after Dutch chemist Johannes van der Waals (1837-1923). **Van der Waals forces** are the weakest intermolecular force and consist of dipole-dipole forces and dispersion forces.

Dipole-Dipole Forces

Dipole-dipole forces are the attractive forces that occur between polar molecules. A molecule of hydrogen chloride has a partially positive hydrogen atom and a partially negative chlorine atom. In a collection of many hydrogen chloride molecules, they will align themselves so that the oppositely charged regions of neighboring molecules are near each other.

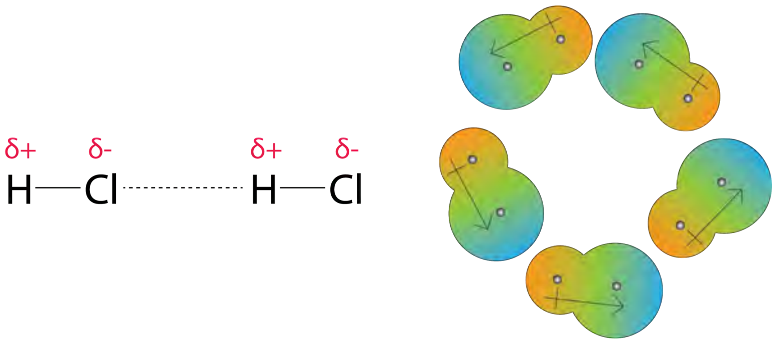


FIGURE 9.43

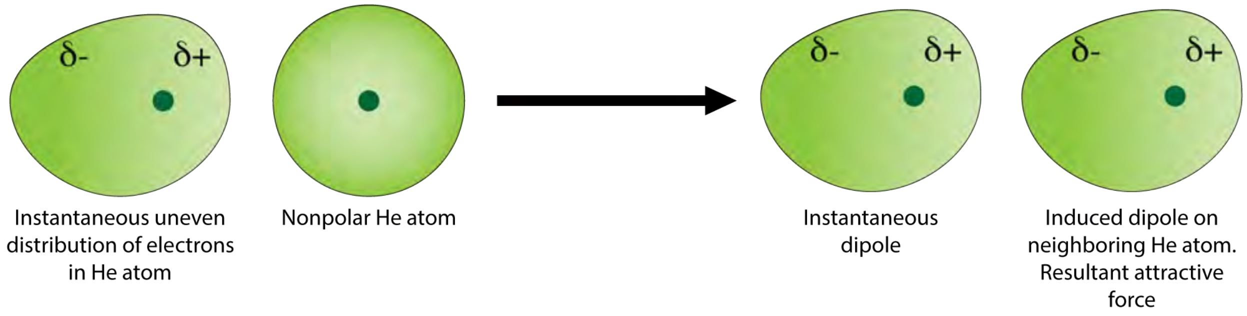
Dipole-dipole forces are a result of the attraction of the positive end of one dipole to the negative end of a neighboring dipole.

Dipole-dipole forces are similar in nature, but much weaker than ionic bonds.

London Dispersion Forces

Dispersion forces are also considered a type of van der Waals force and are the weakest of all intermolecular forces. They are often called London forces after Fritz London (1900-1954), who first proposed their existence in 1930. **London dispersion forces** are the intermolecular forces that occur between atoms and between nonpolar molecules as a result of the motion of electrons.

The electron cloud of a helium atom contains two electrons, which can normally be expected to be equally distributed spatially around the nucleus. However, at any given moment the electron distribution may be uneven, resulting in an instantaneous dipole. This weak and temporary dipole subsequently influences neighboring helium atoms through electrostatic attraction and repulsion. It induces a dipole on nearby helium atoms (see **Figure** 9.44).



Instantaneous uneven distribution of electrons in He atom

Nonpolar He atom

Instantaneous dipole

Induced dipole on neighboring He atom. Resultant attractive force

FIGURE 9.44

A short-lived or instantaneous dipole in a helium atom.

The instantaneous and induced dipoles are weakly attracted to one another. The strength of dispersion forces increases as the number of electrons in the atoms or nonpolar molecules increases.

The halogen group consists of four elements that all take the form of nonpolar diatomic molecules. The **Table** 9.3 shows a comparison of the melting and boiling points for each.

TABLE 9.3: **Melting and Boiling Points of Halogens**

Molecule	**Total Number of Electrons**	**Melting Point (°C)**	**Boiling Point (°C)**	**Physical State at Room Temperature**
F_2	18	-220	-188	gas
Cl_2	34	-102	-34	gas
Br_2	70	-7	59	liquid
I_2	106	114	184	solid

The dispersion forces are strongest for iodine molecules because they have the greatest number of electrons. The relatively stronger forces result in melting and boiling points which are the highest of the halogen group. These forces are strong enough to hold iodine molecules close together in the solid state at room temperature. The dispersion forces are progressively weaker for bromine, chlorine, and fluorine and this is illustrated in their steadily lower melting and boiling points. Bromine is a liquid at room temperature, while chlorine and fluorine are gases, whose molecules are much further apart from one another. Intermolecular forces are nearly nonexistent in the gas state, and so the dispersion forces in chlorine and fluorine only become measurable as the temperature decreases and they condense into the liquid state.

Summary

- Van der Waals forces are weak interactions between molecules that involve dipoles.
- Polar molecules have permanent dipole-dipole interactions.
- Non-polar molecules can interact by way of London dispersion forces.

Practice

Use the link below to answer the following questions:

http://www.chemguide.co.uk/atoms/bonding/vdw.html

1. What are intermolecular attractions?
2. How cold must helium get before it forms a liquid?
3. Can large numbers of molecules be held together by dispersion forces?
4. Do long thin molecules develop stronger or weaker dipoles than short fat molecules?

Review

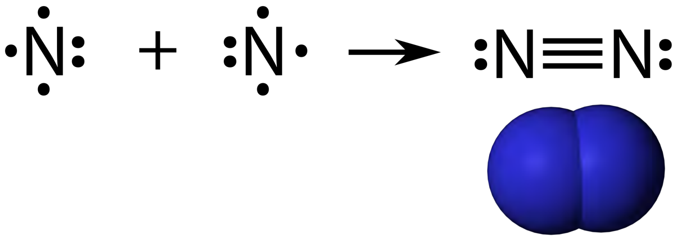
1. What attractive forces develop between polar molecules?
2. What creates London dispersion forces?
3. Are London dispersion forces permanent or temporary?
4. Are the dispersion forces for Cl_2 stronger or weaker than the ones for Br_2?

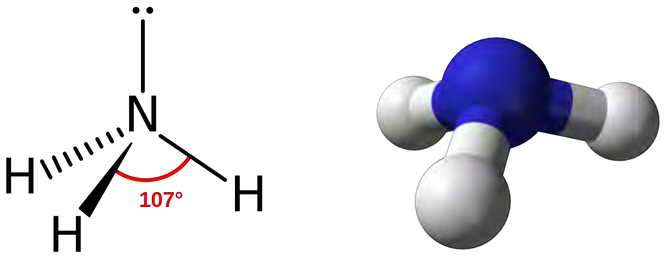
- **dipole-dipole forces:** The attractive forces that occur between polar molecule*s*

- **London dispersion forces:** The intermolecular forces that occur between atoms and between nonpolar molecules as a result of the motion of electrons.
- **Van der Waals forces:** The weakest intermolecular force and consist of dipole-dipole forces and dispersion forces.

9.16 Hydrogen Bonding

- Define hydrogen bond.
- Describe molecular structures that will participate in hydrogen bond formation.





What's the difference between these two molecules?

A rough rule of thumb is that higher molecular-weight materials have higher boiling points than their lower molecular weight counterparts. More energy is needed to move the larger molecule from the liquid state to the vapor state. However, ammonia has a boiling point of -33.34°C and a molecular weight of 17 while nitrogen (molecular weight 28) has a boiling point of -195.8°C. The lighter ammonia molecule must have other factors that influence its physical properties.

Hydrogen Bonding

The attractive force between water molecules is a dipole interaction. The hydrogen atoms are bound to the highly electronegative oxygen atom (which also possesses two lone pair sets of electrons, making for a very polar bond. The partially positive hydrogen atom of one molecule is then attracted to the oxygen atom of a nearby water molecule (see **Figure** 9.45).

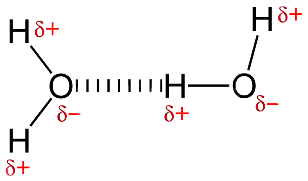


FIGURE 9.45

A hydrogen bond in water occurs between the hydrogen atom of one water molecule and the lone pair of electrons on an oxygen atom of a neighboring water molecule.

A **hydrogen bond** is an intermolecular attractive force in which a hydrogen atom that is covalently bonded to a small, highly electronegative atom is attracted to a lone pair of electrons on an atom in a neighboring molecule. Hydrogen bonds are very strong compared to other dipole interactions. The strength of a typical hydrogen bond is about 5% of that of a covalent 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 in the covalent bond with hydrogen, leaving the H atom very electron-deficient. The H atom nearly acts as a bare proton, leaving it very attracted to lone pair electrons on a nearby atom.

The hydrogen bonding that occurs in water leads to some unusual, but very important properties. Most molecular compounds that have a mass similar to water are gases at room temperature. Because of the strong hydrogen bonds, water molecules are able to stay condensed in the liquid state. The **Figure** 9.46 shows how the bent shape and two hydrogen atoms per molecule allows each water molecule to be able to hydrogen bond to two other molecules.

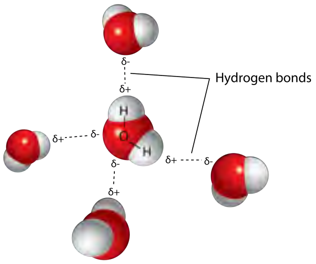


FIGURE 9.46

Multiple hydrogen bonds occur simultaneously in water because of its bent shape and the presence of two hydrogen atoms per molecule.

In the liquid state, the hydrogen bonds of water can break and reform as the molecules flow from one place to another. When water is cooled, the molecules begin to slow down. Eventually, when water is frozen to ice, the hydrogen bonds become permanent and form a very specific network (see **Figure** 9.47).

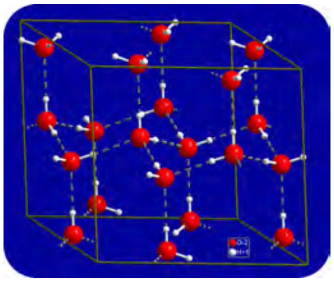


FIGURE 9.47

When water freezes to ice, the hydrogen bonding network becomes permanent. Each oxygen atom has an approximately tetrahedral geometry – two covalent bonds and two hydrogen bonds.

The bent shape of the molecules leads to gaps in the hydrogen bonding network of ice. Ice has the very unusual property that its solid state is less dense than its liquid state. Ice floats in liquid water. Virtually all other substances are denser in the solid state than in the liquid state. Hydrogen bonds play a very important biological role in the physical structures of proteins and nucleic acids.

Summary

- Hydrogen bonds form when a H attached to a N, O, or F atom interacts with another N, O, or F atom.

Practice

Use the link below to answer the following questions:

http://www.elmhurst.edu/ chm/vchembook/161Ahydrogenbond.html

1. What are the features of N and O that cause then to form H bonds with H?
2. Will all H atoms form H-bonds?
3. What is the length of an H-bond compared to the length of a covalent bond?

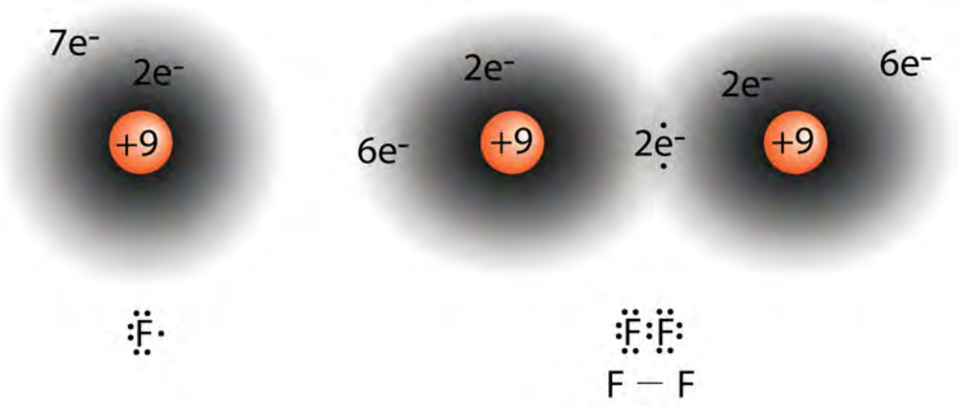
Review

1. How strong is a hydrogen bond?
2. What happens when H is covalently bonded to N, O, or F?
3. How does the shape of the water molecule affect its properties?

- **hydrogen bond:** An intermolecular attractive force in which a hydrogen atom that is covalently bonded to a small, highly electronegative atom is attracted to a lone pair of electrons on an atom in a neighboring molecule.

9.17 Valence Bond Theory

- Define valence bond theory.
- Describe how to use valence bond theory to explain aspects of covalent bonds.



What happens next?

We have seen that the old fish-hook idea of atoms connecting that Democritus liked so much just doesn't work. Electrons don't have little hooks on them, but they are the basis for connecting atoms to form molecules. You have learned how to write Lewis electron-dot structures for molecules and predict their shape using VSEPR theory. Now it is time to apply these abilities to understand how the electrons behave in their atomic orbitals when a covalent bond forms.

Valence Bond Theory

You have learned that a covalent bond forms 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. An optimum distance, equal to the bond length, is eventually attained, and the potential energy reaches a minimum. A stable, single covalent bond has formed between the two hydrogen atoms. 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. In a molecule of HF, the *1s* orbital of the hydrogen atom overlaps with the *2p* orbital of the fluorine atom (see **Figure** 9.48).

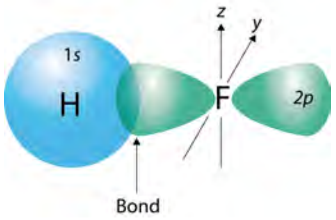


FIGURE 9.48
A molecule of hydrogen fluoride (HF).

In essence, any covalent bond results from the overlap of atomic orbitals. This idea forms the basis for a quantum mechanical theory called valence bond (VB) theory. In **valence bond theory**, the electrons in a molecule are assumed to occupy atomic orbitals of the individual atoms and a bond results from overlap of those orbitals.

Summary

- Electrons occupy atomic orbitals.
- Covalent bonds result from the overlap of atomic orbitals.

Practice

View the presentation at the link below and take the quizzes.

http://www.kentchemistry.com/links/bonding/bondingflash.htm

Review

1. Where are electrons according to valence bond theory?
2. How do covalent bonds form?
3. Do the orbitals of the two electrons involved in the bond need to be the same?

- **valence bond theory:** The electrons in a molecule are assumed to occupy atomic orbitals of the individual atoms and a bond results from overlap of those orbitals.

9.18 Hybrid Orbitals - sp3

- Define hybridization.
- Describe sp^3 hybridization and covalent bond formation.

Do you recognize this plant?

If we were walking on the beach, the plants shown above would look very different. They would be short and sticking out of the sand. When we see them this way, we do not immediately recognize them as beach plants. Often we need to look at the world around us in different ways to understand things better.

Hybrid Orbitals – sp^3

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^3 Hybridization

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 element carbon and the methane (CH_4) molecule. A carbon atom has the electron configuration of $1s^2$ $2s^2$ $2p^2$, 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, with four equivalent C$-$H bonds. To account for this, one of the $2s$ electrons is promoted 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

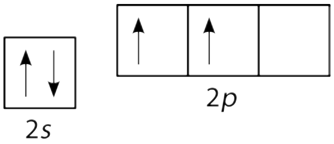


FIGURE 9.49

Orbital configuration for carbon atom.

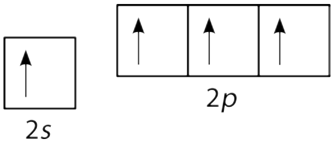


FIGURE 9.50

Promotion of carbon s electron to empty p orbital.

results in a lower overall energy and thus greater stability to 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^o relative to one another. However, as was seen from VSEPR theory, the observed H−C−H bond angle in the tetrahedral CH_4 molecule is actually 109.5^o. 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. In other words, *s* and *p* orbitals can hybridize but *p* orbitals cannot hybridize with other *p* orbitals. **Hybrid orbitals** are the atomic orbitals obtained when two or more nonequivalent orbitals form 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.

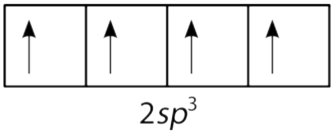


FIGURE 9.51

Carbon sp^3 hybrid orbitals.

The sp^3 hybrids are all equivalent to one another. Spatially, the hybrid orbitals point towards the four corners of a tetrahedron.

Summary

- Electrons hybridize in order to form covalent bonds.
- Nonequivalent orbitals mix to form hybrid orbitals.

Practice

Use the link below to answer the following questions. Read only the sections on ammonia and water hybridization.

http://www.adichemistry.com/general/chemicalbond/vbt/hybridization-illustrations.html

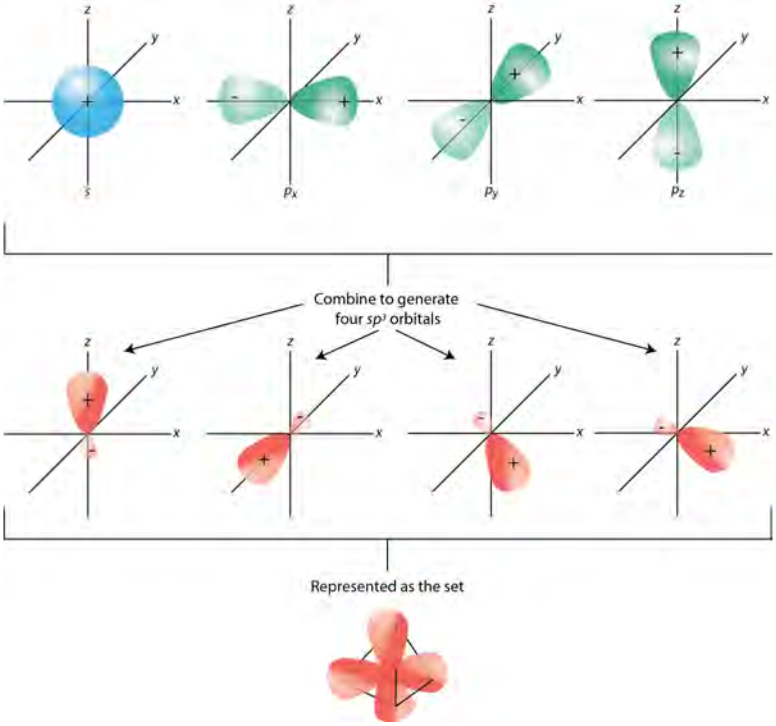


FIGURE 9.52

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 four lobes of each of the sp^3 hybrid orbitals then overlap with the normal unhybridized 1s orbitals of each hydrogen atoms to form the tetrahedral methane molecule.

1. What are the bond angles in ammonia and in water?
2. What contributes to these unexpected bond angles?
3. What happens to the lone pair electrons in ammonia when hybridization occurs?
4. Does the same thing happen with water?

Review

1. Why is carbon expected to form only two covalent bonds?
2. How many covalent bonds does carbon actually form?
3. What needs to happen to allow carbon to form four bonds?

- **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 form the same atom combine in preparation for bond formation.

9.19 Hybrid Orbitals - sp and sp2

- Describe the formation of sp and sp^2 orbitals.

How do you open the closed circle?

Romeo and Juliet were two of the great lovers of all time. Their embrace allowed no other person to be a part of it – they only wanted to be with each other. It took outside intervention (parents are like that!) to get them away from one another. Paired electrons are like that. They do not bond covalently until they are unpaired. Then they can become a part of a larger chemical structure.

Hybrid Orbitals – sp and sp^2

sp Hybridization

A beryllium hydride (BeH_2) molecule is predicted to be linear by VSEPR. The beryllium atom contains all paired electrons and so must also undergo hybridization. One of the *2s* electrons is first promoted to the empty $2p_x$ orbital.

Now the hybridization takes place only with the occupied orbitals and the result is a pair of *sp* hybrid orbitals. The two remaining *p* orbitals (p_y and p_z) do not hybridize and remain unoccupied.

The geometry of the *sp* hybrid orbitals is linear, with the lobes of the orbitals pointing in opposite directions along one axis, arbitrarily defined as the x-axis (see **Figure** 9.55). Each can bond with a *1s* orbital from a hydrogen atom to form the linear BeH_2 molecule.

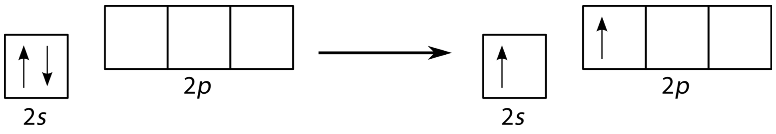


FIGURE 9.53

Promotion of Be 2s electron.

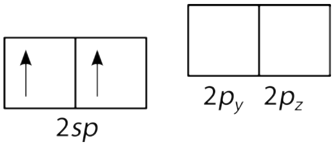


FIGURE 9.54

Be hybrid orbitals.

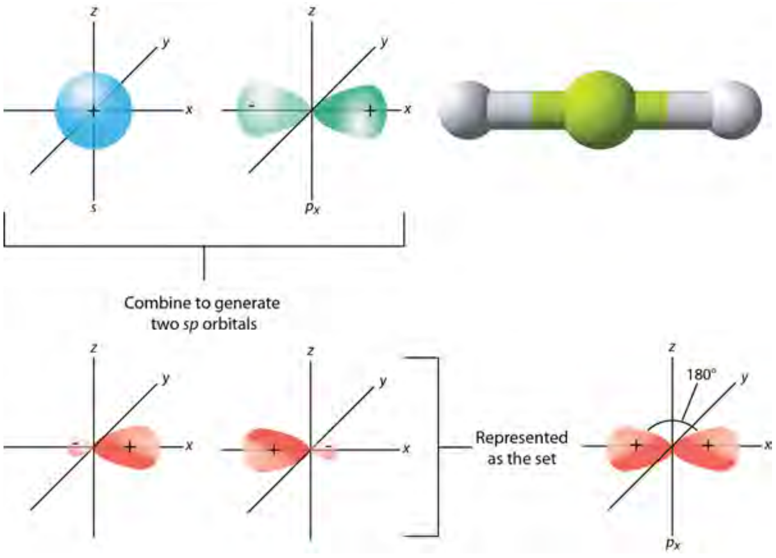


FIGURE 9.55

The process of sp hybridization is the mixing of an s orbital with a single p orbital (the pxorbital by convention), to form a set of two sp hybrids. The two lobes of the sp hybrids point opposite one another to produce a linear 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 in further detail later.

sp^2 Hybridization

Boron trifluoride (BF_3) is predicted to have a trigonal planar geometry by VSEPR. First a paired *2s* electron is promoted to the empty $2p_y$ orbital.

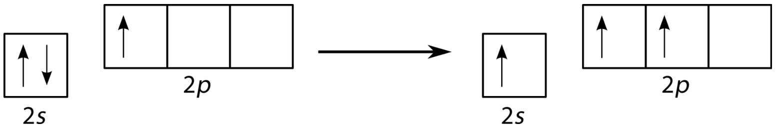


FIGURE 9.56

Promotion of 2s electron.

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.

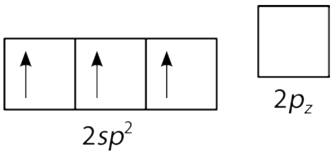


FIGURE 9.57

Formation of sp^2 orbital.

The geometry of the sp^2 hybrid orbitals is trigonal planar, with the lobes of the orbitals pointing towards the corners of a triangle (see **Figure** 9.58). The angle between any two of the hybrid orbital lobes is 120°. Each can bond with a 2*p* orbital from a fluorine atom to form the trigonal planar BF_3 molecule.

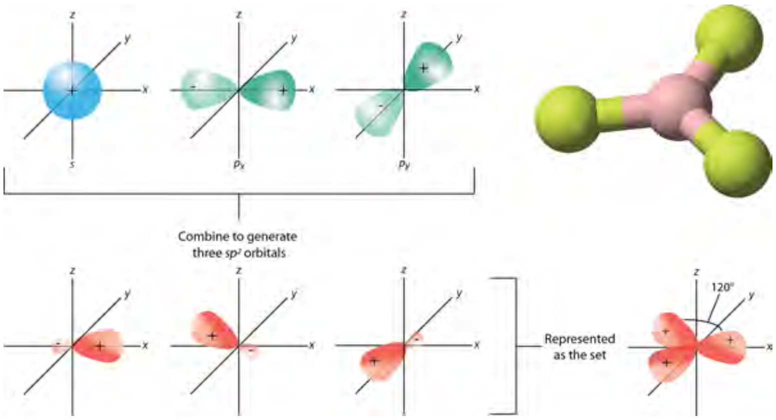


FIGURE 9.58

The process of sp^2 hybridization is the mixing of an 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 planar triangle.

Other molecules with a trigonal planar electron domain geometry form sp^2 hybrid orbitals. Ozone (O_3) is an example of a molecule whose electron domain geometry is trigonal planar, though the presence of a lone pair on the central oxygen makes the molecular geometry bent. The hybridization of the central O atom of ozone is sp^2.

Summary

- Paired electrons can be hybridized and then participate in covalent bonding.

Practice

Use the link below to answer the following questions. Only read the boron section.

http://www.adichemistry.com/general/chemicalbond/vbt/hybridization-illustrations.html

1. How many unpaired electrons are in the ground state of boron?
2. Where does the boron get three unpaired electrons for bonding to form BCl_3?
3. What is the geometry of the BCl_3?

Review

1. Does the ground state beryllium atom contain any unpaired electrons?
2. Why does one 2*s* electron in Be get promoted to a 2*p* orbital?
3. What is the geometry of the two sp orbitals?

9.20 Sigma and Pi Bonds

- Define sigma and pi bonds.
- Describe hybridization of electrons in sigma and pi bonds.

How many people do you think are squeezed into this space?

Our minds can handle two electrons interacting with one another in a sphere of space. But then we start putting in double bonds and triple bonds. The way we draw these bonds on paper suggests we are squeezing more electrons into the same space, and that doesn't work. Electrons don't like to be pushed together (especially since they all have negative charges that repel one another). So we need a more complex picture that works for all these electrons.

Sigma and Pi Bonds

The hybridization model helps explain molecules with double or triple bonds. Ethene (C_2H_4) 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.

As can be seen in the diagram above, the electron domain geometry around *each* carbon independently is trigonal planar. This corresponds to sp^2 hybridization. Previously, we saw carbon undergo sp^3 hybridization in a CH_4 molecule, so the electron promotion is the same for ethene, but the hybridization occurs only between the single *s* orbital and two of the three *p* orbitals. Thus generates a set of three sp^2 hybrids along with an unhybridized $2p_z$ orbital. Each contains one electron and so 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

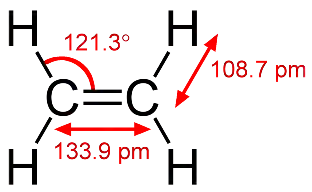


FIGURE 9.59

Geometry of ethene molecule.

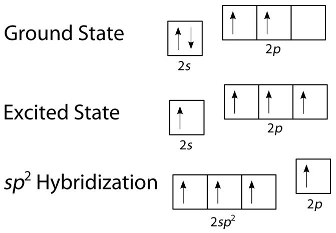


FIGURE 9.60

Hybridization in ethene.

with the identical hybrid orbital on the other carbon atom. The remaining two hybrid orbitals form 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. The **Figure** 9.61 shows the two types of bonding in C_2H_4. The sp^2 hybrid orbitals are purple and the p_z orbital is blue. Three sigma bonds are formed from each carbon atom for a total of six sigma bonds total in the molecule. The pi bond is the "second" bond of the double bonds between the carbon atoms and is shown as an elongated green lobe that extends both above and below the plane of the molecule. This plane contains the six atoms and all of the sigma bonds.

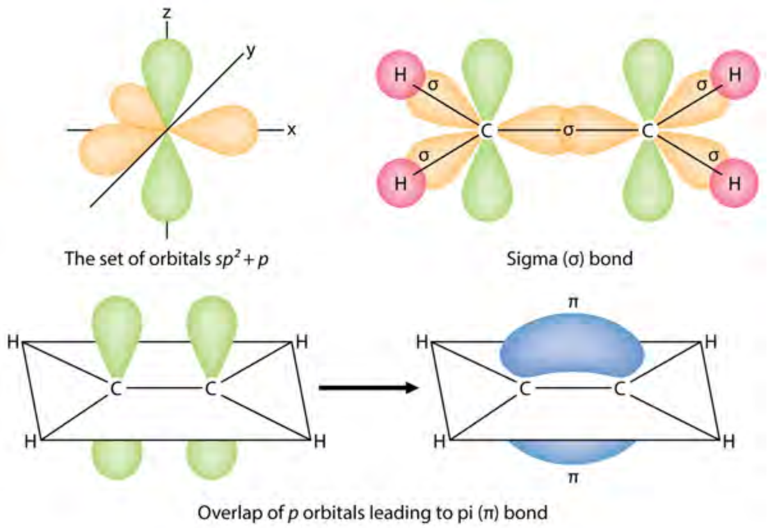


FIGURE 9.61

Sigma and pi bonds.

In a conventional Lewis electron-dot structure, a double bond is shown as a double dash 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. The hybridization is therefore *sp*.

FIGURE 9.62

Ethyne structure.

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.

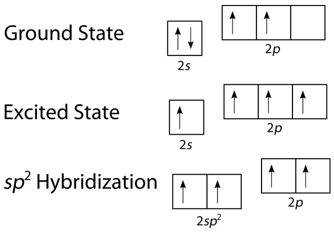
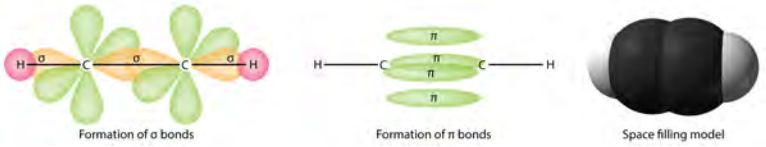


FIGURE 9.63

Hybridization in ethyne.

The *sp* hybrid orbitals form a sigma bond between each other as well as sigma bonds to the hydrogen atoms. Both the p_y and the p_z orbitals on each carbon atom form pi bonds between each other. As with ethene, these side-to-side overlaps are above and below the plane of the molecule. The orientation of the two pi bonds is that they are perpendicular to one another (see **Figure** 9.64). One pi bond is above and below the line of the molecule as shown, while the other is in front of and behind the page.



Formation of σ bonds Formation of π bonds Space filling model

FIGURE 9.64

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.

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.

Summary

- Sigma bonds form between two atoms.
- Pi bonds form from p orbital overlap.

Practice

Use the link below to answer the following questions:

https://sites.google.com/site/ed350201003/Task

1. What kind of overlap makes a sigma bond?
2. What kind of overlap makes a pi bond?
3. Can a sigma bond be formed by overlapping an s and a p orbital?
4. In methane, which carbon electrons are not involved in bonding?

Review

1. What is the hybridization around each carbon in ethene?
2. What are the two bonds in C=C?
3. What is the shape of the ethene molecule?
4. How are the ethyne pi bonds oriented in relation to each other?

- **pi bond (π bond):** 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.
- **sigma bond (σ bond):** 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.

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89. CK-12 Foundation - Zachary Wilson, using 3D molecular structure by Ben Mills (Wikimedia: Benjah-bmm27). 3D model: http://commons.wikimedia.org/wiki/File:Acetylene-CRC-IR-3D-vdW.png. CC-BY-NC-SA 3.0 (3D molecule available under the public domain)

CHAPTER 10

The Mole

Chapter Outline

10.1 Avogadro's Number

- Define mole.
- Define Avogadro's number.

Is there an easier way?

When the weather is nice, many people begin to work on their yards and homes. For many projects, sand is needed as a foundation for a walk or to add to other materials. You could order up twenty million grains of sand and have people really stare at you. You could order by the pound, but that takes a lot of time weighing out. The best bet is to order by the yard, meaning a cubic yard. The loader can scoop up what you need and put it directly in your truck. Very quick, very easy, and everybody knows what you mean.

Avogadro's Number

It certainly is easy to count bananas or to count elephants (as long as you stay out of their way). However, you would be counting grains of sugar from your sugar canister for a long, long time. Atoms and molecules are extremely small – far, far smaller than grains of sugar. Counting atoms or molecules is not only unwise, it is absolutely impossible. One drop of water contains about 10^{22} molecules of water. If you counted 10 molecules every second for 50 years without stopping you would have counted only 1.6×10^{10} molecules. Put another way, at that counting rate, it would take you over 30 trillion years to count the water molecules in one tiny drop.

Chemists needed a name that can stand for a very large number of items. Amedeo Avogadro (1776 - 1856), an Italian scientist, provided just such a number. He is responsible for the counting unit of measure called the mole. A **mole** (mol) is the amount of a substance that contains 6.02×10^{23} representative particles of that substance. The mole is the SI unit for amount of a substance. Just like the dozen and the gross, it is a name that stands for a number. There are therefore 6.02×10^{23} water molecules in a mole of water molecules. There also would be 6.02×10^{23} bananas in a mole of bananas, if such a huge number of bananas ever existed.

The number 6.02×10^{23} is called **Avogadro's number**, the number of representative particles in a mole. It is an experimentally determined number. A **representative particle** is the smallest unit in which a substance naturally

FIGURE 10.1

Italian scientist Amedeo Avogadro, whose work led to the concept of the mole as a counting unit in chemistry.

exists. For the majority of elements, the representative particle is the atom. Iron, carbon, and helium consist of iron atoms, carbon atoms, and helium atoms, respectively. Seven elements exist in nature as diatomic molecules and they are H_2, N_2, O_2, F_2, Cl_2, Br_2, and I_2. The representative particle for these elements is the molecule. Likewise, all molecular compounds such as H_2O and CO_2 exist as molecules and so the molecule is their representative particle. For ionic compounds such as NaCl and $Ca(NO_3)_2$, the representative particle is the formula unit. A mole of any substance contains Avogadro's number (6.02×10^{23}) of representative particles.

FIGURE 10.2

The animal mole is very different than the counting unit of the mole. Chemists nonetheless have adopted the mole as their unofficial mascot. National Mole Day is a celebration of chemistry that occurs on October 23rd (10/23) of each year.

Summary

- A mole of any substance contains Avogadro's number (6.02×10^{23}) of representative particles.

Practice

Use the link below to answer the following questions:

http://www.scientificamerican.com/article.cfm?id=how-was-avogadros-number

1. What was Avogadro's hypothesis?
2. Who first calculated this number?
3. Who coined the term "Avogadro's number"?
4. What contribution did Robert Millikan make to the determination for the value for the number?

Review

1. What is the SI unit for amount of a substance?
2. What is the representative particle for an element?
3. The formula unit is the representative particle for what?

- **Avogadro's number:** The number of representative particles in a mole, 6.02×10^{23}.
- **mole** (mol): The amount of a substance that contains 6.02×10^{23} representative particles of that substance.
- **representative particle**: The smallest unit in which a substance naturally exists.

10.2 Conversion Between Moles and Atoms

- Perform calculations involving conversions between number of moles and number of atoms or molecules.

Big numbers or little numbers?

Do you hate to type subscripts and superscripts? Even with a good word-processing program, having to click on an icon to get a superscript and then remembering to click off after you type the number can be a real hassle. If we did not know about moles and just knew about numbers of atoms or molecules (those big numbers that require lots of superscripts), life would be much more complicated and we would make many more typing errors.

Conversions Between Moles and Atoms

Conversions Between Moles and Number of Particles

Using our unit conversion techniques, we can use the mole label to convert back and forth between the number of particles and moles.

Sample Problem 1: Converting Number of Particles to Moles

The element carbon exists in two primary forms: graphite and diamond. How many moles of carbon atoms is 4.72×10^{24} atoms of carbon?

Step 1: List the known quantities and plan the problem.

Known

- number of C atoms = 4.72×10^{24}

- 1 mole = 6.02×10^{23}atoms

<u>Unknown</u>

- 4.72×10^{24} = ? mol C

One conversion factor will allow us to convert from the number of C atoms to moles of C atoms.

Step 2: Calculate.

$$4.72 \times 10^{24} \text{ atoms C} \times \frac{1 \text{ mol C}}{6.02 \times 10^{23} \text{ atoms C}} = 7.84 \text{ mol C}$$

Step 3: Think about your result.

The given number of carbon atoms was greater than Avogadro's number, so the number of moles of C atoms is greater than 1 mole. Since Avogadro's number is a measured quantity with three significant figures, the result of the calculation is rounded to three significant figures.

Suppose that you wanted to know how many hydrogen atoms were in a mole of water molecules. First, you would need to know the chemical formula for water, which is H_2O. There are two atoms of hydrogen in each molecule of water. How many atoms of hydrogen would there be in two water molecules? There would be 2 × 2 = 4 hydrogen atoms. How about in a dozen? In that case a dozen is 12 so 12 × 2 = 24 hydrogen atoms in a dozen water molecules. To get the answers, (4 and 24) you had to multiply the given number of molecules by two atoms of hydrogen per molecule. So to find the number of hydrogen atoms in a mole of water molecules, the problem could be solved using conversion factors.

$$1 \text{ mol } H_2O \times \frac{6.02 \times 10^{23} \text{ molecules } H_2O}{1 \text{ mol } H_2O} \times \frac{2 \text{ atoms H}}{1 \text{ molecule } H_2O} = 1.20 \times 10^{24} \text{ atoms H}$$

The first conversion factor converts from moles of particles to the number of particles. The second conversion factor reflects the number of atoms contained within each molecule.

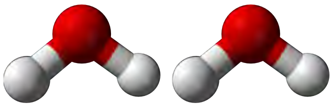


FIGURE 10.3

Two water molecules contain 4 hydrogen atoms and 2 oxygen atoms. A mole of water molecules contains 2 moles of hydrogen atoms and 1 mole of oxygen atoms.

Sample Problem 2: Atoms, Molecules, and Moles

Sulfuric acid has the chemical formula H_2SO_4. A certain quantity of sulfuric acid contains 4.89×10^{25} atoms of oxygen. How many moles of sulfuric acid is the sample?

Step 1: List the known quantities and plan the problem.

<u>Known</u>

- 4.89×10^{25} = O atoms

- 1 mole = 6.02×10^{23} molecules H_2SO_4

Unknown

- mol of H_2SO_4 molecules

Two conversion factors will be used. First, convert atoms of oxygen to molecules of sulfuric acid. Then, convert molecules of sulfuric acid to moles of sulfuric acid.

Step 2: Calculate.

$$4.89 \times 10^{25} \text{ atoms O } \times \frac{1 \text{ molecule } H_2SO_4}{4 \text{ atoms O}} \times \frac{1 \text{ mol } H_2SO_4}{6.02 \times 10^{23} \text{ molecules } H_2SO4} = 20.3 \text{ mol } H_2SO_4$$

Step 3: Think about your result.

The original number of oxygen atoms was about 80 times larger than Avogadro's number. Since each sulfuric acid molecule contains 4 oxygen atoms, there are about 20 moles of sulfuric acid molecules.

Summary

- Methods are described for conversions between moles, atoms, and molecules.

Practice

Read the relevant portions of the following article and do problems 3, 5, 9, 13, and 18. Do not worry about the calculations involving conversions dealing with molar mass (that will come next).

http://faculty.rcc.edu/freitas/1AWorksheets/14GramsToMolesToMolecules.pdf

Review

1. What important number do we need to know to do these conversions?
2. I want to convert atoms to moles. My friend tells me to multiply the number of atoms by 6.02×10^{23} atoms/mole. Is this correct?
3. Why should I know the formula for a molecule in order to calculate the number of moles of one of the atoms?

10.3 Molar Mass

- Define molar mass.
- Perform calculations involving molar mass.

When creating a solution, how do I know how much of each substance to put in?

I want to make a solution that contains 1.8 moles of potassium dichromate. I don't have a balance calibrated in molecules, but I do have one calibrated in grams. If I know the relationship between moles and the number of grams in a mole, I can use my balance to measure out the needed amount of material.

Molar Mass

Molar mass is defined as the mass of one mole of representative particles of a substance. By looking at a periodic table, we can conclude that the molar mass of lithium is 6.94 g, the molar mass of zinc is 65.38 g, and the molar mass of gold is 196.97 g. Each of these quantities contains 6.02×10^{23} atoms of that particular element. The units for molar mass are grams per mole or g/mol.

Molar Masses of Compounds

A molecular formula of the compound 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 mass of one molecule of carbon dioxide by adding together the masses of 1 atom of carbon and 2 atoms of oxygen.

$$12.01 \text{ amu} + 2(16.00 \text{ amu}) = 44.01 \text{ amu}$$

The **molecular mass** of a compound is the mass of one molecule of that compound. The molecular mass of carbon dioxide is 44.01 amu.

The molar mass of any compound is the mass in grams of one mole of that compound. One mole of carbon dioxide molecules has a mass of 44.01 g, while one mole of sodium sulfide formula units has a mass of 78.04 g. The molar masses are 44.01 g/mol and 78.04 g/mol respectively. In both cases, that is the mass of 6.02×10^{23} representative particles. The representative particle of CO_2 is the molecule, while for Na_2S, it is the formula unit.

Sample Problem: Molar Mass of a Compound

Calcium nitrate, $Ca(NO_3)_2$, is used as a component in fertilizer Determine the molar mass of calcium nitrate.

Step 1: List the known and unknown quantities and plan the problem.

Known

- formula = $Ca(NO_3)_2$
- molar mass Ca = 40.08 g/mol
- molar mass N = 14.01 g/mol
- molar mass O = 16.00 g/mol

Unknown

- molar mass $Ca(NO_3)_2$

First we need to analyze the formula. Since the Ca lacks a subscript, there is one Ca atom per formula unit. The 2 outside the parentheses means that there are two nitrate ions per formula unit and each nitrate ion consists of one nitrogen atom and three oxygen atoms. Therefore, there are a total of 1 × 2 = 2 nitrogen atoms and 3 × 2 = 6 oxygen atoms per formula unit. Thus, 1 mol of calcium nitrate contains 1 mol of Ca atoms, 2 mol of N atoms, and 6 mol of O atoms.

Step 2: Calculate.

Use the molar masses of each atom together with the number of atoms in the formula and add together.

$$
\begin{aligned}
&1 \text{ mol Ca} \times \frac{40.08 \text{ g Ca}}{1 \text{ mol Ca}} = 40.08 \text{ g Ca} \\
&2 \text{ mol N} \times \frac{14.01 \text{ g N}}{1 \text{ mol N}} = 28.02 \text{ g N} \\
&6 \text{ mol O} \times \frac{16.00 \text{ g O}}{1 \text{ mol O}} = 96.00 \text{ g O} \\
&\text{molar mass of } Ca(NO_3)_2 = 40.08 \text{ g} + 28.02 \text{ g} + 96.00 \text{ g} = 164.10 \text{ g/mol}
\end{aligned}
$$

Summary

- Calculations are described for the determination of molar mass of an atom or a compound.

Practice

Read the material at the link below and work the problems at the end:

http://misterguch.brinkster.net/molarmass.html

Review

1. What is the molar mass of Pb?
2. Why do we need to include the units in our answer?
3. I want to calculate the molar mass of $CaCl_2$. How many moles of Cl are in one mole of the compound?
4. How many moles of H are in the compound $(NH_4)_3PO_4$?

- **molar mass**: The mass of one mole of representative particles of a substance.
- **molecular mass**: The mass of one molecule of that compound.

10.4 Conversions between Moles and Mass

- Perform calculations dealing with conversions between moles and mass.

How can we get more product?

Chemical manufacturing plants are always seeking to improve their processes. One of the ways this improvement comes about is through measuring the amount of material produced in a reaction. By knowing how much is made, the scientists and engineers can try different ways of getting more product at less cost.

Conversions Between Moles and Mass

The molar mass of any substance is the mass in grams of one mole of representative particles of that substance. The representative particles can be atoms, molecules, or formula units of ionic compounds. This relationship is frequently used in the laboratory. Suppose that for a certain experiment you need 3.00 moles of calcium chloride ($CaCl_2$). Since calcium chloride is a solid, it would be convenient to use a balance to measure the mass that is needed. The molar mass of $CaCl_2$ is 110.98 g/mol. The conversion factor that can be used is then based on the equality that 1 mol = 110.98 g $CaCl_2$. Dimensional analysis will allow you to calculate the mass of $CaCl_2$ that you should measure.

$$3.00 \text{ mol CaCl}_2 \times \frac{110.98 \text{ g CaCl}_2}{1 \text{ mol CaCl}_2} = 333 \text{ g CaCl}_2$$

When you measure the mass of 333 g of $CaCl_2$, you are measuring 3.00 moles of $CaCl_2$.

FIGURE 10.4
Calcium chloride is used as a drying agent and as a road deicer.

Sample Problem: Converting Moles to Mass

Chromium metal is used for decorative electroplating of car bumpers and other surfaces. Find the mass of 0.560 moles of chromium.

Step 1: List the known quantities and plan the problem.

Known

- molar mass of Cr = 52.00 g mol
- 0.560 mol Cr

Unknown

- 0.560 mol Cr = ? g

One conversion factor will allow us to convert from the moles of Cr to mass.

Step 2: Calculate.

$$0.560 \text{ mol Cr} \times \frac{52.00 \text{ g Cr}}{1 \text{ mol Cr}} = 29.1 \text{ g Cr}$$

Step 3: Think about your result.

Since the desired amount was slightly more than one half of a mole, the mass should be slightly more than one half of the molar mass. The answer has three significant figures because of the 0.560 mol.

A similar conversion factor utilizing molar mass can be used to convert from the mass of an substance to moles. In a laboratory situation, you may perform a reaction and produce a certain amount of a product which can be massed. It will often then be necessary to determine the number of moles of the product that was formed. The next problem illustrates this situation.

Sample Problem: Converting Mass to Moles

A certain reaction produces 2.81 g of copper(II) hydroxide, $Cu(OH)_2$. Determine the number of moles produced in the reaction.

Step 1: List the known quantities and plan the problem.

Known

- mass = 2.81 g

Unknown

- mol $Cu(OH)_2$

One conversion factor will allow us to convert from mass to moles.

Step 2: Calculate.

First, it is necessary to calculate the molar mass of $Cu(OH)_2$ from the molar masses of Cu, O, and H. The molar mass is 97.57 g/mol.

$$2.81 \text{ g Cu(OH)}_2 \times \frac{1 \text{ mol Cu(OH)}_2}{97.57 \text{ g Cu(OH)}_2} = 0.0288 \text{ mol Cu(OH)}_2$$

Step 3: Think about your result.

The relatively small mass of product formed results in a small number of moles.

Summary

- Calculations involving conversions between moles of a material and the mass of that material are described.

Practice

Read the material in the link below and work the problems at the end.

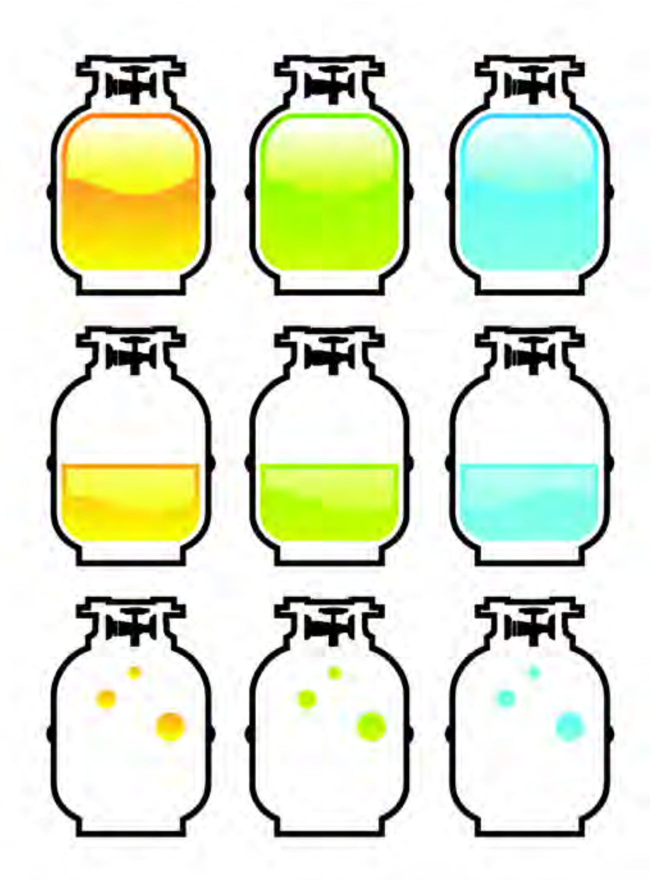
http://www.occc.edu/kmbailey/chem1115tutorials/Stoichiometry_Molar_Mass_Calculations.htm

Review

1. Why would you want to calculate the mass of a material?
2. Why would you want to determine how many moles of material you produced in a reaction?
3. You have 19.7 grams of a material and wonder how many moles were formed. Your friend tells you to multiply the mass by grams/mole. Is your friend correct?

10.5 Conversions between Mass and Number of Particles

- Perform calculations involving conversions of mass and number of particles.



How much gas is there?

Avogadro was interested in studying gases. He theorized that equal volumes of gases under the same conditions contained the same number of particles. Other researchers studied how many gas particles were in a specific volume of gas. Eventually, scientists were able to develop the relationship between number of particles and mass using the idea of moles.

Conversions Between Mass and Number of Particles

In the last lesson, you learned how to convert back and forth between moles and the number of representative particles. Now you have seen how to convert back and forth between moles and mass of a substance in grams. We can combine the two types of problems into one. Mass and number of particles are both related to grams. In order to convert from mass to number of particles or vice-versa, it will first require a conversion to moles.

Sample Problem: Converting Mass to Particles

How many molecules is 20.0 g of chlorine gas, Cl_2?

FIGURE 10.5
Conversion from number of particles to mass or from mass to number of particles requires two steps

Step 1: List the known quantities and plan the problem.

Known

- molar mass Cl_2 = 70.90 g/mol
- 20.0 g Cl_2

Unknown

- number of molecules of Cl_2

Use two conversion factors. The first converts grams of Cl_2 to moles. The second converts moles of Cl_2 to the number of molecules.

Step 2: Calculate.

$$20.0 \text{ g Cl}_2 \times \frac{1 \text{ mol Cl}_2}{70.90 \text{ g Cl}_2} \times \frac{6.02 \times 10^{23} \text{ molecules Cl}_2}{1 \text{ mol Cl}_2} = 1.70 \times 10^{23} \text{ molecules Cl}_2$$

The problem is done using two consecutive conversion factors. There is no need to explicitly calculate the moles of Cl_2.

Step 3: Think about your result.

Since the given mass is less than half of the molar mass of chlorine, the resulting number of molecules is less than half of Avogadro's number.

Summary

- Calculations are illustrated for conversions between mass and number of particles.

Practice

Read the material at the link below and then do practice problems on page 9 and the problem on page 17 (don't peak at the answers until you have tried the problems).

http://schools.fwps.org/decatur-old/staff/adewaraja/chemistry/curriculum%20units/chapter%2010/Lesson5/particle_-mole_mass_calcu.pdf

Review

1. Why can't we convert directly from number of particles to grams?
2. How many atoms of chlorine are present in the problem above?
3. The periodic table says the atomic weight of chlorine is 35.5. Why can't I use that value in my calculations?

10.6 Avogadro's Hypothesis and Molar Volume

- State Avogadro's hypothesis.
- Define standard temperature and pressure.
- Define molar volume.

How do scuba divers know if they will run out of gas?

Knowing how much gas is available for a dive is crucial to the survival of the diver. The tank on the diver's back is equipped with gauges to tell how much gas is present and what the pressure is. A basic knowledge of gas behavior allows the diver to assess how long to stay under water without developing problems.

Avogadro's Hypothesis and Molar Volume

Volume is a third way to measure the amount of matter, after item count and mass. With liquids and solids, volume varies greatly depending on the density of the substance. This is because solid and liquid particles are packed close together with very little space in between the particles. However, gases are largely composed of empty space between the actual gas particles.

In 1811, Amedeo Avogadro explained that the volumes of all gases can be easily determined. **Avogadro's hypothesis** states that equal volumes of all gases at the same temperature and pressure contain equal numbers of particles. Since the total volume that a gas occupies is made up primarily of the empty space between the particles, the actual size of the particles themselves is nearly negligible. A given volume of a gas with small light particles such as hydrogen (H_2) contains the same number of particles as the same volume of a heavy gas with large particles such as sulfur hexafluoride, SF_6.

Gases are compressible, meaning that when put under high pressure, the particles are forced closer to one another. This decreases the amount of empty space and reduces the volume of the gas. Gas volume is also affected

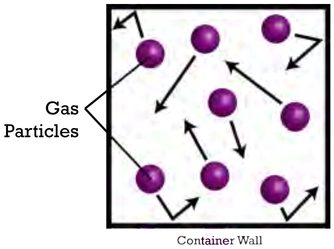


FIGURE 10.6

Gas particles are very small compared to the large amounts of empty space between them.

by temperature. When a gas is heated, its molecules move faster and the gas expands. Because of the variation in gas volume due to pressure and temperature changes, the comparison of gas volumes must be done at one standard temperature and pressure. **Standard temperature and pressure (STP)** is defined as 0°C (273.15 K) and 1 atm pressure. The **molar volume** of a gas is the volume of one mole of a gas at STP. At STP, one mole (6.02×10^{23} representative particles) of any gas occupies a volume of 22.4 L (**Figure** 10.7).

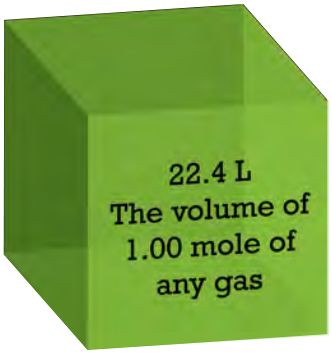


FIGURE 10.7

A mole of any gas occupies 22.4 L at standard temperature and pressure (0 °C and 1 atm).

The **Figure** 10.8 illustrates how molar volume can be seen when comparing different gases. Samples of helium (He), nitrogen (N_2), and methane (CH_4) are at STP. Each contains 1 mole or 6.02×10^{23} particles. However, the mass of each gas is different and corresponds to the molar mass of that gas: 4.00 g/mol for He, 28.0 g/mol for N_2, and 16.0 g/mol for CH_4.

Summary

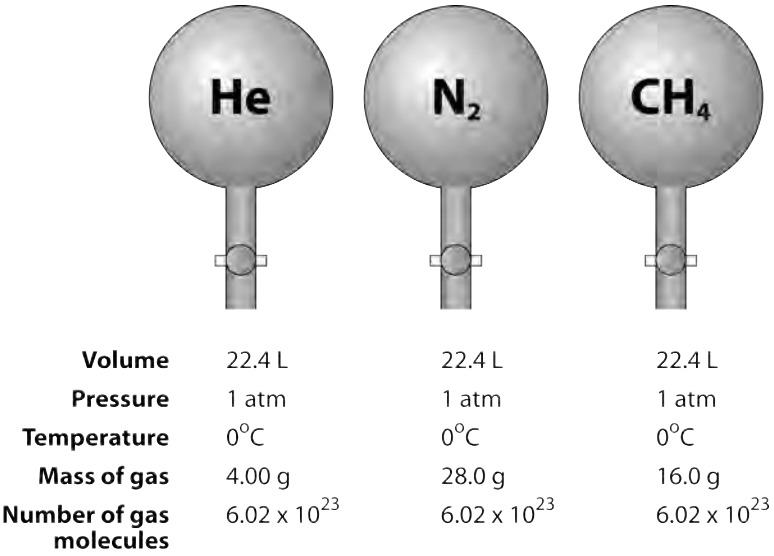
- Equal volumes of gases at the same conditions contain the same number of particles.
- Standard temperature and pressure are defined.

Practice

Use the link below to answer the following questions:

http://chemed.chem.purdue.edu/demos/main_pages/4.6.html

1. What was the volume of each gas that was weighed?
2. What did the experiment find?
3. What was the relationship between gas weight and molecular weight?



	He	N_2	CH_4
Volume	22.4 L	22.4 L	22.4 L
Pressure	1 atm	1 atm	1 atm
Temperature	0°C	0°C	0°C
Mass of gas	4.00 g	28.0 g	16.0 g
Number of gas molecules	6.02×10^{23}	6.02×10^{23}	6.02×10^{23}

FIGURE 10.8

Avogadro's hypothesis states that equal volumes of any gas at the same temperature and pressure contain the same number of particles. At standard temperature and pressure, 1 mole of any gas occupies 22.4 L.

Review

1. What do we know about the space actually taken up by a gas?
2. Why do we need to do all our comparisons at the same temperature and pressure?
3. How can we use this information?

- **Avogadro's hypothesis:** Equal volumes of all gases at the same temperature and pressure contain equal numbers of particles.
- **molar volume:** The volume of one mole of a gas at STP.
- **standard temperature and pressure (STP):** 0°C (273.15 K) and 1 atm pressure.

10.7 Conversions between Moles and Gas Volume

- Make conversions between the volume of a gas and the number of moles of that gas.

How can you tell how much gas is in these containers?

Small gas tanks are often used to supply gases for chemistry reactions. A gas gauge will give some information about how much is in the tank, but quantitative estimates are needed so the reaction will be able to proceed to completion. Knowing how to calculate needed parameters for gases is very helpful to avoid running out too early.

Conversions Between Moles and Gas Volume

Molar volume at STP can be used to convert from moles to gas volume and from gas volume to moles. The equality of 1 mole = 22.4 L is the basis for the conversion factor.

Sample Problem One: Converting Gas Volume to Moles

Many metals react with acids to produce hydrogen gas. A certain reaction produces 86.5 L of hydrogen gas at STP. How many moles of hydrogen were produced?

Step 1: List the known quantities and plan the problem.

Known

- 86.5 L H_2
- 1 mol = 22.4 L

Unknown

- moles of H_2

Apply a conversion factor to convert from liters to moles.

Step 2: Calculate.

$$86.5 \text{ L H}_2 \times \frac{1 \text{ mol H}_2}{22.4 \text{ L H}_2} = 3.86 \text{ mol H}_2$$

Step 3: Think about your result.

The volume of gas produced is nearly four times larger than the molar volume. The fact that the gas is hydrogen plays no role in the calculation.

Sample Problem Two: Converting Moles to Gas Volume

What volume does 4.96 moles of O_2 occupy at STP?

Step 1: List the known quantities and plan the problem.

Known

- 4.6 moles O_2
- 1 mol = 22.4 L

Unknown

- volume of O_2

Step 2: Calculate.

(4.96 moles)(22.4 liters/mole) = 111.1 liters

Step 3: Think about your result.

The volume seems correct given the number of moles.

Sample Problem Three: Converting Volume to Mass

If we know the volume of a gas sample at STP, we can determine how mass is present. Assume we have 867 liters of N_2 at STP. What is the mass of the nitrogen gas?

Step 1: List the known quantities and plan the problem.

Known

- 867 moles L N_2
- 1 mol = 22.4 L
- molar mass of N_2 = 28 g/mol

Unknown

- mass of N_2

Step 2: Calculate.

We start by determining the number of moles of gas present. We know that 22.4 liters of a gas at STP equals one mole, so:

$$867 \text{ litres} \times \frac{1 \text{ mole}}{22.4 \text{ liters}} = 3.87 \text{ moles}$$

We also know the molecular weight of N_2 (28.0 grams/mole), so we can then calculate the weight of nitrogen gas in 867 liters:

$$38.7 \text{ moles} \times \frac{28 \text{ grames}}{\text{mole}} = 1083.6 \text{ grams } N_2$$

Step 3: Think about your result.

In a multi-step problem, be sure that the units check.

Summary

- Conversions between moles and volume of a gas are shown.

Practice

Work the practice problems at the link below. Focus on conversions between volume and moles, but try some of the others:

http://www.sciencegeek.net/Chemistry/taters/Unit4GramMoleVolume.htm

Review

1. Why do the gases need to be at STP?
2. When does the identity of the gas become important?

10.8 Gas Density

- Make calculations dealing with molar mass and density of a gas.

Why does carbon dioxide sink?

When we run a reaction to produce a gas, we expect it to rise into the air. Many students have done experiments where gases such as hydrogen and oxygen are formed. The gas can be trapped in a test tube held upside-down over the reaction. Carbon dioxide, on the other hand, sinks when it is released. Carbon dioxide has a density greater that air, so it will not rise like these other gases would.

Gas Density

As you know, density is defined as the mass per unit volume of a substance. Since gases all occupy the same volume on a per mole basis, the density of a particular gas is dependent on its molar mass. A gas with a small molar mass will have a lower density than a gas with a large molar mass. Gas densities are typically reported in g/L. Gas density can be calculated from molar mass and molar volume.

Sample Problem One: Gas Density

What is the density of nitrogen gas at STP?

Step 1: List the known quantities and plan the problem.

Known

FIGURE 10.9

Balloons filled with helium gas float in air because the density of helium is less than the density of air.

- N_2 = 28.02 g/mol
- 1 mol = 22.4 L

Unknown

- density = ? g/L

Molar mass divided by molar volume yields the gas density at STP.

Step 2: Calculate.

$$\frac{28.02\text{ g}}{1\text{ mol}} \times \frac{1\text{ mol}}{22.4\text{ L}} = 1.25\text{ g/L}$$

When set up with a conversion factor, the mol unit cancels, leaving g/L as the unit in the result.

Step 3: Think about your result.

The molar mass of nitrogen is slightly larger than molar volume, so the density is slightly greater than 1 g/L.

Alternatively, the molar mass of a gas can be determined if the density of the gas at STP is known.

Sample Problem Two: Molar Mass from Gas Density

What is the molar mass of a gas whose density is 0.761 g/L at STP?

Step 1: List the known quantities and plan the problem.

Known

- N_2 = 28.02 g/mol
- 1 mol = 22.4 L

Unknown

- molar mass = ? g/L

Molar mass is equal to density multiplied by molar volume.

Step 2: Calculate.

$$\frac{0.761\text{ g}}{1\text{ L}} \times \frac{22.4\text{ L}}{1\text{ mol}} = 17.0\text{ g/mol}$$

Step 3: Think about your result.

Because the density of the gas is less than 1 g/L, the molar mass is less than 22.4.

Summary

- Calculations are described showing conversions between molar mass and density for gases.

Practice

Use the link below to answer the following questions:

http://employees.oneonta.edu/viningwj/sims/gas_density_s.html

1. Which of the gases has the highest density?
2. Which gas has the lowest density?
3. Would you expect nitrogen to have a higher or lower density that oxygen? Why?

Review

1. How is density calculated?
2. How is molar mass calculated?
3. What would be the volume of 3.5 moles of a gas?

10.9 Mole Road Map

- Perform calculations involving interconversions of mass, moles, and volume of a gas.

How do I get from here to there?

If I want to visit the town of Manteo, North Carolina, out on the coast, I will need a map of how to get there. I may have a printed map or I may download directions from the internet, but I need something to get me going in the right direction. Chemistry road maps serve the same purpose. How do I handle a certain type of calculation? There is a process and a set of directions to help.

Mole Road Map

Previously, we saw how the conversions between mass and number of particles required two steps, with moles as the intermediate. This concept can now be extended to also include gas volume at STP. The resulting diagram is referred to as a mole road map (see **Figure** 10.10).

The mole is at the center of any calculation involving amount of a substance. The sample problem below is one of many different problems that can be solved using the mole road map.

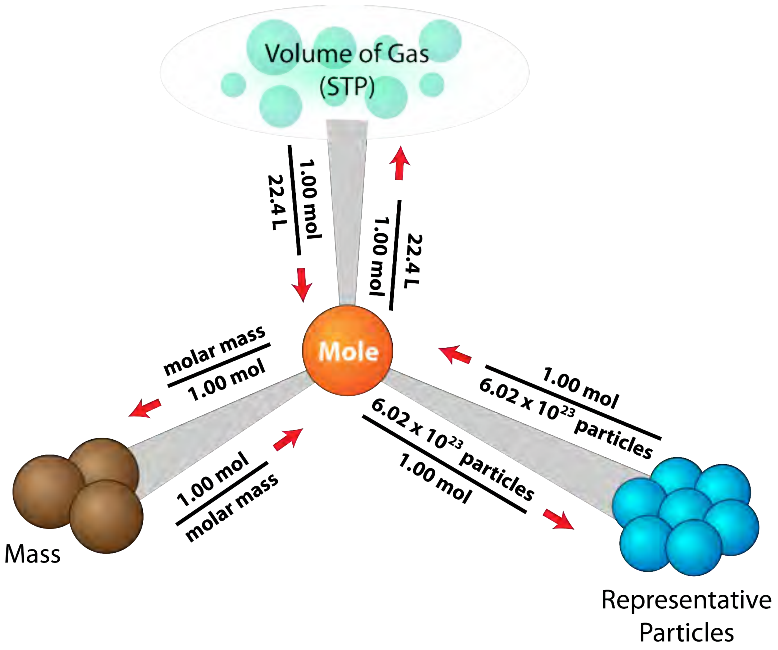


FIGURE 10.10

The mole road map shows the conversion factors needed to interconvert between mass, number of particles, and volume of a gas.

Sample Problem One: Mole Road Map

What is the volume of 79.3 g of neon gas at STP?

Step 1: List the known quantities and plan the problem.

Known

- Ne = 20.18 g/mol
- 1 mol = 22.4 L

Unknown

- volume = ? L

The conversion factors will be grams → moles → gas volume.

Step 2: Calculate.

$$79.3 \text{ g Ne} \times \frac{1 \text{ mol Ne}}{20.18 \text{ g Ne}} \times \frac{22.4 \text{ L Ne}}{1 \text{ mol Ne}} = 88.0 \text{ L Ne}$$

Step 3: Think about your result.

The given mass of neon is equal to about 4 moles, resulting in a volume that is about 4 times larger than molar volume.

Summary

- An overall process is given for calculations involving moles, grams, and gas volume.

Practice

Use the link below to carry out some practice calculations. Do problems 1, 2, and 5 (you can try the others if you are feeling especially brave):

http://www.docbrown.info/page04/4_73calcs/MVGmcTEST.htm

Review

1. In the problem above, what is the formula weight of neon?
2. What value is at the center of all the calculations?
3. If we had 79.3 grams of Xe, would we expect a volume that is greater than or less than that obtained with neon?

10.10 Percent Composition

- Define percent composition.
- Perform percent composition calculations.

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, SOYBEAN), SALT, MOLASSES.

Is there anything healthy in this jar?

Packaged foods that you eat typically have nutritional information provided on the label. The label on a jar of peanut butter (shown above) 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.

Percent Composition

Chemists often need to know what elements are present in a compound and in what percentage. The **percent composition** is the percent by mass of each element in a compound. It is calculated in a similar way that we just saw for the peanut butter.

$$\% \text{ by mass} = \frac{\text{mass of element}}{\text{mass of compound}} \times 100\%$$

Percent Composition from Mass Data

The sample problem below shows the calculation of the percent composition of a compound based on mass data.

Sample Problem One: Percent Composition from Mass

A certain newly synthesized compound is known to contain the elements zinc and oxygen. When a 20.00 g sample of the sample is decomposed, 16.07 g of zinc remains. Determine the percent composition of the compound.

Step 1: List the known quantities and plan the problem.

Known

- mass of compound = 20.00 g
- mass of Zn = 16.07 g

Unknown

- percent Zn = ? %
- percent O = ? %

Subtract to find the mass of oxygen in the compound. Divide each element's mass by the mass of the compound to find the percent by mass.

Step 2: Calculate.

$$\text{Mass of oxygen} = 20.00\text{ g} - 16.07\text{ g} = 3.93\text{ g O}$$
$$\%\text{ Zn} = \frac{16.07\text{ g Zn}}{20.00\text{ g}} \times 100\% = 80.35\%\text{ Zn}$$
$$\%\text{ O} = \frac{3.93\text{ g O}}{20.00\text{ g}} \times 100\% = 19.65\%\text{ O}$$

Step 3: Think about your result.

The calculations make sense because the sum of the two percentages adds up to 100%. By mass, the compound is mostly zinc.

Percent Composition from a Chemical Formula

The percent composition of a compound can also be determined from the formula of the compound. The subscripts in the formula are first used to calculate the mass of each element in one mole of the compound. That is divided by the molar mass of the compound and multiplied by 100%.

$$\%\text{ by mass } = \frac{\text{mass of element in 1 mol}}{\text{molar mass of compound}} \times 100\%$$

The percent composition of a given compound is always the same as long as the compound is pure.

Sample Problem Two: Percent Composition from Chemical Formula

Dichlorineheptoxide (Cl_2O_7) is a highly reactive compound used in some organic synthesis reactions. Calculate the percent composition of dichlorineheptoxide.

Step 1: List the known quantities and plan the problem.

Known

- mass of Cl in 1 mol Cl_2O_7 = 70.90 g
- mass of O in 1 mol Cl_2O_7 = 112.00 g
- molar mass of Cl_2O_7 = 182.90 g/mol

Unknown

- percent Cl = ? %

- percent O = ? %

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%.

Step 2: Calculate.

$$\begin{aligned}\%\ \text{Cl} &= \frac{70.90\ \text{g Cl}}{182.90\ \text{g}} \times 100\% = 38.76\%\ \text{Cl}\\ \%\ \text{O} &= \frac{112.00\ \text{g O}}{182.90\ \text{g}} \times 100\% = 61.24\%\ \text{O}\end{aligned}$$

Step 3: Think about your result.

The percentages add up to 100%.

Percent composition can also be used to determine the mass of a certain element that is contained in any mass of a compound. In the previous sample problem, it was found that the percent composition of dichlorineheptoxide is 38.76% Cl and 61.24% O. Suppose that you needed to know the masses of chlorine and oxygen present in a 12.50 g sample of dichlorineheptoxide. You can set up a conversion factor based on the percent by mass of each element.

$$\begin{aligned}12.50\ \text{g Cl}_2\text{O}_7 \times \frac{38.76\ \text{g Cl}}{100\ \text{g Cl}_2\text{O}_7} &= 4.845\ \text{g Cl}\\ 12.50\ \text{g Cl}_2\text{O}_7 \times \frac{61.24\ \text{g O}}{100\ \text{g Cl}_2\text{O}_7} &= 7.655\ \text{g O}\end{aligned}$$

The sum of the two masses is 12.50 g, the mass of the sample size.

Summary

- Processes are described for calculating the percent composition of a material based on mass or on chemical composition.

Practice

Use the link below to review material and do calculations. Read both parts of the lesson and do as many calculations as you have time for.

http://www.chemteam.info/Mole/Percent-Composition-Part1.html

Review

1. What is the formula for calculating percent composition?
2. What information do you need to calculate percent composition by mass?
3. What do subscripts in a chemical formula tell you?

- **percent composition:** The percent by mass of each element in a compound.

10.11 Percent of Water in a Hydrate

- Define hydrate.
- Calculate the percent water in hydrate when give relevant data.

Why does the color change?

If you look at a typical bottle of copper sulfate, it will be a bluish-green. If someone tells you that copper sulfate is white, you won't believe them. You are both right; it just depends on the copper sulfate. Your blue-green copper sulfate has several water molecules attached to it while your friend's copper sulfate is anhydrous (no water attached). Why the difference? The water molecules interact with some of the d electrons in the copper ion and produce the color. When the water is removed, the electron configuration changes and the coo disappears.

Percent of Water in a Hydrate

Many ionic compounds naturally contain water as part of the crystal lattice structure. A **hydrate** is a compound that has one or more water molecules bound to each formula unit. Ionic compounds that contain a transition metal are often highly colored. Interestingly, it is common for the hydrated form of a compound to be of a different color than the **anhydrous** form, which has no water in its structure. A hydrate can usually be converted to the anhydrous compound by heating. The **Figure** below shows the anhydrous compound cobalt(II) chloride to be blue while the hydrate is a distinctive magenta color.

The hydrated form of cobalt(II) chloride contains six water molecules in each formula unit. The name of the compound is cobalt(II) chloride hexahydrate and its formula is $CoCl_2{\bullet}6H_2O$. The formula for water is set apart at the end of the formula with a dot, followed by a coefficient that represents the number of water molecules per formula unit.

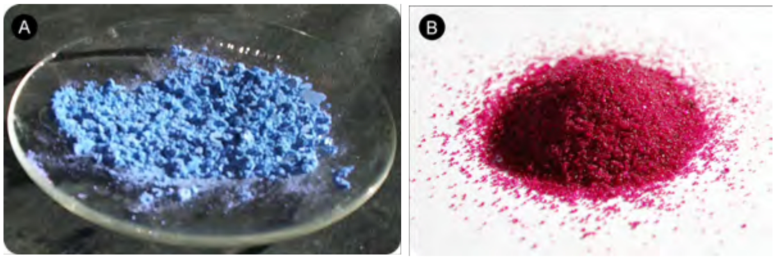


FIGURE 10.11

On the left is anhydrous cobalt(II) chloride, $CoCl_2$. On the right is the hydrated form of the compound called cobalt(II) chloride hexahydrate, $CoCl_2•6H_2O$.

It is useful to know the percent of water contained within a hydrate. The sample problem below demonstrates the procedure.

Sample Problem One: Percent of Water in a Hydrate

Find the percent water in cobalt(II) chloride hexahydrate, $CoCl_2•6H_2O$.

Step 1: List the known quantities and plan the problem.

The mass of water in the hydrate is the coefficient (6) multiplied by the molar mass of H_2O. The molar mass of the hydrate is the molar mass of the $CoCl_2$ plus the mass of water.

Known

- mass of H_2O in 1 mol hydrate = 108.12 g
- molar mass of hydrate = 237.95 g/mol

Unknown

- percent H_2O = ? %

Calculate the percent by mass of water by dividing the mass of H_2O in 1 mole of the hydrate by the molar mass of the hydrate and multiplying by 100%.

Step 2: Calculate.

$$\% \text{ H}_2\text{O} = \frac{108.12 \text{ g H}_2\text{O}}{237.95 \text{ g}} \times 100\% = 45.44\% \text{ H}_2\text{O}$$

Step 3: Think about your result.

Nearly half of the mass of the hydrate is composed of water molecules within the crystal.

Summary

- The process of calculating the percent water in a hydrate is described.

Practice

Use the following link to practice calculating percent water in a hydrate:

http://www.sd84.k12.id.us/shs/departments/science/martz/2007_ssem2/Chemistry/hydrate.htm

Review

1. What is a hydrate?
2. How can you convert a hydrate to an anhydrous compound?
3. What does hexahydrate mean?

- **Anhydrous:** Without water.
- **Hydrate:** A compound that has one or more water molecules bound to each formula unit

10.12 Determining Empirical Formulas

- Define empirical formula.
- Calculate the empirical formula for a compound when given the elemental analysis of the compound.

What is shown in this picture?

In the early days of chemistry, there were few tools for the detailed study of compounds. Much of the information regarding the composition of compounds came from the elemental analysis of inorganic materials. The "new" field of organic chemistry (the study of carbon compounds) faced the challenge of not being able to characterize a compound completely. The relative amounts of elements could be determined, but so many of these materials had carbon, hydrogen, oxygen, and may be nitrogen in simple ratios. We did not know exactly how many of these atoms were actually in a specific molecule.

Determining Empirical Formulas

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, all formulas of ionic compounds are empirical. However, we can also consider the empirical formula of a molecular compound. Ethene is a small hydrocarbon compound with the formula C_2H_4 (see **Figure** 10.12). 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. There are two ways to view that ratio. Considering one molecule of ethene, the ratio is 1 carbon atom for every 2 atoms of hydrogen. Considering one mole of ethene, the ratio is 1 mole of carbon for every 2 moles of hydrogen. So the subscripts in a formula represent the mole ratio of the elements in that formula.

In a procedure called **elemental analysis**, an unknown compound can be analyzed in the laboratory in order to determine the percentages of each element contained within it. These percentages can be transformed into the mole ratio of the elements, which leads to the empirical formula. The steps to be taken are outlined below.

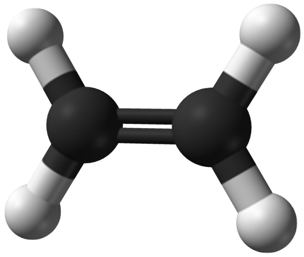


FIGURE 10.12

Ball-and-stick model of ethene, C_2H_4.

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 whichever of the moles from step 2 is the smallest.
4. If all the moles at this point are whole numbers (or very close), the empirical formula can be written with the moles as the subscript of each element.
5. In some cases, one or more of the moles calculated in step 3 will not be whole numbers. Multiply each of the moles by the smallest whole number that will convert each into a whole number. Write the empirical formula.

Sample Problem One: Determining the Empirical Formula of a Compound

A compound of iron and oxygen is analyzed and found to contain 69.94% iron and 30.06% oxygen. Find the empirical formula of the compound.

Step 1: List the known quantities and plan the problem.

Known

- % of Fe = 69.94%
- % of O = 30.06%

Unknown

- Empirical formula = $Fe_?O_?$

Steps to follow are outlined in the text.

Step 2: Calculate.

1. Assume a 100 g sample.

$$\begin{gathered}69.94 \text{ g Fe}\\30.06 \text{ g O}\end{gathered}$$

2. Convert to moles.

$$\begin{aligned}69.94 \text{ g Fe} \times \frac{1 \text{ mol Fe}}{55.85 \text{ g Fe}} &= 1.252 \text{ mol Fe}\\30.06 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} &= 1.879 \text{ mol O}\end{aligned}$$

3. Divide both moles by the smallest of the results.

$$\frac{1.252 \text{ mol Fe}}{1.252} = 1 \text{ mol Fe} \qquad \frac{1.879 \text{ mol O}}{1.252} = 1.501 \text{ mol O}$$

4/5. Since the moles of O, is still not a whole number, both moles can be multiplied by 2, while rounding to a whole number.

$$1 \text{ mol Fe} \times 2 = 2 \text{ mol Fe} \qquad 1.501 \text{ mol O} \times 2 = 3 \text{ mol O}$$

The empirical formula of the compound is Fe_2O_3.

Step 3: Think about your result.

The subscripts are whole numbers and represent the mole ratio of the elements in the compound. The compound is the ionic compound iron(III) oxide.

Summary

- A process is described for the calculation of the empirical formula for a compound based on the percent composition of that compound.

Practice

Use the link below to read about calculating empirical formulas and practice working some problems:

http://www.chemteam.info/Mole/EmpiricalFormula.html

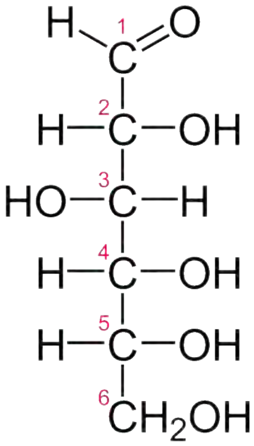
Review

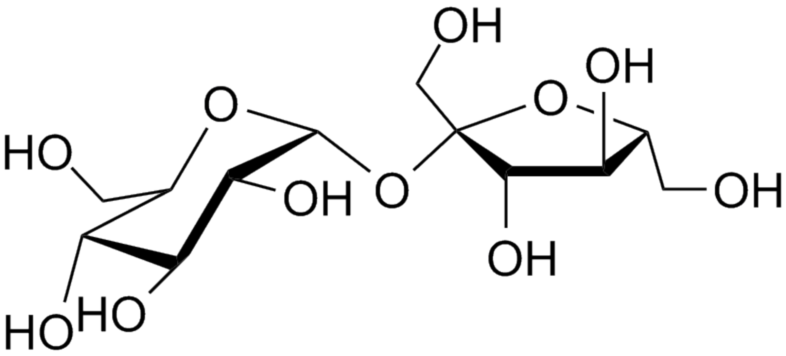
1. What is an empirical formula?
2. What does an empirical formula tell you?
3. What does it not tell you?

- **elemental analysis:** Determines the percentages of each element in a compound.
- **empirical formula:** Shows the lowest whole-number ratio of the elements in a compound.

10.13 Determining Molecular Formulas

- Define molecular formula.
- Determine the molecular formula when give the empirical formula and the molar mass of the compound.





How can you determine the differences between these two molecules?

Above we see two carbohydrates: glucose and sucrose. Sucrose is almost exactly twice the size of glucose, although their empirical formulas would be very similar. Some people could distinguish them on the basis of taste, but it's not a good idea to go around tasting chemicals. The best way is to determine the molecular weights – that approach allows you to easily tell which compound is which.

Molecular Formulas

Molecular formulas give the kind and number of atoms of each element present in a molecular compound. In many cases, the molecular formula is the same as the empirical formula. The molecular formula of methane is CH_4 and because it contains only one carbon atom, 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 is the main component of vinegar. Its molecular formula is $C_2H_4O_2$. Glucose is a simple sugar that cells use as a primary source of energy. Its molecular formula is $C_6H_{12}O_6$. The structures of both molecules are shown in the figure below. They are very different compounds, yet both have the same empirical formula of CH_2O.

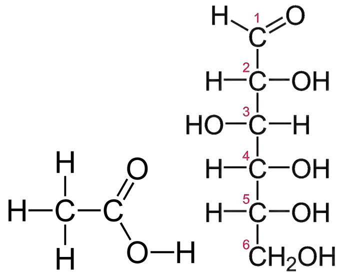


FIGURE 10.13

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 know the molar mass of the compound. Chemists use an instrument called a mass spectrometer to determine the molar mass of compounds. 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 the subscripts in the empirical formula by the whole number found in step 2. The result is the molecular formula.

Sample Problem One: Determining the Molecular Formula of a Compound

The empirical formula of a compound of boron and hydrogen is BH_3. Its molar mass is 27.7 g/mol. Determine the molecular formula of the compound.

Step 1: List the known quantities and plan the problem.

Known

- empirical formula = BH_3
- molar mass = 27.7 g/mol

Unknown

- molecular formula = ?

Steps to follow are outlined in the text.

Step 2: Calculate.

1. The empirical formula mass (EFM) = 13.84 g/mol

2. $\frac{\text{molar mass}}{\text{EFM}} = \frac{27.7}{13.84} = 2$

3. $BH_3 \times 2 = B_2H_6$

The molecular formula of the compound is B_2H_6.

Step 3: Think about your result.

The molar mass of the molecular formula matches the molar mass of the compound.

Summary

- A procedure is described that allows the calculation of the exact molecular formula for a compound.

Practice

Use the link below to access practice problems. Try as many as you have time for:

http://chemistry.about.com/od/chemistry-test-questions/tp/Molecular-Formula-Practice-Test-Questions.htm

Review

1. What is the difference between an empirical formula and a molecular formula?
2. In addition to the elemental analysis, what do you need to know to calculate the molecular formula?
3. What does the empirical formula mass tell you?

- **empirical formula mass (EFM):** The molar mass represented by the empirical formula.
- **molecular formula:** Gives the kind and number of atoms of each element present in a molecular compound.

10.14 References

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3. (left) Michael David Hill, 2005 (Mikiwikipikidikipedia); (right) chrisbb@prodigy.net. (left) http://commons.wikimedia.org/wiki/File:Close-up_of_mole.jpg; (right) http://www.flickr.com/photos/chrisbrenschmidt/436990097/. (left) CC-BY 2.5; (right) CC-BY 2.0
4. Courtesy of Diane A. Reid/National Cancer Institute. http://commons.wikimedia.org/wiki/File:Man_responds_to_telephone_call.jpg. Public Domain
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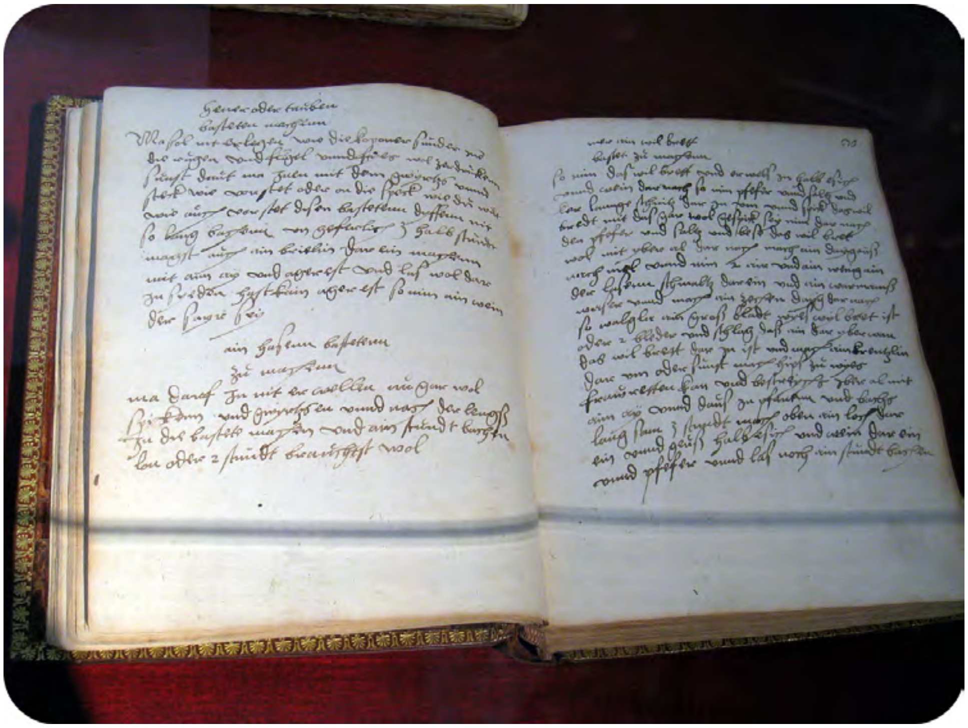
CHAPTER 11 Chemical Reactions

Chapter Outline

11.1 Word Equations

- Write word equations that describe chemical reactions.



What's for dinner?

Various ways of recording recipes have developed over the centuries. The cookbook shown above was written by a woman who probably collected all her own recipes. Later, printed cookbooks became available (even guys had no excuse for not being able to cook). Today we can find recipes on a number of internet sites and can quickly search for information on how to cook anything we want. Reading a recipe sometimes requires we understand a few codes and symbols (what's the difference between a tsp and a Tsp?), but the information on what we start with and what we end up with is there.

Writing Chemical Equations

Chemical reactions are occurring all around you. Plants use sunlight to drive their photosynthetic process and produce energy. Cars and other vehicles burn gasoline in order to power their engines. Batteries use electrochemical reactions to produce energy and power many everyday devices. Many chemical reactions are going on inside you as well, especially during the digestion of food.

In math class, you have written and solved many mathematical equations. Chemists keep track of chemical reactions by writing equations as well. In any chemical reaction one or more substances, called **reactants**, are converted into one or more new substances, called **products**. The general form of the equation for such a process looks like this.

$$\text{Reactants} \rightarrow \text{Products}$$

Unlike in a math equation, a chemical equation does not use an equal sign. Instead the arrow is called a yield sign and so the equation is described as "reactants yield products".

Word Equations

You can describe a chemical reaction by writing a **word equation**. When silver metal is exposed to sulfur it reacts to form silver sulfide. Silver sulfide is commonly known as tarnish and turns the surface of silver objects dark and streaky black (see **Figure** 11.1). The sulfur that contributes to tarnish can come from traces of sulfur in the air or from food such as eggs. The word equation for the process is:

$$\text{Silver} + \text{sulfur} \rightarrow \text{Silver sulfide}$$

The silver and the sulfur are the reactants in the equation, while the silver sulfide is the product.

FIGURE 11.1

The coffee percolator on the left has been tarnished from exposure to sulfur. Tarnish is the chemical compound silver sulfide. The same percolator on the right has been polished with a tarnish removal product in order to restore its silver finish.

Another common chemical reaction is the burning of methane gas. Methane is the major component of natural gas and is commonly burned on a gas stove or in a Bunsen burner (Figure 11.2). Burning is a chemical reaction in which some type of fuel is reacted with oxygen gas. The products of the reaction in the burning of methane as well as other fuels are carbon dioxide and water. The word equation for this reaction is:

$$\text{Methane} + \text{oxygen} \rightarrow \text{carbon dioxide} + \text{water}$$

Word equations can be very useful, but do have one major drawback. They cannot be used for any quantitative work. A word equation does not tell how many moles of each material are needed or how many moles of product are formed.

Summary

- Word equations are used to describe the conversion of reactants to products.

Practice

Read the material at the link below and do the practice problems:

http://www.dynamicscience.com.au/tester/solutions/chemistry/chemical%20equations.htm

FIGURE 11.2

A Bunsen burner is commonly used to heat substances in a chemistry lab. Methane is reacted with oxygen to form carbon dioxide and water.

Review

1. Write the generic form of a chemical reaction.
2. What are reactants?
3. What are products?

- **chemical reaction**: Conversion of reactants to products
- **product:** The result of chemical reaction
- **reactant:** The starting material for a chemical reaction
- **word equation:** A description of a chemical reaction using the names of the compounds.

11.2 Chemical Equations

- Describe the symbols used in a chemical equation.

How do you make Shrimp gumbo?

Shrimp gumbo is one of many enjoyable dishes that are part of the Cajun culture of Louisiana. It's a spicy dish that needs careful control of all the ingredients so that it has a "kick", but is not overwhelming. Recipes tell not only what is in the preparation, but describes how much of each ingredient and details of how to cook the meal. We need this type of information in order to carry out chemical reactions successfully and safely.

Chemical Equations

Word equations are time-consuming to write and do not prove to be convenient for many of the things that chemists need to do with equations. A **chemical equation** is a representation of a chemical reaction that displays the reactants and products with chemical formulas. The chemical equation for the reaction of methane with oxygen is shown:

$$CH_4 + O_2 \rightarrow CO_2 + H_2O$$

The equation above, called a **skeleton equation,** is an equation that shows only the formulas of the reactants and products with nothing to indicate the relative amounts. The first step in writing an accurate chemical equation is to write the skeleton equation, making sure that the formulas of all substances involved are written correctly. All reactants are written to the left of the yield arrow, separated from one another by a plus sign. Likewise, products are written to the right of the yield arrow, also separated with a plus sign.

It is often important to know the physical states of the reactants and products taking part in a reaction. To do this, put the appropriate symbol in parentheses after each formula: (*s*) for solid, (*l*) for liquid, (*g*) for gas, and (*aq*) for an aqueous (water-based) solution. The previous reaction becomes:

$$CH_4(g) + O_2(g) \rightarrow CO_2(g) + H_2O(l)$$

The table below shows a listing of symbols used in chemical equations. Some, such as the double arrow which represents equilibrium, and the use of a catalyst in a reaction, will be treated in detail in other concepts.

TABLE 11.1: Symbols Used in Chemical Equations

Symbol	Description
$+$	Used to separate multiple reactants or products
$\rightarrow$	yield sign; separates reactants from products
$\rightleftarrows$	replaces the yield sign for reversible reactions that reach equilibrium
(s)	reactant or product in the solid state
(l)	reactant or product in the liquid state
(g)	reactant or product in the gas state
(aq)	reactant or product in an aqueous solution (dissolved in water)
$\xrightarrow{Pt}$	formula written above the arrow is used as a catalyst in the reaction
$\xrightarrow{\Delta}$	triangle indicates that the reaction is being heated

Summary

- A chemical equation is described.
- Symbols used in chemical equations are described and explained.

Practice

Watch the video at the link below and do the examples seen in the video:

Your Turn

$CH_4(g) + O_2(g) \rightarrow H_2O(g) + CO_2(g)$

$BaCl_2(aq) + 2AgNO_3(aq) \rightarrow Ba(NO_3)_2(aq) + 2AgCl(s)$

MEDIA

Click image to the left for more content.

http://www.youtube.com/watch?v=lSoRj_iBwYc

Review

1. What does a skeleton equation tell you?
2. Why would you want to know the physical state of materials?

3. What does the symbol $\rightarrow$ mean?
4. If I see Δ over the arrow, what will I do?

- **chemical equation:** A representation of a chemical reaction that displays the reactants and products with chemical formulas
- **skeleton equation:** An equation that shows only the formulas of the reactants and products with nothing to indicate the relative amounts.

11.3 Balancing Equations

- Balance chemical equations when given the skeleton information.

Any Leftovers?

When you cook a meal, quite often there are leftovers because you prepared more than people would eat at one sitting. Sometimes when you repair a piece of equipment, you end up with what are called "pocket parts", small pieces you put in your pocket because you're not sure where they belong. Chemistry tries to avoid leftovers and pocket parts. In normal chemical processes, we cannot create or destroy matter (law of conservation of mass). If we start out with ten carbon atoms, we need to end up with ten carbon atoms. John Dalton' atomic theory said that chemical reactions basically involve the rearrangement of atoms. Chemical equations need to follow these principles in order to be correct.

Balancing Chemical Equations

A **balanced equation** is a chemical equation in which mass is conserved and there are equal numbers of atoms of each element on both sides of the equation. We can write a chemical equation for the reaction of carbon with hydrogen gas to form methane (CH_4).

$$\begin{array}{ccccc} C(s) & + & H_2(g) & \rightarrow & CH_4(g) \\ \text{2 C atoms} & & \text{2 H atoms} & & \text{1 C atom, 4 H atoms} \end{array}$$

In order to write a correct equation, you must first write the correct skeleton equation with the correct chemical formulas. Recall that hydrogen is a diatomic molecule and so is written as H_2.

When we count the number of atoms of both elements, shown under the equation, we see that the equation is not balanced. There are only 2 atoms of hydrogen on the reactant side of the equation, while there are 4 atoms of hydrogen on the product side. We can balance the above equation by adding a coefficient of 2 in front of the formula for hydrogen.

$$\mathrm{C}(s)+2\mathrm{H}_2(g) \rightarrow \mathrm{CH}_4(g)$$

A **coefficient** is a small whole number placed in front of a formula in an equation in order to balance it. The 2 in front of the H_2 means that there are a total of $2 \times 2 = 4$ atoms of hydrogen as reactants. Visually, the reaction looks like:

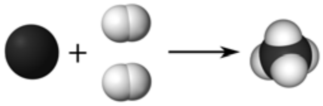


FIGURE 11.3

Reaction between carbon and hydrogen to form methane.

In the balanced equation, there is one atom of carbon and four atoms of hydrogen on both sides of the arrow. Below are guidelines for writing and balancing chemical equations.

1. Determine the correct chemical formulas for each reactant and product.
2. Write the skeleton equation.
3. Count the number of atoms of each element that appears as a reactant and as a product. If a polyatomic ion is unchanged on both sides of the equation, count it as a unit.
4. Balance each element on at a time by placing coefficients in front of the formulas. No coefficient is written for a 1. It is best to begin by balancing elements that only appear in one formula on each side of the equation. NEVER change the subscripts in a chemical formula – you can only balance equations by using coefficients.
5. Check each atom or polyatomic ion to be sure that they are equal on both sides of the equation.
6. Make sure that all coefficients are in the lowest possible ratio. If necessary, reduce to the lowest ratio.

Sample Problem: Balancing Chemical Equations

Aqueous solutions of lead(II) nitrate and sodium chloride are mixed. The products of the reaction are an aqueous solution of sodium nitrate and a solid precipitate of lead(II) chloride.

Step 1: Plan the problem.

Follow the steps for writing and balancing a chemical equation.

Step 2: Solve.

Write the skeleton equation with the correct formulas.

$$\mathrm{Pb(NO_3)_2}(aq)+\mathrm{NaCl}(aq) \rightarrow \mathrm{NaNO_3}(aq)+\mathrm{PbCl_2}(s)$$

Count the number of each atom or polyatomic ion on both sides of the equation.

TABLE 11.2:

reactants	products
1 Pb atom	1 Pb atom
2 NO_3^- ions	1 NO_3^- ions
1 Na atom	1 Na atom
1 Cl atom	2 Cl atoms

The nitrate ions and the chlorine atoms are unbalanced. Start by placing a 2 in front of the NaCl. This increases the reactant counts to 2 Na atoms and 2 Cl atoms. Then place a 2 in front of the $NaNO_3$. The result is:

$$Pb(NO_3)_2(aq) + 2NaCl(aq) \rightarrow 2NaNO_3(aq) + PbCl_2(s)$$

The new count for each atom and polyatomic ion becomes:

TABLE 11.3:

reactants	products
1 Pb atom	1 Pb atom
2 NO_3^- ions	2 NO_3^- ions
2 Na atom	2 Na atom
2 Cl atoms	2 Cl atoms

Step 3: Think about your result.

The equation is now balanced since there are equal numbers of atoms of each element on both sides of the equation.

Summary

- The process of balancing chemical equations is described.

Practice

Get some experience in balancing chemical equations at the following web site:

http://www.sciencegeek.net/APchemistry/APtaters/EquationBalancing.htm

Review

1. What is the law of conservation of mass?
2. How did Dalton describe he profess of a chemical reaction?
3. Why don't we change the subscripts in order to balance an equation?

- **balanced equation:** A chemical equation in which mass is conserved and there are equal numbers of atoms of each element on both sides of the equation.
- **coefficient:** A small whole number placed in front of a formula in an equation in order to balance it.

11.4 Combination Reactions

- Define combination reaction.
- Write products of combination reactions when given the reactants.

Wheel Rim

Car Tire

How useful is a wheel rim?

A wheel rim is not very useful by itself. Driving on the rim can damage it and make for a very rough ride. When the rim is combined with a tire, the product can be put on a car and used for a safe and comfortable ride. The two separate items have combined to make something that improves the car ride.

Combination Reactions

A **combination reaction** is a reaction in which two or more substances combine to form a single new substance. Combination reactions can also be called synthesis reactions. The general form of a combination reaction is:

$$A + B \rightarrow AB$$

One combination reaction is two elements combining to form a compound. Solid sodium metal reacts with chlorine gas to produce solid sodium chloride.

$$2\text{Na}(s) + \text{Cl}_2(g) \rightarrow 2\text{NaCl}(s)$$

Notice that in order to write and balance the equation correctly, it is important to remember the seven elements that exist in nature as diatomic molecules (H_2, N_2, O_2, F_2, Cl_2, Br_2, and I_2).

One sort of combination reaction that occurs frequently is the reaction of an element with oxygen to form an oxide. Metals and nonmetals both react readily with oxygen under most conditions. Magnesium reacts rapidly and dramatically when ignited, combining with oxygen from the air to produce a fine powder of magnesium oxide.

$$2\text{Mg}(s) + \text{O}_2(g) \rightarrow 2\text{MgO}(s)$$

This reaction can be seen in the following video: http://www.youtube.com/watch?v=NnFzHt6l4z8 (0:37).

MEDIA

Click image to the left for more content.

Sulfur reacts with oxygen to form sulfur dioxide.

$$\mathrm{S}(s)+\mathrm{O_2}(g)\rightarrow \mathrm{SO_2}(g)$$

When nonmetals react with one another, the product is a molecular compound. Often, the nonmetal reactants can combine in different ratios and produce different products. Sulfur can also combine with oxygen to produce sulfur trioxide.

$$2\mathrm{S}(s)+3\mathrm{O_2}(g)\rightarrow 2\mathrm{SO_3}(g)$$

Transition metals are capable of adopting multiple positive charges within their ionic compounds. Therefore, most transition metals are capable of forming different products in a combination reaction. Iron reacts with oxygen to form both iron(II) oxide and iron(III) oxide.

$$2\mathrm{Fe}(s)+\mathrm{O_2}(g)\rightarrow 2\mathrm{FeO}(s)$$
$$4\mathrm{Fe}(s)+3\mathrm{O_2}(g)\rightarrow 2\mathrm{Fe_2O_3}(s)$$

Sample Problem: Combination Reactions

Potassium is a very reactive alkali metal that must be stored under oil in order to prevent it from reacting with air. Write the balanced chemical equation for the combination reaction of potassium with oxygen.

Step 1: Plan the problem

Make sure formulas of all reactants and products are correct before balancing the equation. Oxygen gas is a diatomic molecule. Potassium oxide is an ionic compound and so its formula is constructed by the crisscross method. Potassium as an ion becomes $\mathrm{K^+}$, while the oxide ion is $\mathrm{O^{2-}}$.

Step 2: Solve

The skeleton (unbalanced) equation:

$$K(s)+O_2(g)\rightarrow K_2O(s)$$

The equation is then easily balanced with coefficients.

$$4\mathrm{K}(s)+\mathrm{O_2}(g)\rightarrow 2\mathrm{K_2O}(s)$$

Step 3: Think about your result

Formulas are correct and the resulting combination reaction is balanced.

Combination reactions can also take place when an element reacts with a compound to form a new compound composed of a larger number of atoms. Carbon monoxide reacts with oxygen to form carbon dioxide according to the equation:

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$

Two compounds may also react to from a more complex compound. A very common example is the reactions of oxides with water. Calcium oxide reacts readily with water to produce an aqueous solution of calcium hydroxide.

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

Sulfur trioxide gas reacts with water to form sulfuric acid. This is an unfortunately common reaction that occurs in the atmosphere in some places where oxides of sulfur are present as pollutants. The acid formed in the reaction falls to the ground as acid rain.

$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$$

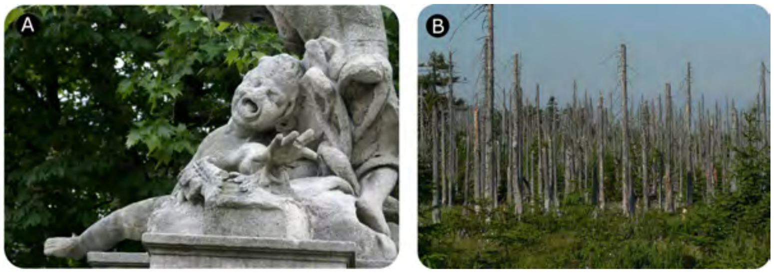


FIGURE 11.4

Acid rain has severe consequences on both natural and man-made objects. Acid rain degrades marble statues like the one on the left (A). The trees in the forest on the right (B) have been killed by acid rain.

Summary

- Combination reactions occur when two or more substances combine to form a new substance.

Practice

Complete the reactions and balance the equations on the worksheet at the link below:

http://www.sciencegeek.net/Chemistry/chempdfs/EquationsWorksheet2.pdf

Review

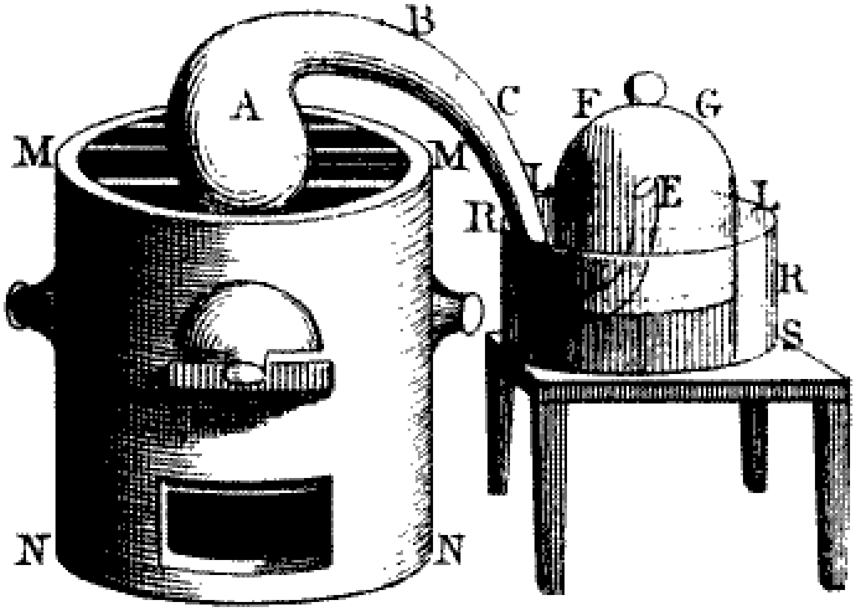
1. What are combination reactions?
2. Write the product of the following reaction: $Mg + H_2O \rightarrow$

3. Is $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ a combination reaction? Explain your answer.

- **combination reaction:** A reaction in which two or more substances combine to form a single new substance.

11.5 Decomposition Reactions

- Define decomposition reaction.
- Write the products of decomposition reactions when given the reactant.
- Write the reactant of a decomposition reaction when given the products.



Antoine Lavoisier is widely known as the "father of modern chemistry". He was one of the first to study chemical reactions in detail. Lavoisier reacted mercury with oxygen to form mercuric oxide as part of his studies on the composition of the atmosphere. He was then able to show that the decomposition of mercuric oxide produced mercury and oxygen. The diagram above shows the apparatus used by Lavoisier to study the formation and decomposition of mercuric oxide.

Decomposition Reactions

A **decomposition reaction** is a reaction in which a compound breaks down into two or more simpler substances. The general form of a decomposition reaction is:

$$AB \rightarrow A + B$$

Most decomposition reactions require an input of energy in the form of heat, light, or electricity.

Binary compounds are compounds composed of just two elements. The simplest kind of decomposition reaction is when a binary compound decomposes into its elements. Mercury(II) oxide, a red solid, decomposes when heated to produce mercury and oxygen gas.

$$2\text{HgO}(s) \rightarrow 2\text{Hg}(l) + \text{O}_2(g)$$

FIGURE 11.5

Mercury(II) oxide is a red solid. When it is heated, it decomposes into mercury metal and oxygen gas.

A reaction is also considered to be a decomposition reaction even when one or more of the products are still compounds. A metal carbonate decomposes into a metal oxide and carbon dioxide gas. For example, calcium carbonate decomposes into calcium oxide and carbon dioxide.

$$\mathrm{CaCO_3}(s) \rightarrow \mathrm{CaO}(s) + \mathrm{CO_2}(g)$$

Metal hydroxides decompose on heating to yield metal oxides and water. Sodium hydroxide decomposes to produce sodium oxide and water.

$$2\mathrm{NaOH}(s) \rightarrow \mathrm{Na_2O}(s) + \mathrm{H_2O}(g)$$

Some unstable acids decompose to produce nonmetal oxides and water. Carbonic acid decomposes easily at room temperature into carbon dioxide and water.

$$\mathrm{H_2CO_3}(aq) \rightarrow \mathrm{CO_2}(g) + \mathrm{H_2O}(l)$$

Sample Problem: Decomposition Reactions

When an electric current is passed through pure water, it decomposes into its elements. Write a balanced equation for the decomposition of water.

Step 1: Plan the problem

Water is a binary compound composed of hydrogen and oxygen. The hydrogen and oxygen gases produced in the reaction are both diatomic molecules.

Step 2: Solve

The skeleton (unbalanced) equation:

$$\mathrm{H_2O}(l) \overset{\text{elec}}{\rightarrow} \mathrm{H_2}(g) + \mathrm{O_2}(g)$$

Note the abbreviation “elec” above the arrow to indicate the passage of an electric current to initiate the reaction. Balance the equation.

$$2H_2O(l) \overset{\text{elec}}{\rightarrow} 2H_2(g) + O_2(g)$$

Step 3: Think about your result

The products are elements and the equation is balanced.

Summary

- A definition of decomposition reaction and example reactions are given.

Practice

Write the reactions (including names and balanced equations) as requested on the following web site:

http://www.sciencegeek.net/Chemistry/chempdfs/EquationsWorksheet3.pdf

Review

1. What is a decomposition reaction?
2. What is usually needed for a decomposition reaction to take place?
3. Are elements always the product of a decomposition reaction?

- **decomposition reaction:** A reaction in which a compound breaks down into two or more simpler substances.

11.6 Combustion Reaction

- Define combustion reaction.
- Write the products of combustion reactions when given the starting materials.

How do you cook the perfect marshmallow?

Roasting marshmallows over an open fire is a favorite past-time for campers, outdoor cook-outs, and just gathering around a fire in the back yard. The trick is to get the marshmallow a nice golden brown without catching it on fire. Too often we are not successful and we see the marshmallow burning on the stick – a combustion reaction taking place right in front of us.

Combustion Reactions

A **combustion reaction** is a reaction in which a substance reactants with oxygen gas, releasing energy in the form of light and heat. Combustion reactions must involve O_2 as one reactant. The combustion of hydrogen gas produces water vapor.

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$$

Notice that this reaction also qualifies as a combination reaction.

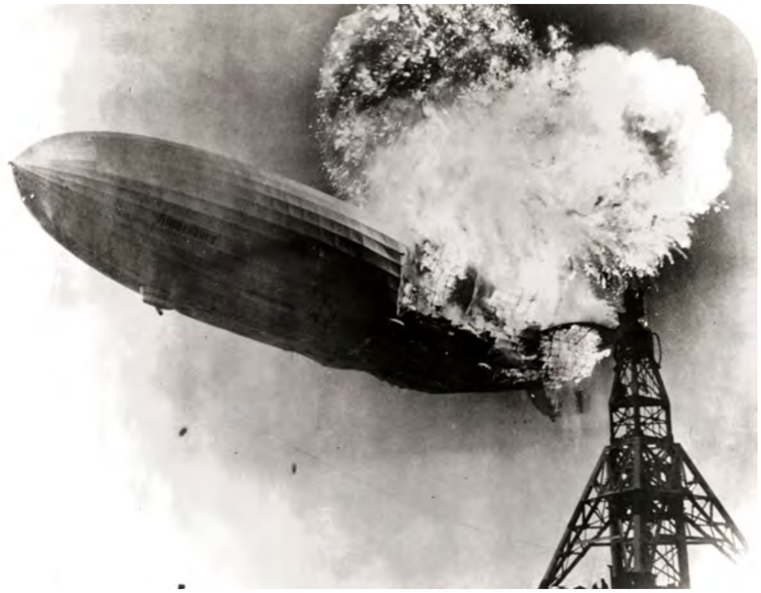


FIGURE 11.6

Explosion of the Hindenberg.

The Hindenburg was a hydrogen-filled airship that suffered an accident upon its attempted landing in New Jersey in 1937. The hydrogen immediately combusted in a huge fireball, destroying the airship and killing 36 people. The chemical reaction was a simple one: hydrogen combining with oxygen to produce water.

Many combustion reactions occur with a hydrocarbon, a compound made up solely of carbon and hydrogen. The products of the combustion of hydrocarbons are carbon dioxide and water. Many hydrocarbons are used as fuel because their combustion releases very large amounts of heat energy. Propane (C_3H_8) is a gaseous hydrocarbon that is commonly used as the fuel source in gas grills.

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$$

Practice Problem: Combustion Reactions

Ethanol can be used as a fuel source in an alcohol lamp. The formula for ethanol is C_2H_5OH. Write the balanced equation for the combustion of ethanol.

Step 1: Plan the problem

Ethanol and oxygen are the reactants. As with a hydrocarbon, the products of the combustion of an alcohol are carbon dioxide and water.

Step 2: Solve

Write the skeleton equation:

$$C_2H_5OH(l) + O_2(g) \rightarrow CO_2(g) + H_2O(g)$$

Balance the equation.

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$$

Step 3: Think about your result

Combustion reactions must have oxygen as a reactant. Note that the water that is produced is in the gas rather than the liquid state because of the high temperatures that accompany a combustion reaction.

Summary

- Combustion reaction is defined and examples are given.

Practice

Write the reactions and balance the equations for the questions on the sheet found on this web site:

http://www.sciencegeek.net/Chemistry/chempdfs/EquationsWorksheet6.pdf

Review

1. What is needed for a combustion reaction to take place?
2. What is formed in any combustion reaction?
3. Mercury reacts with oxygen to form mercuric oxide. Is this a combustion reaction?
4. What are the products of any combustion reaction involving a hydrocarbon?

- **combustion reaction:** A reaction in which a substance reactants with oxygen gas, releasing energy in the form of light and heat.

11.7 Single-Replacement Reactions

- Define single-replacement reaction.
- Give examples of single-displacement reactions.

Why is the silver dark?

The cup shown above provides an example of tarnish, a chemical reaction caused when silver metal reacts with hydrogen sulfide gas produced by some industrial processes or as a result of decaying animal or plant materials:

$$\mathrm{Ag} + \mathrm{H_2S} \rightarrow \mathrm{AgS} + \mathrm{H_2}$$

The tarnish can be removed using a number of polishes, but the process also removes a small amount of silver along with the tarnish.

Single-Replacement Reactions

A **single-replacement reaction** is a reaction in which one element replaces a similar element in a compound. The general form of a single-replacement (also called single-displacement) reaction is:

$$A + BC \rightarrow AC + B$$

In this general reaction, element A is a metal and replaces element B, also a metal, in the compound. When the element that is doing the replacing is a nonmetal, it must replace another nonmetal in a compound, and the general equation becomes:

$$Y + XZ \rightarrow XY + Z$$

Y is a nonmetal and replaces the nonmetal Z in the compound with X.

Metal Replacement

Magnesium is a more reactive metal than copper. When a strip of magnesium metal is placed in an aqueous solution of copper(II) nitrate, it replaces the copper. The products of the reaction are aqueous magnesium nitrate and solid copper metal.

$$\text{Mg}(s) + \text{Cu(NO}_3)_2(aq) \rightarrow \text{Mg(NO}_3)_2(aq) + \text{Cu}(s)$$

This subcategory of single-replacement reactions is called a metal replacement reaction because it is a metal that is being replaced (zinc).

Hydrogen Replacement

Many metals react easily with acids and when they do so, one of the products of the reaction is hydrogen gas. Zinc reacts with hydrochloric acid to produce aqueous zinc chloride and hydrogen (**Figure** 11.7).

$$\text{Zn}(s) + 2\text{HCl}(aq) \rightarrow \text{ZnCl}_2(aq) + \text{H}_2(g)$$

In a hydrogen replacement reaction, the hydrogen in the acid is replaced by an active metal.

Some metals are so reactive that they are capable of replacing the hydrogen in water. The products of such a reaction are the metal hydroxide and hydrogen gas. All group 1 metals undergo this type of reaction. Sodium reacts vigorously with water to produce aqueous sodium hydroxide and hydrogen (see **Figure** 11.8).

$$2\text{Na}(s) + 2\text{H}_2\text{O}(l) \rightarrow 2\text{NaOH}(aq) + \text{H}_2(g)$$

Halogen Replacement

The element chlorine reacts with an aqueous solution of sodium bromide to produce aqueous sodium chloride and elemental bromine.

$$\text{Cl}_2(g) + 2\text{NaBr}(aq) \rightarrow 2\text{NaCl}(aq) + \text{Br}_2(l)$$

The reactivity of the halogen group (group 17) decreases from top to bottom within the group. Fluorine is the most reactive halogen, while iodine is the least. Since chlorine is above bromine, it is more reactive than bromine and can replace it in a halogen replacement reaction.

FIGURE 11.7

Zinc metal reacts with hydrochloric acid to give off hydrogen gas in a single-displacement reaction.

FIGURE 11.8

Sodium metal reacts vigorously with water, giving off hydrogen gas. A large piece of sodium will often generate so much heat that the hydrogen will ignite.

Summary

- The activity series describes the relative reactivities of metals and halogens.

Practice

Read the material at the link below and do the practice problems:

http://www.chemteam.info/Equations/SingleReplacement.html

Review

1. What is a metal replacement reaction?
2. Will a non-metal replace a metal?
3. What is the most reactive halogen?
4. What products will I get if I add potassium metal to water?

- **single-replacement reaction:** A reaction in which one element replaces a similar element in a compound.

11.8 Activity Series

- Define activity series.
- Use the activity series to predict the outcome of reactions.

What's the difference between the above two pictures?

We see above two metals that can be exposed to water. The picture on the left is of sodium, which gives a violent reaction when it comes in contact with water. The picture on the right is of silver, a metal so unreactive with water that it can be made into drinking vessels. Both metals have a single s electron in their outer shell, so you would predict similar reactivities. However, we have a better tool that allows us to make better prediction about what will react with what.

The Activity Series

Single-replacement reactions only occur when the element that is doing the replacing is more reactive than the element that is being replaced. Therefore, it is useful to have a list of elements in order of their relative reactivities. The **activity series** is a list of elements in decreasing order of their reactivity. Since metals replace other metals, while nonmetals replace other nonmetals, they each have a separate activity series. The **Table** 11.4 is an activity series of most common metals and of the halogens.

TABLE 11.4: **Activity Series**

Activity of Metals	Activity of Halogens
Li K React with cold water, replacing Ba hydrogen. Sr Ca Na	F_2 Cl_2 Br_2 I_2
Mg Al React with steam, but not cold Zn water, replacing hydrogen. Cr Fe Cd	

TABLE 11.4: (continued)

Co Ni Sn Pb Do not react with water. React with acids, replacing hydrogen.	
H_2	
Cu Hg Ag Pt Au Unreactive with water or acids.	

For a single-replacement reaction, a given element is capable of replacing an element that is below it in the activity series. This can be used to predict if a reaction will occur. Suppose that small pieces of the metal nickel were placed into two separate aqueous solutions: one of iron(III) nitrate and one of lead(II) nitrate. Looking at the activity series, we see that nickel is below iron, but above lead. Therefore, the nickel metal will be capable of replacing the lead in a reaction, but will not be capable of replacing iron.

$$\begin{aligned}&\text{Ni}(s)+\text{Pb(NO}_3)_2(aq)\rightarrow\text{Ni(NO}_3)_2(aq)+\text{Pb}(s)\\&\text{Ni}(s)+\text{Fe(NO}_3)_3(aq)\rightarrow\text{NR (no reaction)}\end{aligned}$$

In the descriptions that accompany the activity series of metals, a given metal is also capable of undergoing the reactions described below that section. For example, lithium will react with cold water, replacing hydrogen. It will also react with steam and with acids, since that requires a lower degree of reactivity.

Sample Problem: Single-Replacement Reactions

Use the activity series to predict if the following reactions will occur. If not, write NR. If the reaction does occur, write the products of the reaction and balance the equation.

A. $\text{Al}(s)+\text{Zn(NO}_3)_2(aq)\rightarrow$

B. $\text{Ag}(s)+\text{HCl}(aq)\rightarrow$

Step 1: Plan the problem

For A, compare the placements of aluminum and zinc on the activity series. For B, compare the placements of silver and hydrogen.

Step 2: Solve

Since aluminum is above zinc, it is capable of replacing it and a reaction will occur. The products of the reaction will be aqueous aluminum nitrate and solid zinc. Take care to write the correct formulas for the products before balancing the equation. Aluminum adopts a 3+ charge in an ionic compound, so the formula for aluminum nitrate is $\text{Al(NO}_3)_3$. The balanced equation is:

$$2\text{Al}(s)+3\text{Zn(NO}_3)_2(aq)\rightarrow2\text{Al(NO}_3)_3(aq)+3\text{Zn}(s)$$

Since silver is below hydrogen, it is not capable of replacing hydrogen in a reaction with an acid.

$$\text{Ag}(s) + \text{HCl}(aq) \rightarrow \text{NR}$$

Summary

- Metals and halogens are ranked according to their ability to displacement other metals or halogens below them in the series.

Practice

Take the quiz on the web site below:

http://www.sophia.org/chemical-reactions-activity-series-concept

Review

1. What does the activity series tell us?
2. Can a metal undergo any of the reactions listed below it in the series?
3. List two metals that cobalt will displace and tow that will displace it.

- **activity series:** A list of elements in decreasing order of their reactivity.

11.9 Double-Replacement Reactions

- Define double-replacement reaction.
- Predict products of double-replacement reactions when given the reactants.

THE COUNTRY EDITOR—PAYING THE YEARLY SUBSCRIPTION.—[DRAWN BY F. S. CHURCH.]

Wanna swap?

The practice of barter (trading one thing for another) has been in existence from the beginning of time. In the illustration above, Items like chickens were bartered for newspapers. You have something I want, and I have something you want. So we trade and we each have something new. Some chemical reactions are like that. Compounds swap parts and you have new materials.

Double-Replacement Reactions

A **double-replacement reaction** is a reaction in which the positive and negative ions of two ionic compounds exchange places to form two new compounds. The general form of a double-replacement (also called double-displacement) reaction is:

$$AB + CD \rightarrow AD + CB$$

In this reaction, A and C are positively-charged cations, while B and D are negatively-charged anions. Double-replacement reactions generally occur between substances in aqueous solution. In order for a reaction to occur, one of the products is usually a solid precipitate, a gas, or a molecular compound such as water.

Formation of a Precipitate

A precipitate forms in a double-replacement reaction when the cations from one of the reactants combine with the anions from the other reactant to form an insoluble ionic compound. When aqueous solutions of potassium iodide and lead(II) nitrate are mixed, the following reaction occurs.

$$2\mathrm{KI}(aq) + \mathrm{Pb(NO_3)_2}(aq) \rightarrow 2\mathrm{KNO_3}(aq) + \mathrm{PbI_2}(s)$$

There are very strong attractive forces that occur between Pb^{2+} and I^- ions and the result is a brilliant yellow precipitate (see **Figure** 11.9). The other product of the reaction, potassium nitrate, remains soluble.

FIGURE 11.9

Formation of lead iodide precipitate.

Formation of a Gas

Some double-replacement reactions produce a gaseous product which then bubbles out of the solution and escapes into the air. When solutions of sodium sulfide and hydrochloric acid are mixed, the products of the reaction are aqueous sodium chloride and hydrogen sulfide gas.

$$\mathrm{Na_2S}(aq) + 2\mathrm{HCl}(aq) \rightarrow 2\mathrm{NaCl}(aq) + \mathrm{H_2S}(g)$$

Formation of a Molecular Compound

Another kind of double-replacement reaction is one that produces a molecular compound as one of its products. Many examples in this category are reactions that produce water. When aqueous hydrochloric acid is reacted with aqueous sodium hydroxide, the products are aqueous sodium chloride and water.

$$\mathrm{HCl}(aq) + \mathrm{NaOH}(aq) \rightarrow \mathrm{NaCl}(aq) + \mathrm{H_2O}(l)$$

Sample Problem: Double-Replacement Reactions

Write a complete and balanced chemical equation for the following double-replacement reactions. One product is indicated as a guide.

A. $\mathrm{NaCN}(aq)+\mathrm{HBr}(aq)\rightarrow$ (hydrogen cyanide gas is formed)

B. $\mathrm{(NH_4)_2SO_4}(aq)+\mathrm{Ba(NO_3)_2}(aq)\rightarrow$ (a precipitate of barium sulfate forms)

Step 1: Plan the problem

In A, the production of a gas drives the reaction. In B, the production of a precipitate drives the reaction. In both cases, use the ionic charges of both reactants to construct the correct formulas of the products.

Step 2: Solve

A. The cations of both reactants are +1 charged ions, while the anions are -1 charged ions. After exchanging partners, the balanced equation is:

$$\mathrm{NaCN}(aq)+\mathrm{HBr}(aq)\rightarrow\mathrm{NaBr}(aq)+\mathrm{HCN}(g)$$

B. Ammonium ion and nitrate ion are 1+ and 1− respectively, while barium and sulfate are 2+ and 2−. This must be taken into account when exchanging partners and writing the new formulas. Then, the equation is balanced.

$$\mathrm{(NH_4)_2SO_4}(aq)+\mathrm{Ba(NO_3)_2}(aq)\rightarrow 2\mathrm{NH_4NO_3}(aq)+\mathrm{BaSO_4}(s)$$

Step 3: Think about your result

Both are double-replacement reactions. All formulas are correct and the equations are balanced. Occasionally, a reaction will produce both a gas and a molecular compound. The reaction of a sodium carbonate solution with hydrochloric acid produces aqueous sodium chloride, carbon dioxide gas, and water.

$$\mathrm{Na_2CO_3}(aq)+2\mathrm{HCl}(aq)\rightarrow 2\mathrm{NaCl}(aq)+\mathrm{CO_2}(g)+\mathrm{H_2O}(l)$$

Summary

- The double-replacement reaction is described.
- Examples of the double-replacement reaction are shown.

Practice

Read the material at the web site below and do the practice problems:

http://www.chemteam.info/Equations/DoubleReplacement.html

Review

1. What are the usual reactants in a double-replacement reaction?
2. List the three possible types of products.
3. Why would you not expect two ionic products?

- **double-replacement reaction:** A reaction in which the positive and negative ions of two ionic compounds exchange places to form two new compounds.

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CHAPTER 12

Stoichiometry

Chapter Outline

12.1 Everyday Stoichiometry

- Define stoichiometry.
- Describe everyday applications of the concept of stoichiometry.

How much equipment do you need for an experiment?

You are in charge of setting out the lab equipment for a chemistry experiment. If you have twenty students in the lab (and they will be working in teams of two) and the experiment calls for three beakers and two test tubes, how much glassware do you need to set out? Figuring this out involves a type of balanced equation and the sort of calculations you would do for a chemical reaction.

Everyday Stoichiometry

You have learned about chemical equations and the techniques used in order to balance them. Chemists use balanced equations to allow them to manipulate chemical reactions in a quantitative manner. Before we look at a chemical reaction, let's consider the equation for the ideal ham sandwich.

FIGURE 12.1

The ideal ham sandwich.

Our ham sandwich is composed of 2 slices of ham (H), a slice of cheese (C), a slice of tomato (T), 5 pickles (P), and 2 slices of bread (B). The equation for our sandwich is shown below:

$$2\text{H}+\text{C}+\text{T}+5\text{P}+2\text{B} \rightarrow \text{H}_2\text{CTP}_5\text{B}_2$$

Now let us suppose that you are having some friends over and need to make five ham sandwiches. How much of each sandwich ingredient do you need? You would take the number of each ingredient required for one sandwich (its coefficient in the above equation) and multiply by five. Using ham and cheese as examples and using a conversion factor, we can write:

$$5\text{H}_2\text{CTP}_5\text{B}_2 \times \frac{2\ \text{H}}{1\ \text{H}_2\text{CTP}_5\text{B}_2} = 10\ \text{H}$$

$$5\text{H}_2\text{CTP}_5\text{B}_2 \times \frac{1\ \text{C}}{1\ \text{H}_2\text{CTP}_5\text{B}_2} = 5\ \text{C}$$

The conversion factors contain the coefficient of each specific ingredient as the numerator and the formula of on sandwich as the denominator. The result is what you would expect. In order to make five ham sandwiches, you would need 10 slices of ham and 5 slices of cheese.

This type of calculation demonstrates the use of stoichiometry. **Stoichiometry** is the calculation of amounts of substances in a chemical reaction from the balanced equation. The sample problem below is another stoichiometry problem involving ingredients of the ideal ham sandwich.

Sample Problem: Ham Sandwich Stoichiometry

Kim looks in the refrigerator and finds that she has 8 slices of ham. In order to make as many sandwiches as possible, how many pickles does she need? Use the equation above.

Step 1: List the known quantities and plan the problem.

Known

- have 8 ham slices (H)

- 2 H = 5 P (conversion factor)

Unknown

- How many pickles (P) needed?

The coefficients for the two reactants (ingredients) are used to make a conversion factor between ham slices and pickles.

Step 2: Solve.

$$8\ H \times \frac{5\ P}{2\ H} = 20\ P$$

Since 5 pickles combine with 2 ham slices in each sandwich, 20 pickles are needed to fully combine with 8 ham slices.

Step 3: Think about your result.

The 8 ham slices will make 4 ham sandwiches. With 5 pickles per sandwich, the 20 pickles are used in the 4 sandwiches.

Summary

- An example of everyday stoichiometry is given.

Practice

Use the link below to answer the following questions:

http://www.chem4kids.com/files/react_stoichio.html

1. What does stoichiometry help you figure out?
2. What are all reactions dependent upon?
3. If I have ten hydrogen molecules and three oxygen molecules, how many molecules of water can I make?
4. What will be left over and how much?

Review

1. I don’t like pickles. What would my ideal ham sandwich be?
2. How does that change the equation?
3. Will this change affect the amounts of other materials?

- **stoichiometry:** The calculation of amounts of substances in a chemical reaction from the balanced equation.

12.2 Mole Ratios

- Define mole ratio.
- Use mole ratios to determine amounts of materials involved in a reaction.

What does this porch need?

You want to add some sections to the porch seen above. Before you go to the hardware store to buy lumber, you need to determine the unit composition (the material between two large uprights). You count how many posts, how many boards, how many rails – then you decide how many sections you want to add before you calculate the amount of building material needed for your porch expansion.

Mole Ratios

Stoichiometry problems can be characterized by two things: (1) the information *given* in the problem, and (2) the information that is to be solved for, referred to as the *unknown*. The given and the unknown may both be reactants, both be products, or one may be a reactant while the other is a product. The amounts of the substances can be expressed in moles. However, in a laboratory situation, it is common to determine the amount of a substance by finding its mass in grams. The amount of a gaseous substance may be expressed by its volume. In this lesson, we will focus on the type of problem where both the given and the unknown quantities are expressed in moles.

Chemical equations express the amounts of reactants and products in a reaction. The coefficients of a balanced equation can represent either the number of molecules or the number of moles of each substance. The production of ammonia (NH_3) from nitrogen and hydrogen gases is an important industrial reaction called the Haber process, after German chemist Fritz Haber.

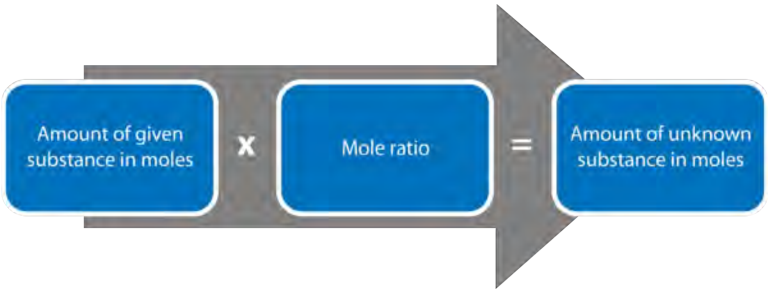
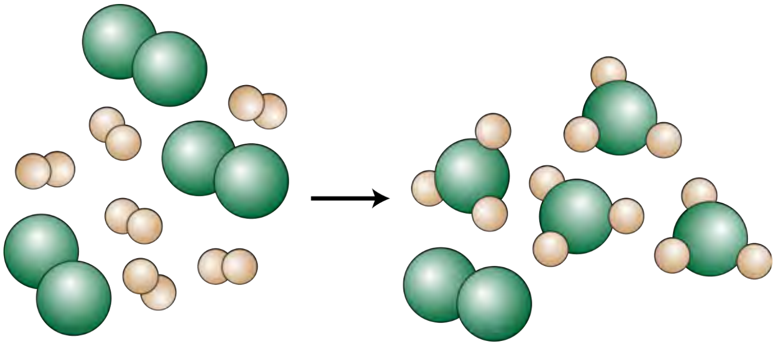


FIGURE 12.2

Mole ratio relationship.

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

The balanced equation can be analyzed in several ways, as shown in the **Figure** 12.3.



	Reactants		Products
Before reaction	3 mol N_2	6 mol H_2	0 mol NH_3
After reaction	1 mol N_2	0 mol H_2	4 mol NH_3

FIGURE 12.3

This representation of the production of ammonia from nitrogen and hydrogen show several ways to interpret the quantitative information of a chemical reaction.

We see that 1 molecule of nitrogen reacts with 3 molecules of nitrogen to form 2 molecules of ammonia. This is the smallest possible relative amounts of the reactants and products. To consider larger relative amounts, each coefficient can be multiplied by the same number. For example, 10 molecules of nitrogen would react with 30 molecules of hydrogen to produce 20 molecules of ammonia.

The most useful quantity for counting particles is the mole. So if each coefficient is multiplied by a mole, the balanced chemical equation tells us that 1 mole of nitrogen reacts with 3 moles of hydrogen to produce 2 moles of ammonia. This is the conventional way to interpret any balanced chemical equation.

Finally, if each mole quantity is converted to grams by using the molar mass, we can see that the law of conservation of mass is followed. 1 mol of nitrogen has a mass of 28.02 g, while 3 mol of hydrogen has a mass of 6.06 g, and 2 mol of ammonia has a mass of 34.08 g.

$$28.02 \text{ g } N_2 + 6.06 \text{ g } H_2 \rightarrow 34.08 \text{ g } NH_3$$

Mass and the number of atoms must be conserved in any chemical reaction. The number of molecules is not necessarily conserved.

FIGURE 12.4

Apparatus for running Haber process.

A **mole ratio** is a conversion factor that relates the amounts in moles of any two substances in a chemical reaction. The numbers in a conversion factor come from the coefficients of the balanced chemical equation. The following six mole ratios can be written for the ammonia forming reaction above.

$$\frac{1 \text{ mol } N_2}{3 \text{ mol } H_2} \quad or \quad \frac{3 \text{ mol } H_2}{1 \text{ mol } N_2}$$

$$\frac{1 \text{ mol } N_2}{2 \text{ mol } NH_3} \quad or \quad \frac{2 \text{ mol } NH_3}{1 \text{ mol } N_2}$$

$$\frac{3 \text{ mol } H_2}{2 \text{ mol } NH_3} \quad or \quad \frac{2 \text{ mol } NH_3}{3 \text{ mol } H_2}$$

In a mole ratio problem, the given substance, expressed in moles, is written first. The appropriate conversion factor is chosen in order to convert from moles of the given substance to moles of the unknown.

Sample Problem: Mole Ratio

How many moles of ammonia are produced if 4.20 moles of hydrogen are reacted with an excess of nitrogen?

Step 1: List the known quantities and plan the problem.

Known

- given: H_2 = 4.20 mol

Unknown

- mol of NH_3

The conversion is from mol $H_2 \rightarrow NH_3$. The problem states that there is an excess of nitrogen, so we do not need to be concerned with any mole ratio involving N_2. Choose the conversion factor that has the NH_3 in the numerator and the H_2 in the denominator.

Step 2: Solve.

$$4.20 \text{ mol H}_2 \times \frac{2 \text{ mol NH}_3}{3 \text{ mol H}_2} = 2.80 \text{ mol NH}_3$$

The reaction of 4.20 mol of hydrogen with excess nitrogen produces 2.80 mol of ammonia.

Step 3: Think about your result.

The result corresponds to the 3:2 ratio of hydrogen to ammonia from the balanced equation.

Summary

- Mole ratios allow comparison of the amounts of any two materials in a balanced equation.
- Calculations can be made to predict how much product can be obtained from a given number of moles of reactant.

Practice

Do problems 1-4 at the link below:

http://myweb.astate.edu/mdraganj/Moles1.html

Review

1. If a reactant is in excess, why do we not worry about the mole ratios involving that reactant?
2. What is the mole ratio of H to N in the ammonia molecule?
3. The formula for ethanol is CH_3CH_2OH. What is the mole ratio of H to C in this molecule?

- **mole ratio:** A conversion factor that relates the amounts in moles of any two substances in a chemical reaction.

12.3 Mass-Mole and Mole-Mass Stoichiometry

- Perform calculations involving conversions of mass to moles.
- Perform calculations involving conversion of moles to mass.

Need nails?

When you are doing a large construction project, you have a good idea of how many nails you will need (lots!). When you go to the hardware store, you don't want to sit there and count out several hundred nails. You can buy nails by weight, so you determine how many nails are in a pound, calculate how many pounds you need, and you're on your way to begin building.

While the mole ratio is ever-present in all stoichiometry calculations, amounts of substances in the laboratory are most often measured by mass. Therefore, we need to use mole-mass calculations in combination with mole ratios to solve several different types of mass-based stoichiometry problems.

Mass to Moles Problems

In this type of problem, the mass of one substance is given, usually in grams. From this, you are to determine the amount in moles of another substance that will either react with or be produced from the given substance.

$$\text{mass of } \textit{given} \rightarrow \text{moles of } \textit{given} \rightarrow \text{moles of } \textit{unknown}$$

The mass of the given substance is converted into moles by use of the molar mass of that substance from the periodic table. Then, the moles of the given substance are converted into moles of the unknown by using the mole ratio from the balanced chemical equation.

Sample Problem: Mass-Mole Stoichiometry

Tin metal reacts with hydrogen fluoride to produce tin(II) fluoride and hydrogen gas according to the following balanced equation.

$$\mathrm{Sn}(s)+2\mathrm{HF}(g)\rightarrow \mathrm{SnF_2}(s)+\mathrm{H_2}(g)$$

How many moles of hydrogen fluoride are required to react completely with 75.0 g of tin?

Step 1: List the known quantities and plan the problem.

Known

- given: 75.0 g Sn
- molar mass of Sn = 118.69 g/mol
- 1 mol Sn = 2 mol HF (mole ratio)

Unknown

- mol HF

Use the molar mass of Sn to convert the grams of Sn to moles. Then use the mole ratio to convert from mol Sn to mol HF. This will be done in a single two-step calculation.

g Sn → mol Sn → mol HF

Step 2: Solve.

$$75.0 \text{ g Sn} \times \frac{1 \text{ mol Sn}}{118.69 \text{ g Sn}} \times \frac{2 \text{ mol HF}}{1 \text{ mol Sn}} = 1.26 \text{ mol HF}$$

Step 3: Think about your result.

The mass of tin is less than one mole, but the 1:2 ratio means that more than one mole of HF is required for the reaction. The answer has three significant figures because the given mass has three significant figures.

Moles to Mass Problems

In this type of problem, the amount of one substance is given in moles. From this, you are to determine the mass of another substance that will either react with or be produced from the given substance.

$$\text{moles of } \textit{given} \rightarrow \text{moles of } \textit{unknown} \rightarrow \text{mass of } \textit{unknown}$$

The moles of the given substance are first converted into moles of the unknown by using the mole ratio from the balanced chemical equation. Then, the moles of the unknown are converted into mass in grams by use of the molar mass of that substance from the periodic table.

Sample Problem: Mole-Mass Stoichiometry

Hydrogen sulfide gas burns in oxygen to produce sulfur dioxide and water vapor.

$$2H_2S(g) + 3O_2(g) \rightarrow 2SO_2(g) + 2H_2O(g)$$

What mass of oxygen gas is consumed in a reaction that produces 4.60 mol SO_2?

Step 1: List the known quantities and plan the problem.

Known

- given: 4.60 mol SO_2
- 2 mol SO_2 = 3 mol O_2 (mole ratio)
- molar mass of O_2 = 32.00 g/mol

Unknown

- mass O_2 = ? g

Use the mole ratio to convert from mol SO_2 to mol O_2. Then convert mol O_2 to grams. This will be done in a single two-step calculation.

mol SO_2 → mol O_2 → g O_2

Step 2: Solve.

$$4.60 \text{ mol } SO_2 \times \frac{3 \text{ mol } O_2}{2 \text{ mol } SO_2} \times \frac{32.00 \text{ g } O_2}{1 \text{ mol } O_2} = 221 \text{ g } O_2$$

Step 3: Think about your result.

According to the mole ratio, 6.90 mol O_2 is produced with a mass of 221 g. The answer has three significant figures because the given number of moles has three significant figures.

Summary

- Calculations involving conversions of mass to moles and moles to mass are described.

Practice

Work problems 11-20 at the link below:

http://myweb.astate.edu/mdraganj/Moles1.html

Review

1. In the first problem, what would happen if you multiply grams Sn by 118.69 grams/mole Sn?
2. Why is a balanced equation needed?
3. Does the physical form of the material matter for these calculations?

- **mass-mole calculations:** mass of given → moles of given → moles of unknown
- **mole-mass calculations:** moles of given → moles of unknown → mass of unknown

12.4 Mass-Mass Stoichiometry

- Perform calculations involving the determination of the mass of product based on the mass of the reactant.

How many walnuts are 250 grams worth?

I want to send 250 grams of shelled walnuts to a friend (don't ask why – just go with the question). How many walnuts in shells do I need to buy? To figure this out, I need to know how much the shell of a walnut weighs (about 40% of the total weight of the unshelled walnut). I can then calculate the mass of walnuts that will give me 250 grams of shelled walnuts and then determine how many walnuts I need to buy.

Mass to Mass Problems

Mass-mass calculations are the most practical of all mass-based stoichiometry problems. Moles cannot be measured directly, while the mass of any substance can generally be easily measured in the lab. This type of problem is three steps and is a combination of the two previous types.

$$\text{mass of } \textit{given} \rightarrow \text{moles of } \textit{given} \rightarrow \text{moles of } \textit{unknown} \rightarrow \text{mass of } \textit{unknown}$$

The mass of the given substance is converted into moles by use of the molar mass of that substance from the periodic table. Then, the moles of the given substance are converted into moles of the unknown by using the mole ratio from the balanced chemical equation. Finally, the moles of the unknown are converted to mass by use of its molar mass.

Sample Problem: Mass-Mass Stoichiometry

Ammonium nitrate decomposes to dinitrogen monoxide and water according to the following equation.

$$NH_4NO_3(s) \rightarrow N_2O(g) + 2H_2O(l)$$

In a certain experiment, 45.7 g of ammonium nitrate is decomposed. Find the mass of each of the products formed.

Step 1: List the known quantities and plan the problem.

Known

- given: 45.7 g NH_4NO_3
- 1 mol NH_4NO_3 = 1 mol N_2O = 2 mol H_2O (mole ratios)
- molar mass of NH_4NO_3 = 80.06 g/mol
- molar mass of H_2O = 18.02 g/mol

Unknown

- mass N_2O = ? g
- mass H_2O = ? g

Perform two separate three-step mass-mass calculations as shown below.

$$\begin{gathered} \text{g } NH_4NO_3 \rightarrow \text{mol } NH_4NO_3 \rightarrow \text{mol } N_2O \rightarrow \text{g } N_2O \\ \text{g } NH_4NO_3 \rightarrow \text{mol } NH_4NO_3 \rightarrow \text{mol } H_2O \rightarrow \text{g } H_2O \end{gathered}$$

Step 2: Solve.

$$\begin{gathered} 45.7 \text{ g } NH_4NO_3 \times \frac{1 \text{ mol } NH_4NO_3}{80.06 \text{ g } NH_4NO_3} \times \frac{1 \text{ mol } N_2O}{1 \text{ mol } NH_4NO_3} \times \frac{44.02 \text{ g } N_2O}{1 \text{ mol } N_2O} = 25.1 \text{ g } N_2O \\ 45.7 \text{ g } NH_4NO_3 \times \frac{1 \text{ mol } NH_4NO_3}{80.06 \text{ g } NH_4 \ NO_3} \times \frac{2 \text{ mol } H_2O}{1 \text{ mol } NH_4NO_3} \times \frac{18.02 \text{ g } H_2O}{1 \text{ mol } H_2O} = 20.6 \text{ g } N_2O \end{gathered}$$

Step 3: Think about your result.

The total mass of the two products is equal to the mass of ammonium nitrate which decomposed, demonstrating the law of conservation of mass. Each answer has three significant figures.

Summary

- Mass-mass calculations involve converting the mass of a reactant to moles of reactant, then using mole ratios to determine moles of product which can then be converted to mass of product.

Practice

Read the material at the link below, then do the mass-mass problems at the link found at the bottom of the page:

http://www.chemteam.info/Stoichiometry/Mass-Mass.html

Review

1. If matter is neither created nor destroyed, why can't we just go directly from grams of reactant to grams of product?
2. Why is it important to get the subscripts correct in the formulas?
3. Why do the coefficients need to be correct?

- **mass-mass calculations:** mass of given → moles of given → moles of unknown → mass of unknown

12.5 Volume-Volume Stoichiometry

- Perform calculations involving volume relationships among gases.

How much propane is left in the tank?

As the weather gets warmer, more and more people want to cook out on the back deck or back yard. Many folks still use charcoal for grilling because of the added flavor. But increasing numbers of back yard cooks like to use a propane grill. The gas burns clean, the grill is ready to go as soon as the flame is lit – but how do you know how much propane is left in the tank? You can buy gauges at hardware stores that measure gas pressure and tell you how much is left in the tank.

Volume-Volume Stoichiometry

Avogadro's hypothesis states that equal volumes of all gases at the same temperature and pressure contain the same number of gas particles. Further, one mole of any gas at standard temperature and pressure (0°C and 1 atm) occupies a volume of 22.4 L. These characteristics make stoichiometry problems involving gases at STP very straightforward. Consider the reaction of nitrogen and oxygen cases to form nitrogen dioxide.

$$\begin{array}{llll} N_2(g) & + \; 2O_2(g) & \rightarrow & 2NO_2(g) \\ \text{1 molecule} & \text{2 molecules} & & \text{2 molecules} \\ \text{1 mol} & \text{2 mol} & & \text{2 mol} \\ \text{1 volume} & \text{2 volumes} & & \text{2 volumes} \end{array}$$

Because of Avogadro's work, we know that the mole ratios between substances in a gas-phase reaction are also volume ratios. The six possible volume ratios for the above equation are:

1. $\frac{\text{1 volume } N_2}{\text{2 volumes } O_2}$ *or* $\frac{\text{2 volumes } O_2}{\text{1 volume } N_2}$
2. $\frac{\text{1 volume } N_2}{\text{2 volumes } NO_2}$ *or* $\frac{\text{2 volumes } NO_2}{\text{1 volume } N_2}$
3. $\frac{\text{2 volumes } O_2}{\text{2 volumes } NO_2}$ *or* $\frac{\text{2 volumes } NO_2}{\text{2 volumes } O_2}$

The volume ratios above can easily be used when the volume of one gas in a reaction is known and you need to determine the volume of another gas that will either react with or be produced from the first gas. The pressure and temperature conditions of both gases need to be the same.

Sample Problem: Volume-Volume Stoichiometry

The combustion of propane gas produces carbon dioxide and water vapor.

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$$

What volume of oxygen is required to completely combust 0.650 L of propane? What volume of carbon dioxide is produced in the reaction?

Step 1: List the known quantities and plan the problem.

Known

- given: 0.650 L C_3H_8
- 1 volume C_3H_8 = 5 volumes O_2
- 1 volume C_3H_8 = 3 volumes CO_2

Unknown

- volume O_2 = ? L
- volume CO_2 = ? L

Two separate calculations can be done using the volume ratios.

Step 2: Solve.

$$0.650 \text{ L } C_3H_8 \times \frac{5 \text{ L } O_2}{1 \text{ L } C_3H_8} = 3.25 \text{ L } O_2$$
$$0.650 \text{ L } C_3H_8 \times \frac{3 \text{ L } CO_2}{1 \text{ L } C_3H_8} = 1.95 \text{ L } CO_2$$

Step 3: Think about your result.

Because the coefficients of the O_2 and the CO_2 are larger than that of the C_3H_8, the volumes for those two gases are greater. Note that total volume is not necessarily conserved in a reaction because moles are not necessarily conserved. In this reaction, 6 total volumes of reactants become 7 total volumes of products.

Summary

- Calculations of volume-volume ratios are based on Avogadro's hypothesis.
- Pressures and temperatures of the gases involved need to be the same.

Practice

Read the material and work the Example One practice problems at the link below:

http://web.gccaz.edu/ ksmith8/rev130_files/Notes%2010.pdf

Review

1. What is Avogadaro's hypothesis?
2. How much volume is occupied by one mole of a gas at STP?
3. In the sample problem above, assume we combust 1.3 L of propane. How much CO_2 will be produced?

- **volume-volume stoichiometry:** At the same pressure and temperature, equal volumes of gases contain the same number of molecules.

12.6 Mass-Volume and Volume-Mass Stoichiometry

- Perform mass to volume and volume to mass calculations involving gases.

How much azide is needed to fill an air bag?

Cars and many other vehicles have air bags in them. In case of a collision, a reaction is triggered so that the rapid decomposition of sodium azide produces nitrogen gas, filling the air bag. If too little sodium azide is used, the air bag will not fill completely and will not protect the person in the vehicle. Too much sodium azide could cause the formation of more gas that the bag can safely handle. If the bag breaks from the excess gas pressure, all protection is lost.

Mass to Volume and Volume to Mass Problems

Chemical reactions frequently involve both solid substances whose mass can be measured as well as gases for which measuring the volume is more appropriate. Stoichiometry problems of this type are called either mass-volume or volume-mass problems.

$$\text{mass of } \textit{given} \rightarrow \text{moles of } \textit{given} \rightarrow \text{moles of } \textit{unknown} \rightarrow \text{volume of } \textit{unknown}$$
$$\text{volume of } \textit{given} \rightarrow \text{moles of } \textit{given} \rightarrow \text{moles of } \textit{unknown} \rightarrow \text{mass of } \textit{unknown}$$

Because both types of problems involve a conversion from either moles of gas to volume or vice-versa, we can use the molar volume of 22.4 L/mol provided that the conditions for the reaction are STP.

Sample Problem: Mass-Volume Stoichiometry

Aluminum metal reacts rapidly with aqueous sulfuric acid to produce aqueous aluminum sulfate and hydrogen gas.

$$2\text{Al}(s) + 3\text{H}_2\text{SO}_4(aq) \rightarrow \text{Al}_2(\text{SO}_4)_3(aq) + 3\text{H}_2(g)$$

Determine the volume of hydrogen gas produced at STP when a 2.00 g piece of aluminum completely reacts.

Step 1: List the known quantities and plan the problem.

Known

- given: 2.00 g Al
- molar mass Al = 26.98 g/mol
- 2 mol Al = 3 mol H_2

Unknown

- volume H_2 = ?

The grams of aluminum will first be converted to moles. Then the mole ratio will be applied to convert to moles of hydrogen gas. Finally, the molar volume of a gas will be used to convert to liters of hydrogen.

$$\text{g Al} \rightarrow \text{mol Al} \rightarrow \text{mol H}_2 \rightarrow \text{L H}_2$$

Step 2: Solve.

$$2.00 \text{ g Al} \times \frac{1 \text{ mol Al}}{26.98 \text{ g Al}} \times \frac{3 \text{ mol H}_2}{2 \text{ mol Al}} \times \frac{22.4 \text{ L H}_2}{1 \text{ mol H}_2} = 2.49 \text{ L H}_2$$

Step 3: Think about your result.

The volume result is in liters. For much smaller amounts, it may be convenient to convert to milliliters. The answer here has three significant figures. Because the molar volume is a measured quantity of 22.4 L/mol, three is the maximum number of significant figures for this type of problem.

Sample Problem: Volume-Mass Stoichiometry

Calcium oxide is used to remove sulfur dioxide generated in coal-burning power plants according to the following reaction.

$$2\text{CaO}(s) + 2\text{SO}_2(g) + \text{O}_2(g) \rightarrow 2\text{CaSO}_4(s)$$

What mass of calcium oxide is required to react completely with 1.2×10^3 L of sulfur dioxide?

Step 1: List the known quantities and plan the problem.

Known

- given: 1.2×10^3 L = SO_2
- 2 mol SO_2 = 2 mol CaO
- molar mass CaO = 56.08 g/mol

Unknown

- mass CaO = ? g

The volume of SO_2 will be converted to moles, followed by the mole ratio, and finally a conversion of moles of CaO to grams.

$$\text{L SO}_2 \rightarrow \text{mol SO}_2 \rightarrow \text{mol CaO} \rightarrow \text{g CaO}$$

Step 2: Solve.

$$1.4 \times 10^3 \text{ L SO}_2 \times \frac{1 \text{ mol SO}_2}{22.4 \text{ L SO}_2} \times \frac{2 \text{ mol CaO}}{2 \text{ mol SO}_2} \times \frac{56.08 \text{ g CaO}}{1 \text{ mol CaO}} = 3.5 \times 10^3 \text{ g CaO}$$

Step 3: Think about your result.

The resultant mass could be reported as 3.5 kg, with two significant figures. Even though the 2:2 mole ratio does not mathematically affect the problem, it is still necessary for unit conversion.

Summary

- Calculations are described for determining the amount of gas formed in a reaction.
- Calculations are described for determining amounts of a material needed to react with a gas.

Practice

Answer the questions at the link below:

http://www.docbrown.info/page04/4_73calcs/MVGmcTEST.htm

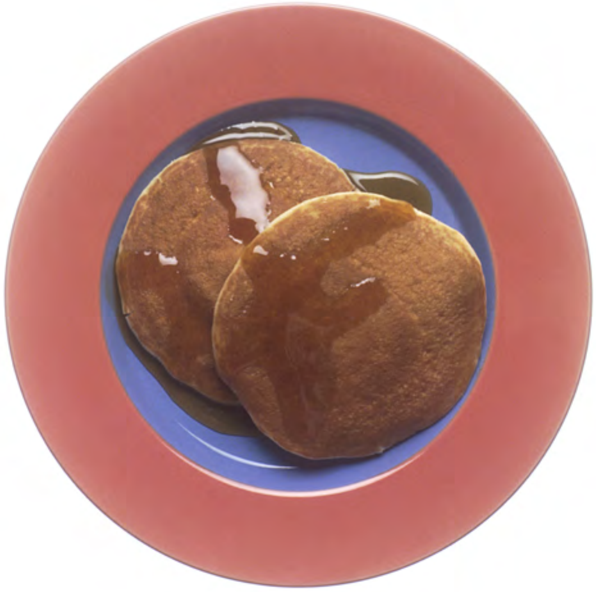
Review

1. What are the conditions for all gases in these calculations?
2. How can you tell if all the ratios were set up correctly?
3. Why was 2 mol CaO/2mol SO_2 included in the second example if it did not affect the final number?

- **mass-volume stoichiometry:** calculations involving determination of amount of gas formed from solid materials.
- **volume-mass stoichiometry:** calculations involving determination of amount of gas needed for reaction with solid materials.

12.7 Limiting Reactant

- Define limiting reactant.
- Describe how to determine which component in a reaction is the limiting reactant.



Don't you hate running out of cooking ingredients?

Cooking is a great example of everyday chemistry. In order to correctly follow a recipe, a cook needs to make sure that he has plenty of all the necessary ingredients in order to make his dish. Let us suppose that you are deciding to make some pancakes for a large group of people. The recipe on the box indicates that the following ingredients are needed for each batch of pancakes:

1 cup of pancake mix

$\frac{3}{4}$ cup milk

1 egg

1 tablespoon vegetable oil

Now you check the pantry and the refrigerator and see that you have the following ingredients available:

2 boxes of pancake mix (8 cups)

Half gallon of milk (4 cups)

2 eggs

Full bottle of vegetable oil (about 3 cups)

The question that you must ask is: How many batches of pancakes can I make? The answer is two. Even though you have enough pancake mix, milk, and oil to make many more batches of pancakes, you are *limited* by the fact that you only have two eggs. As soon as you have made two batches of pancakes, you will be out of eggs and your "reaction" will be complete.

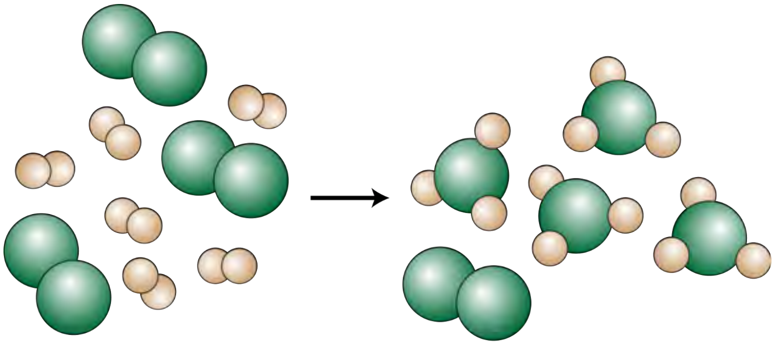
Limiting Reactant

For a chemist, the balanced chemical equation is the recipe that must be followed. As you have seen earlier, the Haber process is a reaction in which nitrogen gas is combined with hydrogen gas to form ammonia. The balanced equation is shown below.

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

We know that the coefficients of the balanced equation tell us the mole ratio that is required for this reaction to occur. One mole of N_2 will react with three moles of H_2 to form two moles of NH_3.

Now let us suppose that a chemist were to react three moles of N_2 with six moles of H_2.



	Reactants		Products
Before reaction	3 mol N_2	6 mol H_2	0 mol NH_3
After reaction	1 mol N_2	0 mol H_2	4 mol NH_3

FIGURE 12.5

Reaction in presence of limiting reagent.

So what happened in this reaction? The chemist started with 3 moles of N_2. You may think of this as being 3 times as much as the "recipe" (the balanced equation) requires since the coefficient for the N_2 is a 1. However, the 6 moles of H_2 that the chemist started with is only two times as much as the "recipe" requires, since the coefficient for the H_2 is a 3 and $3 \times 2 = 6$. So the hydrogen gas will be completely used up while there will be 1 mole of nitrogen gas left over after the reaction is complete. Finally, the reaction will produce 4 moles of NH_3 because that is also two times as much as shown in the balanced equation. The overall reaction that occurred in words:

$$2 \text{ mol } N_2 + 6 \text{ mol } H_2 \rightarrow 4 \text{ mol } NH_3$$

All the amounts are doubled from the original balanced equation.

The **limiting reactant (or limiting reagent)** is the reactant that determines the amount of product that can be formed in a chemical reaction. The reaction proceeds until the limiting reactant is completely used up. In our example above, the H_2 is the limiting reactant. The **excess reactant (or excess reagent)** is the reactant that is initially present in a greater amount than will eventually be reacted. In other words, there is always excess reactant left over after the reaction is complete. In the above example, the N_2 is the excess reactant.

Summary

- The amount of limiting reactant determines how much product will be formed in a chemical reaction.

Practice

Watch the video at the link below and answer the following questions:

http://www.sophia.org/limiting-reactant-definition/limiting-reactant-definition--2-tutorial

1. What reaction is occurring?
2. How is the reaction measured?
3. What do the balloons tell us?

Review

1. In the Haber reaction illustrated above, how do we know that hydrogen is the limiting reactant?
2. What if hydrogen were left over?
3. Which material would be limiting if no hydrogen or nitrogen were left over?

- **excess reactant (or excess reagent):** The reactant that is initially present in a greater amount than will eventually be reacted.
- **limiting reactant (or limiting reagent):** The reactant that determines the amount of product that can be formed in a chemical reaction.

12.8 Determining the Limiting Reactant

- Perform calculations to determine the limiting reactant in a chemical reaction.

Who's coming for dinner?

You have ten people that show up for a dinner party. One of the guest brings twenty brownies for dessert. The decision about serving dessert is easy: two brownies are placed on every plate. If someone wants more brownies, they will have to wait until they go to the store. There are only enough brownies for everyone to have two.

Determining the Limiting Reactant

In the real world, amounts of reactants and products are typically measured by mass or by volume. It is first necessary to convert the given quantities of each reactant to moles in order to identify the limiting reactant.

Sample Problem: Determining the Limiting Reactant

Silver metal reacts with sulfur to form silver sulfide according to the following balanced equation:

$$2\text{Ag}(s) + \text{S}(s) \rightarrow \text{Ag}_2\text{S}(s)$$

What is the limiting reactant when 50.0 g Ag is reacted with 10.0 g S?

Step 1: List the known quantities and plan the problem.

Known

- given: 50.0 g Ag

- given: 10.0 g S

Unknown

- limiting reactant

Use the atomic masses of Ag and S to determine the number of moles of each present. Then, use the balanced equation to calculate the number of moles of sulfur that would be needed to react with the number of moles of silver present. Compare this result to the actual number of moles of sulfur present.

Step 2: Solve.

First, calculate the number of moles of Ag and S present:

$$50.0 \text{ g Ag} \times \frac{1 \text{ mol Ag}}{107.87 \text{ g Ag}} = 0.464 \text{ mol Ag}$$
$$10.0 \text{ g S} \times \frac{1 \text{ mol S}}{32.07 \text{ g S}} = 0.312 \text{ mol S}$$

Second, find the moles of S that would be required to react with all of the given Ag:

$$0.464 \text{ mol Ag} \times \frac{1 \text{ mol S}}{2 \text{ mol Ag}} = 0.232 \text{ mol S (required)}$$

The amount of S actually present is 0.312 moles. The amount of S that is required to fully react with all of the Ag is 0.232 moles. Since there is more sulfur present than what is required to react, the sulfur is the excess reactant. Therefore, silver is the limiting reactant.

Step 3: Think about your result.

The balanced equation indicates that the necessary mole ratio of Ag to S is 2:1. Since there were not twice as many moles of Ag present in the original amounts, that makes silver the limiting reactant.

There is a very important point to consider about the preceding problem. Even though the mass of silver present in the reaction (50.0 g) was greater than the mass of sulfur (10.0 g), silver was the limiting reactant. This is because chemists must always convert to molar quantities and consider the mole ratio from the balanced chemical equation.

There is one other thing that we would like to be able to determine in a limiting reactant problem - the quantity of the excess reactant that will be left over after the reaction is complete. We will go back to the sample problem above to answer this question.

Sample Problem: Determining the Amount of Excess Reactant Left Over

What is the mass of excess reactant remaining when 50.0 g Ag reacts with 10.0 g S?

$$2\text{Ag}(s) + \text{S}(s) \rightarrow \text{Ag}_2\text{S}(s)$$

Step 1: List the known quantities and plan the problem.

Known

- Excess reactant = 0.312 mol S (from sample problem 12.9)

- Amount of excess reactant needed = 0.232 mol S (from sample problem 12.9)

Unknown

- Mass of excess reactant remaining after the reaction = ? g

Subtract the amount (in moles) of the excess reactant that will react from the amount that is originally present. Convert moles to grams.

Step 2: Solve.

$$0.312 \text{ mol S} - 0.232 \text{ mol S} = 0.080 \text{ mol S (remaining after reaction)}$$

$$0.080 \text{ mol S} \times \frac{32.07 \text{ g S}}{1 \text{ mol S}} = 2.57 \text{ g S}$$

There are 2.57 g of sulfur remaining when the reaction is complete.

Step 3: Think about your result.

There were 10.0 g of sulfur present before the reaction began. If 2.57 g of sulfur remains after the reaction, then 7.43 g S reacted.

$$7.43 \text{ g S} \times \frac{1 \text{ mol S}}{32.07 \text{ g S}} = 0.232 \text{ mol S}$$

This is the amount of sulfur that reacted. The problem is internally consistent.

Summary

- Determining the limiting reactant requires that all mass quantities first be converted to moles to evaluate the equation.

Practice

Carry out the calculations on the problem set at the link below:

http://msweb.asub.edu/haines/lim-reag%20worksheet.pdf

Review

1. Why do all mass values need to be converted to moles before determining the limiting reactant?
2. If we used 0.7 moles Ag, would it still be the limiting reactant?
3. If we ran the reaction using the original amounts of Ag and S and had 5.22 grams S left over, what might we assume about the reaction?

12.9 Theoretical Yield and Percent Yield

- Define theoretical yield.
- Define percent yield.
- Calculate theoretical yield.
- Calculate percent yield.

Can we save some money?

The world of pharmaceutical production is an expensive one. Many drugs have several steps in their synthesis and use costly chemicals. A great deal of research takes place to develop better ways to make drugs faster and more efficiently. Studying how much of a compound is produced in any given reaction is an important part of cost control.

Percent Yield

Chemical reactions in the real world don't always go exactly as planned on paper. In the course of an experiment, many things will contribute to the formation of less product than would be predicted. Besides spills and other experimental errors, there are usually losses due to an incomplete reaction, undesirable side reactions, etc. Chemists need a measurement that indicates how successful a reaction has been. This measurement is called the percent yield.

To compute the percent yield, it is first necessary to determine how much of the product should be formed based on stoichiometry. This is called the **theoretical yield**, the maximum amount of product that could be formed from the given amounts of reactants. The **actual yield** is the amount of product that is actually formed when the reaction is carried out in the laboratory. The **percent yield** is the ratio of the actual yield to the theoretical yield, expressed as a percentage.

$$\text{Percent Yield} = \frac{\text{Actual Yield}}{\text{Theoretical Yield}} \times 100\%$$

Percent yield is very important in the manufacture of products. Much time and money is spent improving the percent yield for chemical production. When complex chemicals are synthesized by many different reactions, one step with a low percent yield can quickly cause a large waste of reactants and unnecessary expense.

Typically, percent yields are understandably less than 100% because of the reasons indicated earlier. However, percent yields greater than 100% are possible if the measured product of the reaction contains impurities that cause its mass to be greater than it actually would be if the product was pure. When a chemist synthesizes a desired chemical, he or she is always careful to purify the products of the reaction.

Sample Problem: Calculating the Theoretical Yield and the Percent Yield

Potassium chlorate decomposes upon slight heating in the presence of a catalyst according to the reaction below:

$$2\text{KClO}_3(s) \rightarrow 2\text{KCl}(s) + 3\text{O}_2(g)$$

In a certain experiment, 40.0 g $KClO_3$ is heated until it completely decomposes. What is the theoretical yield of oxygen gas? The experiment is performed and the oxygen gas is collected and its mass is found to be 14.9 g. What is the percent yield for the reaction?

***Part 12.11A*:** First, we will calculate the theoretical yield based on the stoichiometry.

Step 1: List the known quantities and plan the problem.

Known

- given: mass of $KClO_3$ = 40.0 g
- molar mass $KClO_3$ = 122.55 g/mol
- molar mass O_2 = 32.00 g/mol

Unknown

- theoretical yield O_2 = ? g

Apply stoichiometry to convert from the mass of a reactant to the mass of a product:

$$\text{g KClO}_3 \rightarrow \text{mol KClO}_3 \rightarrow \text{mol O}_2 \rightarrow \text{g O}_2$$

Step 2: Solve.

$$40.0 \text{ g KClO}_3 \times \frac{1 \text{ mol KClO}_3}{122.55 \text{ g KClO}_3} \times \frac{3 \text{ mol O}_2}{2 \text{ mol KClO}_3} \times \frac{32.00 \text{ g O}_2}{1 \text{ mol O}_2} = 15.7 \text{ g O}_2$$

The theoretical yield of O_2 is 15.7 g.

Step 3: Think about your result.

The mass of oxygen gas must be less than the 40.0 g of potassium chlorate that was decomposed.

Part 12.11B**:** Now we use the actual yield and the theoretical yield to calculate the percent yield.

Step 1: List the known quantities and plan the problem.

Known

- Actual yield = 14.9 g
- Theoretical yield = 15.7 g (from Part 12.11A)

Unknown

- Percent yield = ? %

$$\text{Percent Yield} = \frac{\text{Actual Yield}}{\text{Theoretical Yield}} \times 100\%$$

Use the percent yield equation above.

Step 2: Solve.

$$\text{Percent Yield} = \frac{14.9 \text{ g}}{15.7 \text{ g}} \times 100 = 94.9\%$$

Step 3: Think about your result.

Since the actual yield is slightly less than the theoretical yield, the percent yield is just under 100%.

Summary

- Theoretical yield is calculated based on the stoichiometry of the chemical equation.
- The actual yield is experimentally determined.
- The percent yield is determined by calculating the ratio of actual yield/theoretical yield.

Practice

Work the problems found on the link below:

http://science.widener.edu/svb/tutorial/percentyieldcsn7.html

Review

1. What do we need in order to calculate theoretical yield?
2. If I spill some of the product before I weigh it, how will that affect the actual yield?
3. How will spilling some of the product affect the percent yield?
4. I make a product and weigh it before it is dry. How will that affect the actual yield?

- **actual yield:** The amount of product that is actually formed when the reaction is carried out in the laboratory.
- **percent yield:** The ratio of the actual yield to the theoretical yield, expressed as a percentage.
- **theoretical yield:** The maximum amount of product that could be formed from the given amounts of reactants.

12.10 References

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CHAPTER 13

States of Matter

Chapter Outline

13.1 Kinetic-Molecular Theory

- List the points of the kinetic-molecular-theory.

Approximately 20% of the atmosphere is oxygen. This gas is essential for life. In environments where oxygen is in low supply, it can be provided from a tank. Since gases are very compressible, a large amount of oxygen can be stored in a relatively small container. When it is released, the volume expands and the pressure decreases. The gas is then available for breathing under normal pressure.

The Kinetic-Molecular Theory

The kinetic-molecular theory is a theory that explains the states of matter and is based on the idea that matter is composed of tiny particles that are always in motion. The theory helps explain observable properties and behaviors of solids, liquids, and **gases**. However, the theory is most easily understood as it applies to gases and it is with gases that we will begin our detailed study. The theory applies specifically to a model of a gas called an **ideal gas**. An ideal gas is an imaginary gas whose behavior perfectly fits all the assumptions of the kinetic-molecular theory. In reality, gases are not ideal, but are very close to being so under most everyday conditions.

The kinetic-molecular theory as it applies to gases has five basic assumptions.

1. **Gases consist of very large numbers of tiny spherical particles that are far apart from one another compared to their size**. The particles of a gas may be either atoms or molecules. The distance between the particles of a gas is much, much greater than the distances between the particles of a liquid or a solid. Most of the volume of a gas, therefore, is composed of the empty space between the particles. In fact, the volume of the particles themselves is considered to be insignificant compared to the volume of the empty space.
2. **Gas particles are in constant rapid motion in random directions**. The fast motion of gas particles gives them a relatively large amount of kinetic energy. Recall that kinetic energy is the energy that an object possesses because of its motion. The particles of a gas move in straight-line motion until they collide with another particle or with one of the walls of its container.

3. **Collisions between gas particles and between particles and the container walls are elastic collisions**. An elastic collision is one in which there is no overall loss of kinetic energy. Kinetic energy may be transferred from one particle to another during an elastic collision, but there is no change in the total energy of the colliding particles.
4. **There are no forces of attraction or repulsion between gas particles**. Attractive forces are responsible for particles of a real gas condensing together to form a liquid. It is assumed that the particles of an ideal gas have no such attractive forces. The motion of each particle is completely independent of the motion of all other particles.
5. **The average kinetic energy of gas particles is dependent upon the temperature of the gas.** As the temperature of a sample of gas is increased, the speeds of the particles are increased. This results in an increase in the kinetic energy of the particles. Not all particles of gas in a sample have the same speed and so they do not have the same kinetic energy. The temperature of a gas is proportional to the average kinetic energy of the gas particles.

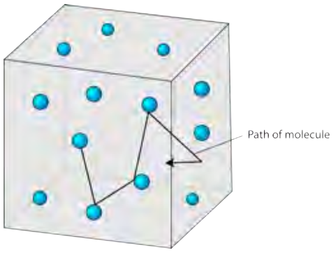


FIGURE 13.1

Gas particles are in random straight-line motion according to the kinetic-molecular theory. The space between particles is very large compared to the particle size.

Summary

- Assumptions of the kinetic-molecular theory:
  - Gases consist of very large numbers of tiny spherical particles that are far apart from one another compared to their size.
  - Gas particles are in constant rapid motion in random directions.
  - Collisions between gas particles and between particles and the container walls are elastic collisions.
  - There are no forces of attraction or repulsion between gas particles.
  - The average kinetic energy of gas particles is dependent upon the temperature of the gas.

Practice

Use the link below to answer the following questions:

http://www.chem.ufl.edu/ itl/2045/lectures/lec_d.html

1. Who developed the kinetic-molecular theory?
2. How many molecules are involved in most collisions?
3. What assumption is made about the volume of a mole of an ideal gas?

Review

1. What kind of motion are gases in?
2. What kind of collisions occurs?
3. What does the kinetic energy depend upon?

- **gas:** Consists of very large numbers of tiny spherical particles that are far apart from one another compared to their size.
- **ideal gas:** An imaginary gas whose behavior perfectly fits all the assumptions of the kinetic-molecular theory.

13.2 Gas Pressure

- Define gas pressure.

Many people enjoy riding in hot air balloons. Some use them for romantic picnics and marriage proposals. Others race in competitions. Being above the earth gives a whole new perspective on the world around us. As the beginning of a hot air balloon ride, the balloon is flat because the pressure inside the balloon equals the pressure outside. When the air inside the balloon is heated, the speed of movement of those air molecules increases and the pressure goes up. After a while the balloon is completely expanded and the flight is ready to take off.

Gas Pressure

Pressure is defined as the force per unit area on a surface.

$$\text{Pressure} = \frac{\text{force}}{\text{area}}$$

When a person stands on the floor, his feet exert pressure on the surface. That pressure is related to both the mass of the person and the surface area of his feet. If the person were holding a heavy object, the pressure would increase because of a greater force. Alternatively, if the person stands on his toes, the pressure also increases because of a decrease in the surface area.

Gas molecules also exert pressure. Earth's atmosphere exerts pressure because gravity acts on the huge number of gas particles contained in the atmosphere, holding it in place. Pressure is also exerted by a small sample of gas, such as that which is contained in a balloon. Gas pressure is the pressure that results from **collisions** of gas particles with an object. Inside the balloon, the gas particles collide with the balloon's inner walls. It is those collisions which keep the balloon inflated. If the gas particles were to suddenly stop moving, the balloon would instantly deflate. The **Figure** 13.2 is an illustration of gas particles exerting pressure inside a container.

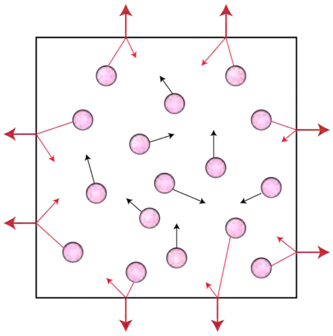


FIGURE 13.2

Collision of gas particles with container wall.

The pressure inside the hot air balloon is affected by temperature. As the molecules heat up, they move faster and strike the inside wall of the balloon harder. This increased motion of the gas particles increases the force on an area of the balloon, producing a rise in the pressure.

Summary

- Pressure is defined as $\frac{\text{force}}{\text{volume}}$.
- Gas pressure is the result of collisions between gas particles and an object.
- An increase in temperature will produce an increase in pressure of a gas.

Practice

Use the link below to answer the following questions:

http://www.grc.nasa.gov/WWW/k-12/airplane/pressure.html

1. What physical properties does a gas particle possess?
2. When applying pressure to a gas, how are the forces in the container affected?
3. What determines the momentum of a single molecule?

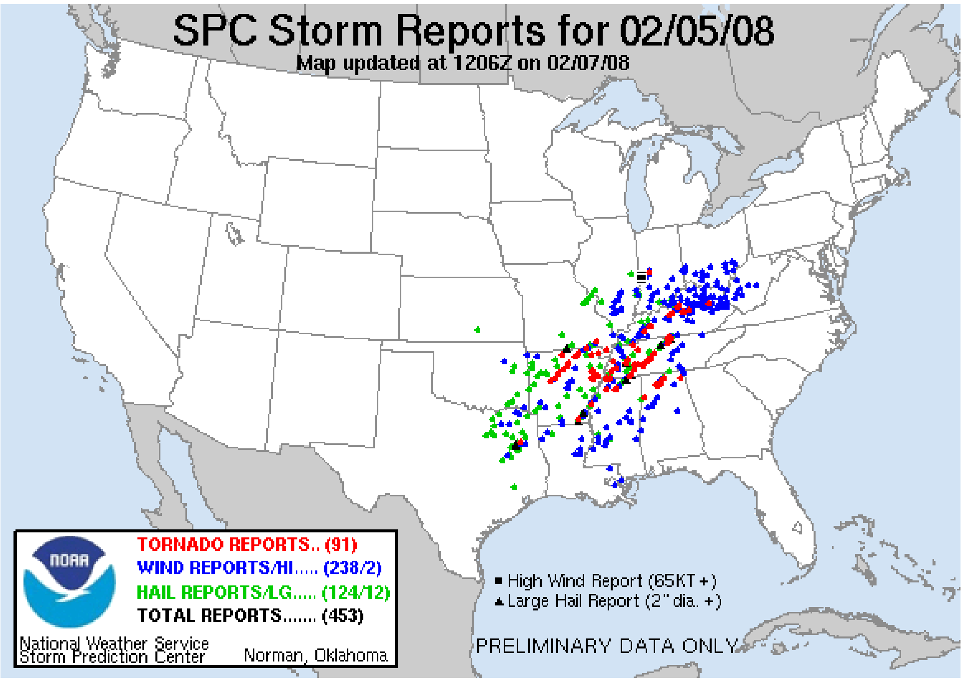
Review

1. What is pressure?
2. What causes pressure by a gas?
3. What would happen to the pressure if gas particles suddenly stopped moving?
4. How does temperature affect pressure?

- **pressure:** Defined as $\frac{\text{force}}{\text{volume}}$.
- **collision:** When gas particles collide with objects it produces gas pressure.

13.3 Atmospheric Pressure

- Define atmospheric pressure.
- Describe how atmospheric pressure changes with elevation above sea level.
- Describe the use of a barometer.



The pressure in the atmosphere is an important factor in determining what the weather will be like. If the barometric pressure is high in an area, this will cause air to move to a region of lower pressure. The greater the difference in pressure between the two areas, the stronger the winds will develop. Under certain conditions, the winds can produce a tornado (a violent rotating column of air that reaches from a thunderstorm down to the ground).

Atmospheric Pressure

Atmospheric pressure is the pressure exerted by gas particles in Earth's atmosphere as those particles collide with objects. A **barometer** is an instrument used to measure atmospheric pressure. A traditional mercury barometer consists of an evacuated tube immersed in a container of mercury. Air molecules push down on the surface of the mercury. Because the inside of the tube is a vacuum, the mercury rises inside the tube. The height to which the mercury rises is dependent on the external air pressure.

A more convenient barometer, called an **aneroid barometer**, measures pressure by the expansion and contraction of a small spring within an evacuated metal capsule.

Atmospheric Pressure and Altitude

At sea level, a mercury column will rise a distance of 760 mm. This **atmospheric pressure** is reported as 760 mmHg (millimeters of mercury). At higher altitudes, the atmospheric pressure is decreased and so the column of

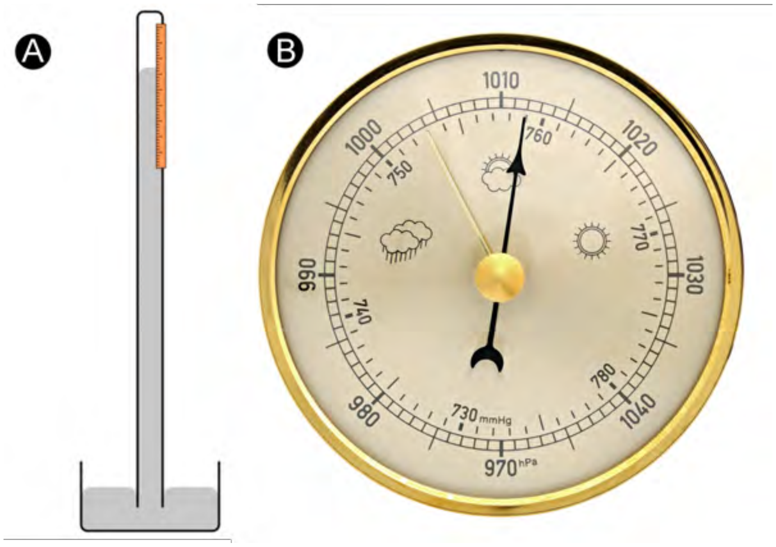


FIGURE 13.3
(A) A barometer measures atmospheric pressure as the height of a column of mercury. (B) A modern aneroid barometer in the form of a dial is used by meteorologists to help them predict upcoming weather.

mercury will not rise as high. On the summit of Mt. Everest (elevation of 8848 m), the air pressure is 253 mmHg. Atmospheric pressure is slightly dependent on weather conditions. From the graph we can see the decrease in atmospheric pressure as the altitude increases. At sea level, the atmospheric pressure would be a little over 100 kPa (one atmosphere or 760 mm Hg). If we climb to the top of Mount Everest (the highest mountain in the world at 29,029 feet or 8848 meters), the atmospheric pressure will drop to slightly over 30 kPa (about 0.30 atmospheres or 228 mm Hg). This marked decrease in atmospheric pressure results in much lower levels of oxygen. Teams that climb this mountain must bring supplies of oxygen with them in order to breathe at these high altitudes.

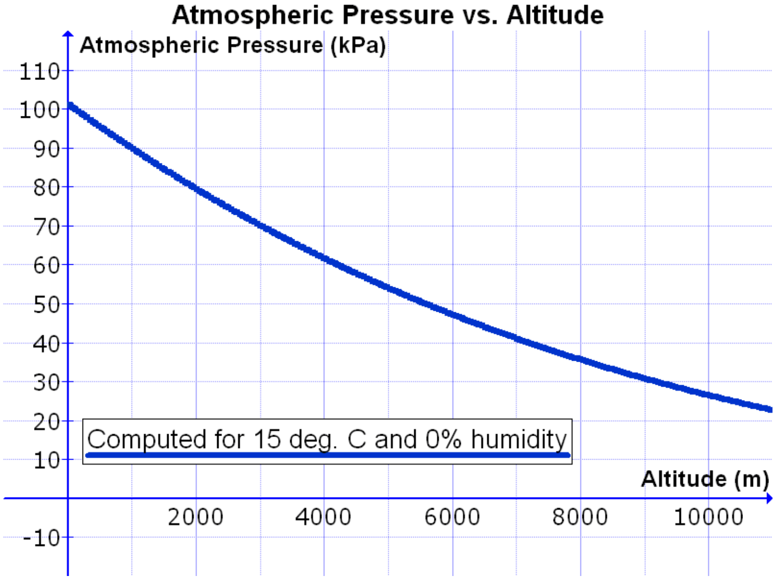


FIGURE 13.4
Effect of altitude on atmospheric pressure.

Summary

- Atmospheric pressure is the pressure exerted by gas particles in Earth's atmosphere as those particles collide with objects.

- A barometer measures atmospheric pressure.
- Atmospheric pressure decreases as the altitude increases.

Practice

Use the link below to answer the following questions:

http://www.sciencecompany.com/-W135.aspx

1. Who invented the mercury barometer?
2. List two factors that will affect how closely your barometer will agree with the local weather station.
3. Your barometer reading is 29.95 inches and falling. What might your weather prediction be?

Review

1. Define atmospheric pressure.
2. What is an aneroid barometer?
3. How does the atmospheric pressure change as the altitude increases?

- **aneroid barometer:** Measures pressure by the expansion and contraction of a small spring within an evacuated metal capsule.
- **atmospheric pressure:** The pressure exerted by gas particles in Earth's atmosphere as those particles collide with objects.
- **barometer:** Measures atmospheric pressure.

13.4 Pressure Units and Conversions

- Be able to convert between different units of pressure.

There are several benefits to maintaining the proper air pressure in a car tire. The ride is smoother and safer than with lowered pressure. The car gets better gas mileage and the tires don't wear out as fast. The recommended pressure for that model of car (usually somewhere between 32-35 psi) is usually listed in the owner's manual or stamped somewhere inside the door. The pressure on the tire is the maximum pressure for that tire, not the recommended one. Tire pressure is best measured when the tire is cold since driving the car for a while will heat up the air in the tire and increase the pressure.

Pressure Units and Conversion

A barometer measures gas pressure by the height of the column of mercury. One unit of gas pressure is the millimeter of mercury (mmHg). An equivalent unit to the mmHg is called the torr, in honor of the inventor of the barometer, Evangelista Torricelli. The **pascal** (Pa) is the standard unit of pressure. A pascal is a very small amount of pressure, so the more useful unit for everyday gas pressures is the kilopascal (kPa). A kilopascal is equal to 1000 pascals. Another commonly used unit of pressure is the **atmosphere** (atm). Standard atmospheric pressure is called 1 atm of pressure and is equal to 760 mmHg and 101.3 kPa. Atmospheric pressure is also often stated as pounds/square inch (psi). The atmospheric pressure at sea level is 14.7 psi.

$$1\text{ atm} = 760\text{ mmHg} = 760\text{ torr} = 101.3\text{ KPa} = 14.7\text{ psi}$$

It is important to be able to convert between different units of pressure. To do so, we will use the equivalent standard pressures shown above.

Sample Problem: Pressure Unit Conversions

The atmospheric pressure in a mountainous location is measured to be 613 mmHg. What is this pressure in atm and in kPa?

Step 1: List the known quantities and plan the problem.

Known

- given: 613 mmHg
- 1 atm = 760 mmHg
- 101.3 kPa = 760 mmHg

Unknown

- pressure = ? atm
- pressure = ? kPa

Use conversion factors from the equivalent pressure units to convert from mmHg to atm and from mmHg to kPa.

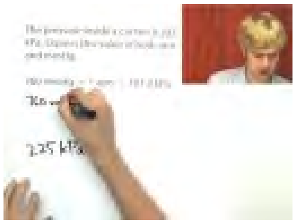
Step 2: Solve.

$$613 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 0.807 \text{ atm}$$
$$613 \text{ mmHg} \times \frac{101.3 \text{ kPa}}{760 \text{ mmHg}} = 81.7 \text{ kPa}$$

Step 3: Think about your result.

The air pressure is about 80% that of standard atmospheric pressure at sea level. For significant purposes, the standard pressure of 760 mmHg has three significant figures.

Watch the video to learn more about conversion factors:



MEDIA

Click image to the left for more content.

http://www.youtube.com/watch?v=qv81QCGNnVo

Summary

- Calculations are described for converting between different pressure units.

Practice

Use the link below to practice conversion calculations:

http://www.kentchemistry.com/links/GasLaws/Pressure.htm

Review

1. Who invented the barometer?

2. One atm = ___ torr?
3. 14.7 psi = ___ kPa
4. 760 mm = ___ psi?
5. The pressure in a car tire is 35 psi. How many atmospheres is that?

- **atmosphere:** Common unit of pressure. Abbreviated as “atm.”
- **pascal:** The standard unit of pressure. Abbreviated as “Pa.”

13.5 Average Kinetic Energy

- Define kinetic energy.
- Describe how temperature influences kinetic energy of particles.
- Define aboslute zero.

Kinetic energy is the energy of motion. Any object that is moving possesses kinetic energy. Baseball involves a great deal of kinetic energy in the game. The pitcher throws a ball, imparting kinetic energy to the ball. When the batter swings, the motion of swinging creates kinetic energy in the bat. The collision of the bat with the ball changes the direction and speed of the ball, with the idea of kinetic energy being involved again.

Kinetic Energy and Temperature

As stated in the kinetic-molecular theory, the temperature of a substance is related to the average **kinetic energy** of the particles of that substance. When a substance is heated, some of the absorbed energy is stored within the particles, while some of the energy increases the motion of the particles. This is registered as an increase in the temperature of the substance.

Average Kinetic Energy

At any given temperature, not all of the particles of a sample of matter have the same kinetic energy. Instead, the particles display a wide range of kinetic energies. Most of the particles have a kinetic energy near the middle of the range. However, a small number of particles have kinetic energies a great deal lower or a great deal higher than the average (see **Figure** 13.5).

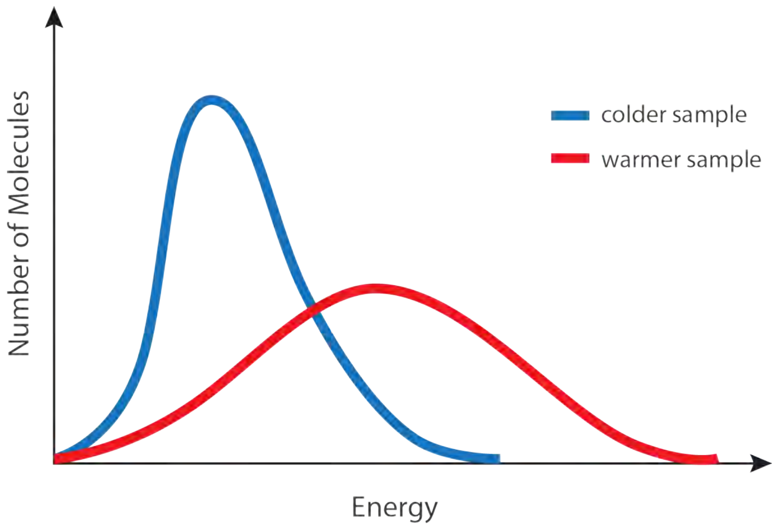


FIGURE 13.5
A distribution of molecular kinetic energies as a function of temperature. The blue curve is for a low temperature, while the red curve is for a high temperature.

The blue curve in the figure above is for a sample of matter at a relatively low temperature, while the red curve is for a sample at a relatively high temperature. In both cases, most of the particles have intermediate kinetic energies, close to the average. Notice that as temperature increases, the range of kinetic energies increases and the distribution curve "flattens out." At a given temperature, the particles of any substance have the same average kinetic energy.

Absolute Zero

As a sample of matter is continually cooled, the average kinetic energy of its particles decreases. Eventually, one would expect the particles to stop moving completely. **Absolute zero** is the temperature at which the motion of particles theoretically ceases. Absolute zero has never been attained in the laboratory, but temperatures on the order of 1×10^{-10} K have been achieved. The **Kelvin** temperature scale is the scale that is based on molecular motion and so absolute zero is also called 0 K. The Kelvin temperature of a substance is directly proportional to the average kinetic energy of the particles of the substance. For example, the particles in a sample of hydrogen gas at 200 K have twice the average kinetic energy as the particles in a hydrogen sample at 100 K.

Summary

- Kinetic energy is the energy of motion.
- At a given temperature, individual particles of a substance have a range of kinetic energies.
- The motion of particles theoretically ceases at absolute zero.

Practice

Watch the presentation and take the quiz at the end:

http://www.wisc-online.com/Objects/ViewObject.aspx?ID=GCH4904

FIGURE 13.6

Helium gas liquefies at 4 K or four degrees above absolute zero. Liquid helium is used as a coolant for large superconducting magnets and must be stored in insulated metal canisters. Pictured here is a large liquid helium container used to cool the magnet of a particle accelerator.

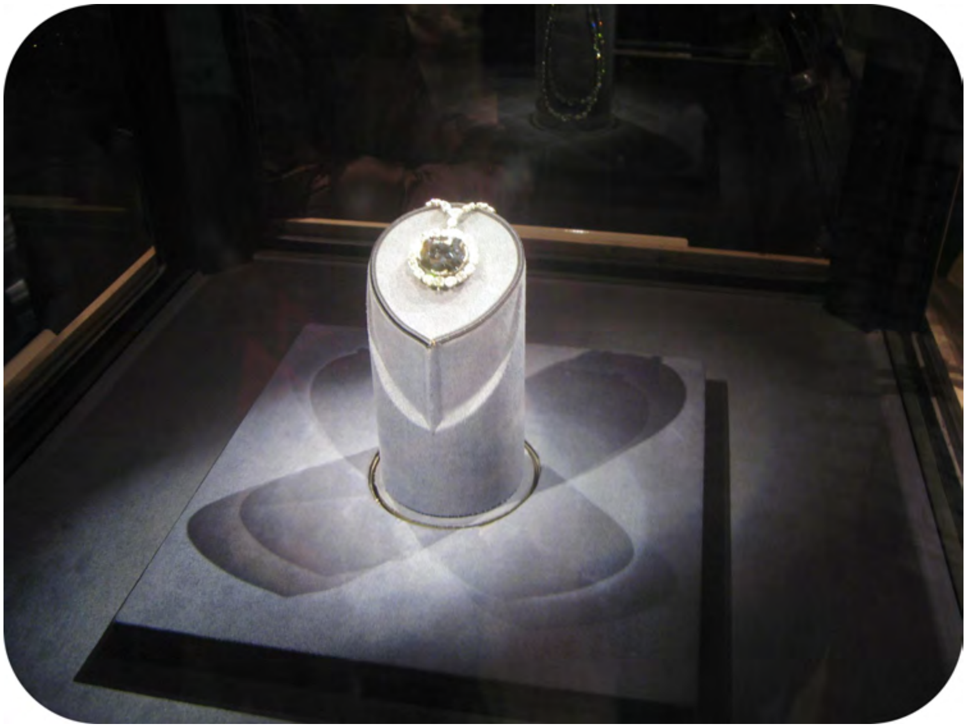
Review

1. What is kinetic energy?
2. If the temperature increases, will particles move faster or slower that they would ata lower temperature?
3. What is absolute zero?
4. List one use for liquid helium.

- **absolute zero:** The temperature at which the motion of particles theoretically ceases.
- **Kelvin scale:** The scale that is based on molecular motion and so absolute zero is also called 0 K.
- **kinetic energy:** The energy of motion.

13.6 Physical Properties and Intermolecular Forces

- List properties of ionic and molecular compounds.
- Explain differences in physical properties of molecular and ionic compounds based on types of intermolecular forces present in the compounds.



Carbon is an interesting and versatile element. There are over twenty million known compounds containing carbon, encompassed in the growing field of organic chemistry. The element itself can exist in two major forms. Diamond is a form of carbon that is extremely hard and is one of the few things that can scratch glass. The other form of carbon is graphite, a very soft material that we find in "lead" pencils. The two forms differ mainly in how the carbon atoms are connected to one another. The differences in the arrangement of atoms affect the properties of the material.

Physical Properties and Intermolecular Forces

The physical state and properties of a particular compound depends in large part on the type of chemical bonding it displays. **Molecular compounds**, sometimes called covalent compounds, display a wide range of physical properties due to the different types of intermolecular attractions such as different kinds of polar interactions. The melting and boiling points of molecular compounds are generally quite low compared to those of **ionic compounds**. This is because the energy required to disrupt the **intermolecular forces** between molecules is far less than the energy required to break the ionic bonds in a crystalline ionic compound. Since molecular compounds are composed of neutral molecules, their electrical conductivity is generally quite poor, whether in the solid or liquid state. Ionic compounds do not conduct electricity in the solid state because of their rigid structure, but conduct well when either molten or dissolved into a solution. The water solubility of molecular compounds is variable and depends primarily on the type of intermolecular forces involved. Substances that exhibit hydrogen bonding or dipole-dipole forces are generally water soluble, whereas those that exhibit only London dispersion forces are generally insoluble. Most, but not all, ionic compounds are quite soluble in water. The **Table** 13.1 summarizes some of the differences between ionic and molecular compounds.

TABLE 13.1: Comparison of Ionic and Molecular Compounds

Property	Ionic Compounds	Molecular Compounds
Type of elements	metal and nonmetal	nonmetals only
Bonding	ionic – transfer of electron(s) between atoms	covalent – sharing of pair(s) of electrons between atoms
Representative unit	formula unit	molecule
Physical state at room temp.	solid	gas, liquid, or solid
Water solubility	usually high	variable
Melting and boiling temps	generally high	generally low
Electrical conductivity	good when molten or in solution	poor

One type of molecular compound behaves quite differently than that described so far. A covalent network solid is a compound in which all of the atoms are connected to one another by covalent bonds. Diamond is composed entirely of carbon atoms, each bonded to four other carbon atoms in a tetrahedral geometry. Melting a covalent network solid is not accomplished by overcoming the relatively weak intermolecular forces. Rather, all of the covalent bonds must be broken, a process that requires extremely high temperatures. Diamond, in fact, does not melt at all. Instead, it vaporizes to a gas at temperatures above 3500°C.

Summary

- The physical properties of a material are affected by the intermolecular forces holding the molecules together.

Practice

Use the link below to answer the following questions:

http://www.elmhurst.edu/ chm/vchembook/160Aintermolec.html

1. What physical properties of materials are influenced by intermolecular forces?
2. What are the strongest intermolecular forces?
3. What kind of molecule is HCl?
4. What forces exist between essentially non-polar molecules?

Review

1. Are melting points of molecular compounds generally higher or lower than those of ionic compounds?
2. Do ionic compounds conduct electricity in the solid state?
3. What types of substances are generally water-soluble?
4. Are most ionic compounds water-soluble?

- **intermolecular force:** Forces between molecules.
- **ionic compound:** Ionic bonds composed in a lattice structure.
- **molecular compound:** Display a wide range of physical properties due to the different types of intermolecular attractions such as different kinds of polar interactions.

13.7 Surface Tension

- Define surface tension.
- Describe role of intermolecular forces in affecting surface tension.

The next time you are by a still body of water, take a close look at what is scooting along on the surface. You may see insects seemingly floating on top of the water. These creatures are known by a variety of names including water skaters, water striders, pond skaters, and other equally descriptive names. They take advantage of a property called surface tension to stay above the water and not sink. The force they exert downward is less than the forces exerted among the water molecules on the surface of the pond, so the insect does not penetrate beneath the surface of the water.

Surface Tension

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 (see A in **Figure** 13.7). The **surface tension** of a liquid is a measure of the elastic force in the liquid's surface. Liquids that have strong intermolecular forces, like the hydrogen bonding in water, exhibit the greatest surface tension. Surface tension allows objects that are denser than water, such as the paper clip shown in B in **Figure** 13.7, to nonetheless float on its surface. It is also responsible for the beading up of water droplets on a freshly waxed car because there are no attractions between the polar water molecules and the nonpolar wax.

Other liquids, such as diethyl ether, do not demonstrate strong surface tension interactions. The intermolecular forces for the ether are the relatively weak dipole-dipole interactions that do not draw the molecules together as tightly as hydrogen bonds would.

Watch a short video of water striders in a pond:

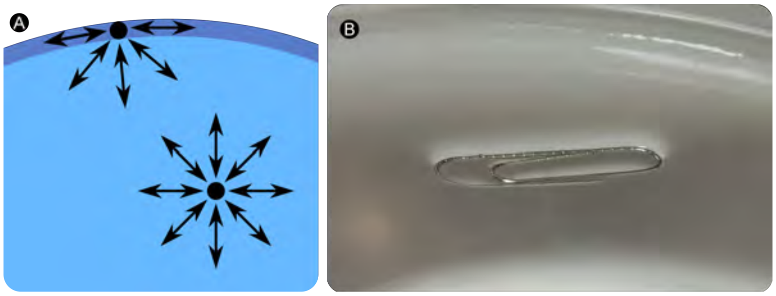


FIGURE 13.7

(A) Molecules at the surface of a liquid are pulled downwards into the liquid, creating a tightened surface. (B) Surface tension allows a paper clip to float on water's surface.

MEDIA

Click image to the left for more content.

http://www.youtube.com/watch?v=mCd6zIuACLw

Summary

- The surface tension of a liquid is a measure of the elastic force in the liquid's surface.
- Liquids with strong intermolecular forces have higher surface tensions than liquids with weaker forces.

Practice

Use the link below to answer the following questions:

http://www.ehow.com/about_6584563_can-certain-bugs-walk-water_.html

1. Do water-walking insects produce a wax that keeps their legs from getting wet?
2. What is on these insects legs that helps them walk on water?
3. How do other insects keep from sinking in the water?

Review

1. Define surface tension.
2. What is responsible for the strong surface tension in water?
3. Does diethyl ether have a stronger or weaker surface tension than water?

- **surface tension:** A measure of the elastic force in the liquid's surface.

13.8 Evaporation

- Define evaporation.
- Define condensation.
- Describe the effect of temperature on the rate of evaporation.

On the roof of the house in the picture above is a device known as a "swamp cooler." This piece of equipment traces its origin back to the ancient Egyptians who hung wet blankets across the doors of their homes. As the warm air passed through the blankets, water would evaporate and cool the air. The royalty went one step further and had servants fan wet cloths over jugs of water to get more evaporation and cooling.

The origin of the term "swamp cooler" is not known – they certainly don't work in a swamp. Best conditions for cooling include a high temperature (over 80°F) and a low humidity (preferably less than 30%). These coolers work well in desert areas, but don't provide any cooling in the humid areas of the country.

Evaporation

A puddle of water left undisturbed eventually disappears. The liquid molecules escape into the gas phase, becoming water vapor. **Vaporization** is the process in which a liquid is converted to a gas. **Evaporation** is the conversion of a liquid to its vapor below the boiling temperature of the liquid. If the water is instead kept in a closed container, the water vapor molecules do not have a chance to escape into the surroundings and so the water level does not change. As some water molecules become vapor, an equal number of water vapor molecules condense back into the liquid state. **Condensation** is the change of state from a gas to a liquid.

In order for a liquid molecule to escape into the gas state, the molecule must have enough kinetic energy to overcome the intermolecular attractive forces in the liquid. Recall that a given liquid sample will have molecules with a wide

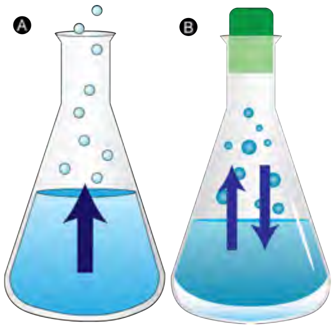


FIGURE 13.8

Evaporation (A) and condensation (B).

range of kinetic energies. Liquid molecules that have this certain threshold kinetic energy escape the surface and become vapor. As a result, the liquid molecules that remain now have a lower average kinetic energy. As evaporation occurs, the temperature of the remaining liquid decreases. You have observed the effects of evaporative cooling. On a hot day, the water molecules in your perspiration absorb body heat and evaporate from the surface of your skin. The evaporating process leaves the remaining perspiration cooler, which in turn absorbs more heat from your body.

A given liquid will evaporate more quickly when it is heated. This is because the heating process results in a greater fraction of the liquid's molecules having the necessary kinetic energy to escape the surface of the liquid. The **Figure** 13.9 shows the kinetic energy distribution of liquid molecules at two temperatures. The numbers of molecules that have the required kinetic energy to evaporate are shown in the shaded area under the curve at the right. The higher temperature liquid (T_2) has more molecules that are capable of escaping into the vapor phase than the lower temperature liquid (T_1).

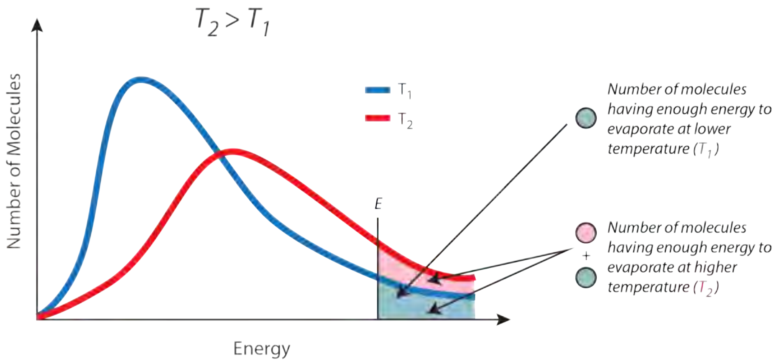


FIGURE 13.9

Kinetic energy distribution curves for a liquid at two temperatures T_1 and T_2. The shaded area is the molecules with enough kinetic energy to escape the liquid and become vapor.

Summary

- Evaporation is the conversion of a liquid to its vapor below the boiling temperature of the liquid.
- Condensation is the change of state from a gas to a liquid.
- As the temperature increases, the rate of evaporation increases.

Practice

Use the link below to answer the following questions:

http://ga.water.usgs.gov/edu/watercycleevaporation.html

1. What is the primary pathway that water moves from the liquid state back into the water cycle as atmospheric water vapor?
2. What percentage of the moisture in the atmosphere comes from evaporation?
3. How long does a water molecule spend in the air after evaporation?
4. What chemicals can be obtained from the Dead Sea?

Review

1. Define vaporization.
2. Define evaporation.
3. Define condensation.
4. How does temperature affect the rate of evaporation?

- **condensation:** The change of state from a gas to a liquid.
- **evaporation:** The conversion of a liquid to its vapor below the boiling temperature of the liquid.
- **vaporization:** The process in which a liquid is converted to a gas.

13.9 Vapor Pressure

- Define vapor pressure.
- Describe the relationship between the intermolecular forces in a liquid and its vapor pressure.
- Describe the relationship between the vapor pressure of a liquid and temperature.

The drinking duck is a toy that many kids (and adults) enjoy playing with. You can see the drinking duck in action in the video at the link below:

MEDIA

Click image to the left for more content.

http://www.youtube.com/watch?v=Bzw0kWvfVkA&feature=player_embedded

The motion of the duck illustrates a physical principle called vapor pressure. As the vapor pressure changes, the liquid in the duck moves up and down, causing the duck to move.

Vapor Pressure

When a partially filled container of liquid is sealed with a stopper, some liquid molecules at the surface evaporate into the **vapor phase**. However, the vapor molecules cannot escape from the container and so after a certain amount of time, the space above the liquid reaches a point where it cannot hold any more vapor molecules. Now some of the vapor molecules condense back into a liquid. The system reaches the point where the rate of evaporation is equal to the rate of condensation (see **Figure** 13.10). This is called a dynamic equilibrium between the liquid and vapor phases.

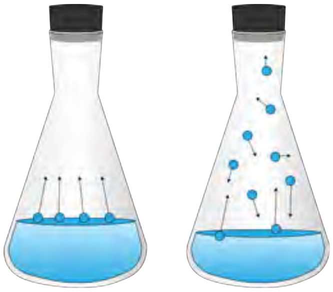


FIGURE 13.10

Equilibrium between liquid phase and vapor phase.

A dynamic equilibrium can be illustrated by an equation with a double arrow, meaning that the reaction is occurring in both directions and at the same rate.

$$H_2O(l) \rightleftharpoons H_2O(g)$$

The forward direction represents the evaporation process, while the reverse direction represents the condensation process.

Because they cannot escape the container, the vapor molecules above the surface of the liquid exert a pressure on the walls of the container. The **vapor pressure** is a measure of the force exerted by a gas above a liquid in a sealed container. Vapor pressure is a property of a liquid based on the strength of its intermolecular forces. A liquid with weak intermolecular forces evaporates more easily and has a high vapor pressure. A liquid with stronger intermolecular forces does not evaporate easily and thus has a lower vapor pressure. For example, diethyl ether is a nonpolar liquid with weak dispersion forces. Its vapor pressure at 20°C is 58.96 kPa. Water is a polar liquid whose molecules are attracted to one another by relatively strong hydrogen bonding. The vapor pressure of water at 20°C is only 2.33 kPa, far less than that of diethyl ether.

Vapor Pressure and Temperature

Vapor pressure is dependent upon temperature. When the liquid in a closed container is heated, more molecules escape the **liquid phase** and evaporate. The greater number of vapor molecules strike the container walls more frequently, resulting in an increase in pressure. The **Table** 13.2 shows the temperature dependence of the vapor pressure of three liquids.

TABLE 13.2: **Vapor Pressure (in kPa) of Three Liquids at Different Temperatures**

	0°C	**20°C**	**40°C**	**60°C**	**80°C**	**100°C**
Water	0.61	2.33	7.37	19.92	47.34	101.33
Ethanol	1.63	5.85	18.04	47.02	108.34	225.75
Diethyl ether	24.70	58.96	122.80	230.65	399.11	647.87

Notice that the temperature dependence of the vapor pressure is not linear. From 0°C to 80°C, the vapor pressure of water increases by 46.73 kPa, while it increases by 53.99 kPa in only a span of twenty degrees from 80°C to 100°C.

Summary

- Vapor pressure is a measure of the force exerted by a gas above a liquid in a sealed container.
- Strong intermolecular forces produce a lower rate of evaporation and a lower vapor pressure.
- Weak intermolecular forces produce a higher rate of evaporation and a higher vapor pressure.
- As the temperature increases, the vapor pressure increases.

Practice

Use the link below to answer the following questions:

http://www.chem.purdue.edu/gchelp/liquids/vpress.html

1. What material has the highest vapor pressure at 25°C?
2. What material has the lowest vapor pressure at 25°C?
3. What device is used to measure vapor pressure?
4. Does the surface area of the liquid affect the vapor pressure?

Review

1. Define vapor pressure.
2. How do intermolecular forces affect vapor pressure?

3. How does temperature affect vapor pressure?

- **liquid phase:** A substance in the liquid state of matter.
- **vapor phase:** A substance in the gaseous state of matter.
- **vapor pressure:** A measure of the force exerted by a gas above a liquid in a sealed container.

13.10 Boiling Point

- Define boiling point.
- Describe the effect of altitude on boiling point.

At 29,029 feet (8,848 m), Mount Everest in the Himalayan range on the border between China and Nepal is the highest point on the earth. Its altitude presents many practical problems to climbers. The oxygen content of the air is much lower that at sea level, making it necessary to bring oxygen tanks along (although a few climbers have reached the peak without oxygen). One other problem is that of boiling water for cooking food. Although water boils at 100°C at sea level, the boiling point on top of Mount Everest is only about 70°C. This difference makes it very difficult to get a decent cup of tea (which definitely frustrated some of the British climbers).

Boiling Point

As a liquid is heated, the average kinetic energy of its particles increases. The rate of evaporation increases as more and more molecules are able to escape the liquid's surface into the vapor phase. Eventually a point is reached when the molecules all throughout the liquid have enough kinetic energy to **vaporize**. At this point the liquid begins to boil. The **boiling point** is the temperature at which the vapor pressure of a liquid is equal to the external pressure. The **Figure** 13.11 illustrates the boiling of liquid.

In the picture on the left, the liquid is below its boiling point, yet some of the liquid evaporates. On the right, the temperature has been increased until bubbles begin to form in the body of the liquid. When the vapor pressure inside the bubble is equal to the external atmospheric pressure, the bubbles rise to the surface of liquid and burst. The temperature at which this process occurs is the boiling point of the liquid.

The normal boiling point is the temperature at which the vapor pressure of the liquid is equal to standard pressure. Because atmospheric pressure can change based on location, the boiling point of a liquid changes with the external pressure. The normal boiling point is a constant because it is defined relative to the standard atmospheric pressure of 760 mmHg (or 1 atm or 101.3 kPa).

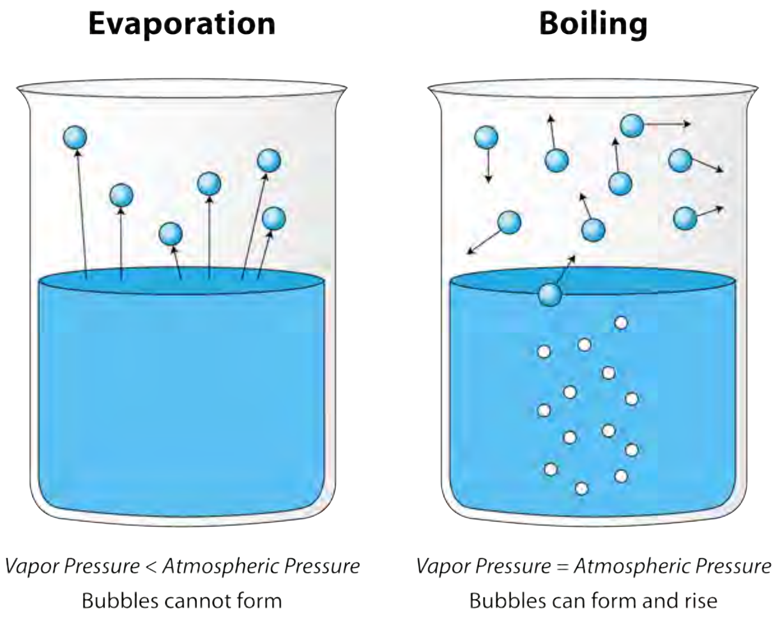


FIGURE 13.11
Comparison between evaporation and boiling.

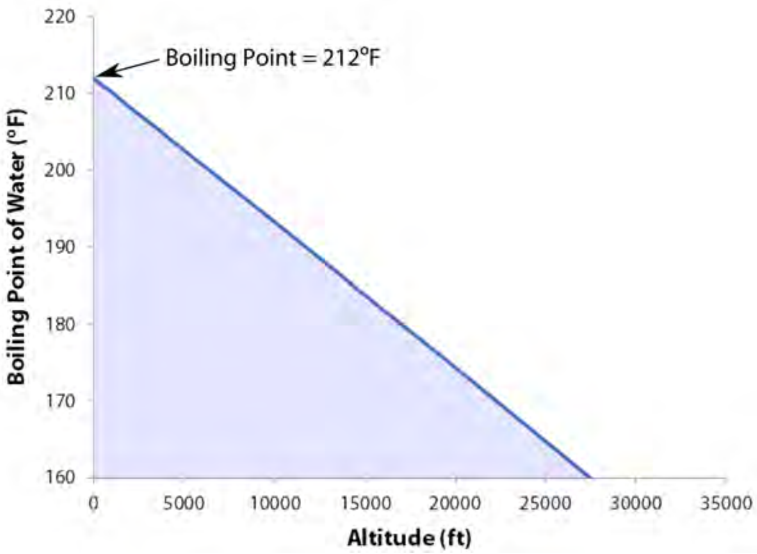


FIGURE 13.12
Influence of altitude on the boiling point of water.

Summary

- The boiling point is the temperature at which the vapor pressure of a liquid is equal to the external pressure.
- As the altitude increases, the boiling point decreases.

Practice

1. What is the boiling point of water in degrees Celsius and Fahrenheit?
2. How does the boiling point of water change at altitudes below sea level?
3. Does water containing impurities boil at a higher or lower temperature than pure water?

Review

1. What happens when a liquid is heated?
2. What is the boiling point?
3. What is the pressure at which the normal boiling point is determined?

- **boiling point:** The temperature at which the vapor pressure of a liquid is equal to the external pressure.
- **vaporize:** When a substance turns from liquid into a gas.

13.11 Vapor Pressure Curves

One of the first lessons in cooking is how to boil water. Yes, it sounds simple, but there are a couple of hints that speed things up. One hint is to put a lid on the pot. The picture above has water boiling uncovered with the steam escaping to the atmosphere. If the lid is on the pot, less water will be boiled off and the water will boil faster. The buildup of pressure inside the pot helps speed up the boiling process.

Vapor Pressure Curves

The boiling points of various liquids can be illustrated in a **vapor pressure curve** (**Figure** 13.13). A vapor pressure curve is a graph of vapor pressure as a function of temperature. To find the normal boiling point of a liquid, a horizontal line is drawn from the left at a pressure equal to standard pressure. At whatever temperature that line intersects the vapor pressure curve of a liquid is the boiling point of that liquid.

The boiling points of liquid also correlate to the strength of the intermolecular forces. Recall that diethyl ether has weak dispersion forces, which meant that the liquid has a high vapor pressure. The weak forces also mean that it does not require a large an input of energy to make diethyl ether boil and so it has a relatively low normal boiling point of 34.6°C. Water, with its much stronger hydrogen bonding, has a low vapor pressure and a higher normal boiling point of 100°C.

As stated earlier, boiling points are affected by external pressure. At higher altitudes, the atmospheric pressure is lower. With less pressure pushing down on the surface of the liquid, it boils at a lower temperature. This can also be seen from the vapor pressure curves. If one draws a horizontal line at a lower vapor pressure, it intersects each curve at a lower temperature. The boiling point of water is 100°C at sea level, where the atmospheric pressure is standard. In Denver, Colorado at 1600 m above sea level, the atmospheric pressure is about 640 mmHg and water boils at about 95°C. On the summit of Mt. Everest the atmospheric pressure is about 255 mmHg and water boils at only 70°C. On the other hand, water boils at greater than 100°C if the external pressure is higher than standard. Pressure cookers do not allow the vapor to escape and the vapor pressure increases. Since water now boils at a temperature above 100°C, the food cooks more quickly.

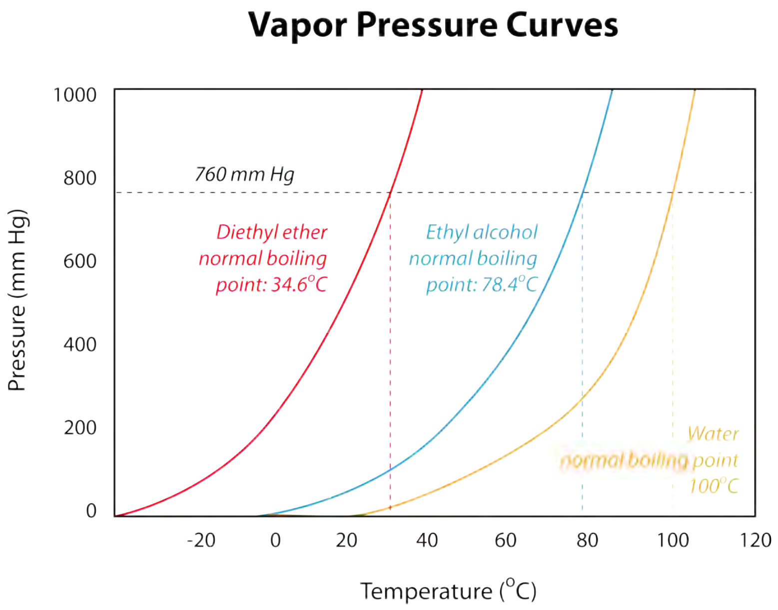


FIGURE 13.13

Vapor pressure curves.

FIGURE 13.14

Pressure cooker.

The effect of decreased air pressure can be demonstrated by placing a beaker of water in a vacuum chamber. At a low enough pressure, about 20 mmHg, water will boil at room temperature.

Summary

- A vapor pressure curve is a graph of vapor pressure as a function of temperature.
- Boiling points are affected by external pressure.

Practice

Use the video below to answer the following questions:

MEDIA
Click image to the left for more content.

http://www.youtube.com/watch?v=Cshd5MVGpfk&feature=player_embedded.

1. What does a vacuum pump do?
2. What is the role of the O-ring?
3. What happens when the vacuum pump is turned on?
4. What happened when the vacuum pump was turned on?
5. What was the temperature of this boiling water?

Review

1. What does a vapor pressure curve show?
2. Why does diethyl ether have a low boiling point?
3. What intermolecular forces hold water molecules together?
4. Why does water boil at a lower temperature when at a high altitude?

- **vapor pressure curve:** A graph of vapor pressure as a function of temperature.

13.12 Melting Point

- Define melting point.
- Describe the process of particle movement in melting.
- Describe the forces that influence the melting point of a material.

In the winter, many people find the snow and ice to be beautiful. They enjoy getting out to ski or ice-skate. Others don't find that time of year to be so much fun. When the snow melts, the roads get very sloppy and messy. Those people look forward to spring when all the ice and snow are gone and the weather is warmer.

Melting Point

Solids are similar to liquids in that both are condensed states, with particles that are far closer together than those of a gas. However, while liquids are fluid, solids are not. The particles of most solids are packed tightly together in an orderly arrangement. The motion of individual atoms, ions, or molecules in a solid is restricted to **vibrational motion** about a fixed point. Solids are almost completely **incompressible** and are the densest of the three states of matter.

As a solid is heated, its particles vibrate more rapidly as the solid absorbs kinetic energy. Eventually, the organization of the particles within the solid structure begins to break down and the solid starts to melt. The **melting point** is the temperature at which a solid changes into a liquid. At its melting point, the disruptive vibrations of the particles of the solid overcome the attractive forces operating within the solid. As with boiling points, the melting point of a solid is dependent on the strength of those attractive forces. Sodium chloride (NaCl) is an ionic compound that consists of a multitude of strong ionic bonds. Sodium chloride melts at 801°C. Ice (solid H_2O) is a molecular compound whose molecules are held together by hydrogen bonds. Though hydrogen bonds are the strongest of the intermolecular forces, the strength of hydrogen bonds is much less than that of ionic bonds. The melting point of ice is 0°C.

The melting point of a solid is the same as the freezing point of the liquid. At that temperature, the solid and liquid states of the substance are in equilibrium. For water, this equilibrium occurs at 0°C.

$$H_2O(s) \rightleftarrows H_2O(l)$$

We tend to think of solids as those materials that are solid at room temperature. However, all materials have melting points of some sort. Gases become solids at extremely low temperatures, and liquids will also become solid if the temperature is low enough. The **Table** 13.3 gives the melting points of some common materials.

TABLE 13.3: **Melting Points of Common Materials**

Material	**Melting Point (°C)**
hydrogen	-259
oxygen	-219
diethyl ether	-116
ethanol	-114
water	0
pure silver	961
pure gold	1063
iron	1538

Summary

- The melting point is the temperature at which a solid changes into a liquid.
- Intermolecular forces have a strong influence on melting point.

Practice

Use the link below to answer the following questions

http://chemwiki.ucdavis.edu/Organic_Chemistry/Organic_Chemistry_With_a_Biological_Emphasis/Chapter__2%3a_Introduction_to_organic_structure_and_bonding_II/Section_2.4%3a_Solubility%2c_melting_points_and_boiling_points

1. To what degree of accuracy can melting points be measured?
2. How can we use melting point data to help identify a compound?
3. How can we use melting points to assess the purity of a compound?

Review

1. Define melting point.
2. What happens when a material melts?
3. Would you expect ethane (C_2H_6) to have a higher or lower melting point than water? Explain your answer.

- **incompressible:** Unable to be compressed.
- **melting point:** The temperature at which a solid changes into a liquid.
- **vibrational motion:** Back and forth movement.

13.13 Sublimation

- Define sublimation.
- Define deposition.
- Give examples of materials that undergo sublimation.

How did the early settlers do their laundry in the winter?

Of course, they could wash the clothes inside, but where to dry them? There were no dryers available, so the clothes had to be hung up to dry. In the winter, you would expect that ice would form on the clothes, but that didn't happen. Even in freezing weather, the water might freeze initially, but would eventually go off as a vapor – from solid ice directly to the gas stage. There are still families today who have to rely on this cumbersome process to get their laundry done.

Sublimation

Vapor Pressure of a Solid

In the last lesson, you learned about the vapor pressure of a liquid and its dependence upon temperature. Solids also have a vapor pressure, though it is generally much less than that of a liquid. A snow bank will gradually disappear even if the temperature stays below 0°C. The snow does not melt, but instead passes directly from the solid state to the vapor state. **Sublimation** is the change of state from a solid to a gas without passing through the liquid state.

Iodine is an example of a substance that sublimes readily at room temperature. This is because the vapor pressure of solid iodine at room temperature is nearly equal to atmospheric pressure. Iodine is a bluish-black solid, but its vapor is a distinctive purple color. Ferrocene (an iron-containing compound) is usually purified by sublimation by gentle warming at atmospheric pressure. In the **Figure** 13.15, you can see the reddish ferrocene crystals deposited on the outside of that tube. **Deposition** is the change of state from a gas to a solid.

FIGURE 13.15

Ferrocene purified by sublimation.

Carbon dioxide is another substance that sublimes at atmospheric pressures. Carbon dioxide in the solid state is known as dry ice. Dry ice is very cold (−78°C) and so is used as a coolant for goods such as ice cream that must remain frozen during shipment. Because the dry ice sublimes rather than melting, there is no liquid mess associated with its change of state as the dry ice warms.

Summary

- Sublimation is the change of state from a solid to a gas without passing through the liquid state.
- Deposition is the change of state from a gas to a solid.
- Iodine and carbon dioxide are two examples of material that undergo sublimation.

Practice

Use the link below to answer the following questions:

http://www.newworldencyclopedia.org/entry/Sublimation_%28chemistry%29

1. How is sublimation used by chemists?
2. Describe the process of purification by sublimation.
3. What is lyophilization?

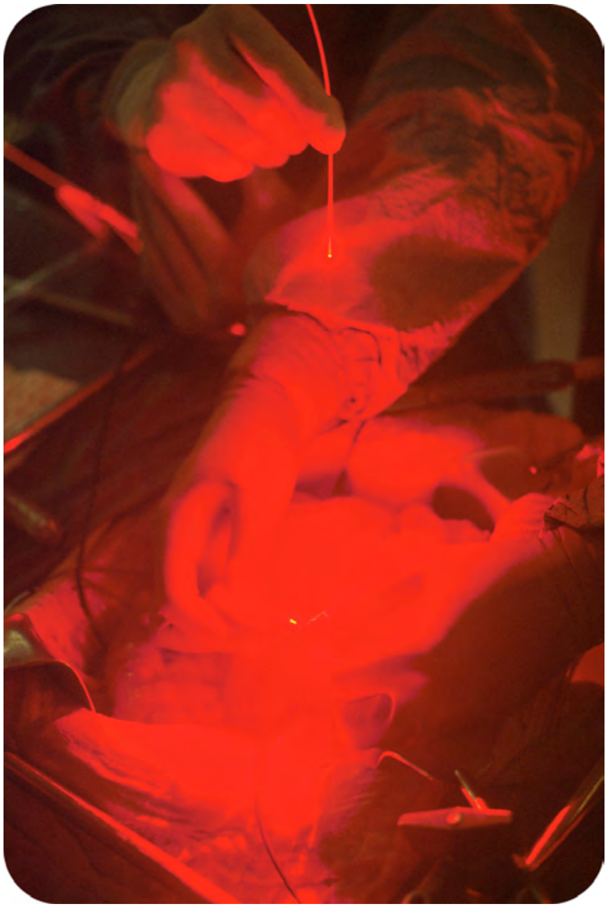
Review

1. Define sublimation.
2. How is ferreocene purified?
3. Name two substances that can undergo sublimation.

- **deposition:** The change of state from a gas to a solid.
- **sublimation:** The change of state from a gas to a solid.

13.14 Crystal Systems

- Define crystal.
- Define crystal lattice.



The development of modern lasers has opened many doors to both research and applications. A laser beam was used to measure the distance from the Earth to the moon. Lasers are important components of CD players. As the image above illustrates, lasers can provide precise focusing of beams to selectively destroy cancer cells in patients. The ability of a laser to focus precisely is due to high-quality crystals that help give rise to the laser beam. A variety of techniques are used to manufacture pure crystals for use in lasers.

Crystalline Solids

The majority of solids are crystalline in nature. A **crystal** is a substance in which the particles are arranged in an orderly, repeating, three-dimensional pattern. Particles of a solid crystal may be ions, atoms, or molecules, depending on the type of substance. The three-dimensional arrangement of a solid crystal is referred to as the **crystal lattice**. Different arrangements of the particles within a crystal cause them to adopt several different shapes.

Crystal Systems

Crystals are classified into general categories based on their shapes. A crystal is defined by its faces, which intersect with one another at specific angles, which are characteristic of the given substance. The seven **crystal systems** are shown below, along with an example of each. The edge lengths of a crystal are represented by the letters a, b, and c. The angles at which the faces intersect are represented by the Greek letters α, β, and γ. Each of the seven crystal systems differs in terms of the angles between the faces and in the number of edges of equal length on each face.

TABLE 13.4: Seven Basic Crystal Systems and Example of Each

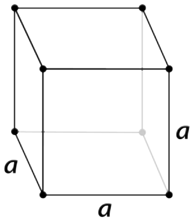
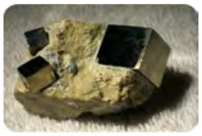
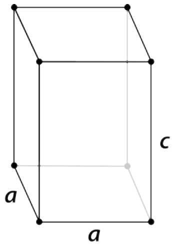
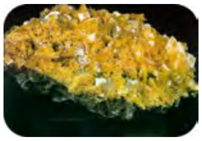
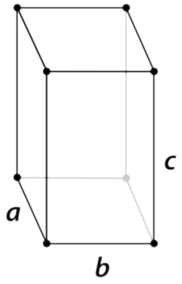
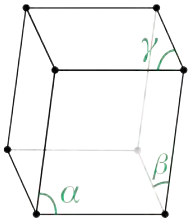
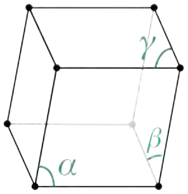
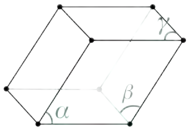
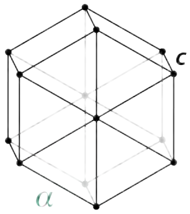
Crystal System	Diagram	Example
Cubic $a = b = c$; $\alpha = \beta = \gamma = 90°$		 Pyrite
Tegragonal $a = b \neq c$; $\alpha = \beta = \gamma = 90°$		 Wulfenite
Orthorhombic $a \neq b \neq c$; $\alpha = \beta = \gamma = 90°$		 Aragonite
Monoclinic $a \neq b \neq c$; $\alpha \neq 90° = \beta = \gamma$		 Azurite

TABLE 13.4: (continued)

Rhombohedral $a = b = c$; $\alpha = \beta = \gamma \neq 90^\circ$		 Calcite
Triclinc $a \neq b \neq c$; $\alpha \neq \beta \neq \gamma \neq 90^\circ$		 Microcline
Hexagonal $a = b \neq c$; $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$		 Beryl

Summary

- A crystal is a substance in which the particles are arranged in an orderly, repeating, three-dimensional pattern.
- The crystal lattice is the three-dimensional arrangement of a solid crystal.

Practice

Use the link below to answer the following questions:

http://www.bookrags.com/research/crystals-and-crystallography-woes-01/

1. What is crystallography?
2. What is a lattice?
3. What types of atomic bonds can exist in crystals?

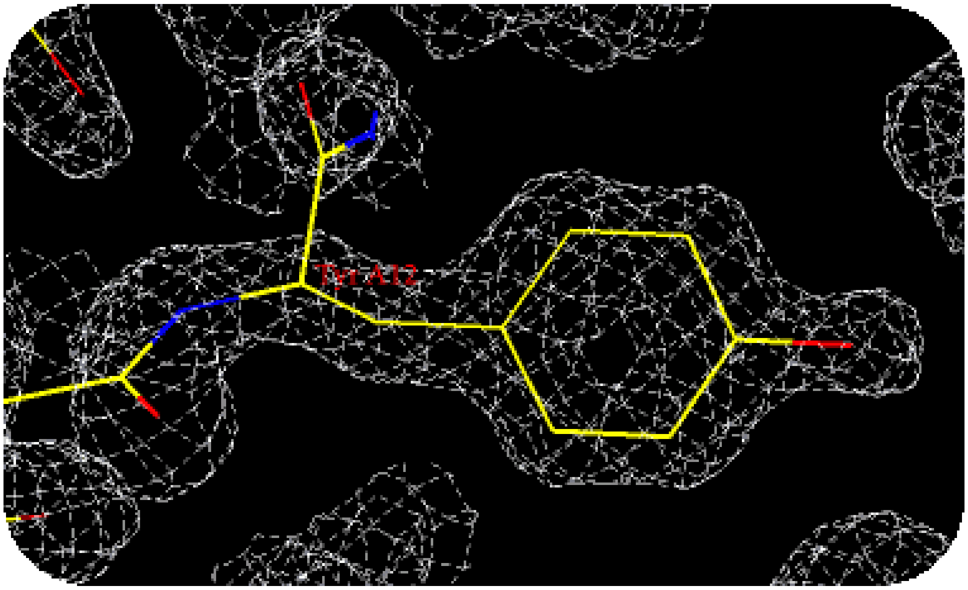
Review

1. What is a crystal?
2. List the seven crystal systems.

- **crystal:** A substance in which the particles are arranged in an orderly, repeating, three-dimensional pattern.
- **crystal lattice:** The three-dimensional arrangement of a solid crystal.
- **crystal system:** A classification of crystals. There are seven systems.

13.15 Unit Cells

- Define unit cell.
- Describe the three cubic crystal system unit cells.



We have many data tables available to us in chemistry. If we wanted to know the size of the lithium atom, we can easily look it up and find that this atom is 134 picometers across. If we remove the outer electron, the lithium ion is now only 90 picometers in size. How do we know this? We don't have a ruler small enough to measure these tiny distances. But we can use a technique called x-ray diffraction to shine beams of x-rays through a crystal of a lithium compound. By measuring how much the beams are bent after they come through the crystal, we can calculate the size of the molecule. This technique works both for small materials like lithium compounds and equally well for very large protein molecules.

Unit Cells

A **unit cell** is the smallest portion of a crystal lattice that shows the three-dimensional pattern of the entire crystal. A crystal can be thought of as the same unit cell repeated over and over in three dimensions. The **Figure** 13.16 illustrates the relationship of a unit cell to the entire crystal lattice.

Unit cells occur in many different varieties. As one example, the cubic crystal system is composed of three different types of unit cells: (1) **simple cubic**, (2) **face-centered cubic**, and (3) **body-centered cubic**. These are shown in three different ways below:

Pay special attention to the last diagram for each type of cell. You will notice that the atoms or ions at the edges of each face or at the corners are not complete spheres. In the simple cubic cell, each particle is shared by three adjacent cells, one on top and one on each side of the particle. The same situation exists for the edge or corner particles in the face-centered and body-centered cubic forms. In addition, each of the particles more in the center of the face-centered cubic cell is also shared with one adjacent cell.

Note that we have only considered the unit cells of a cubic crystal. Other crystal forms also have unit cells. These unit cells are listed below:

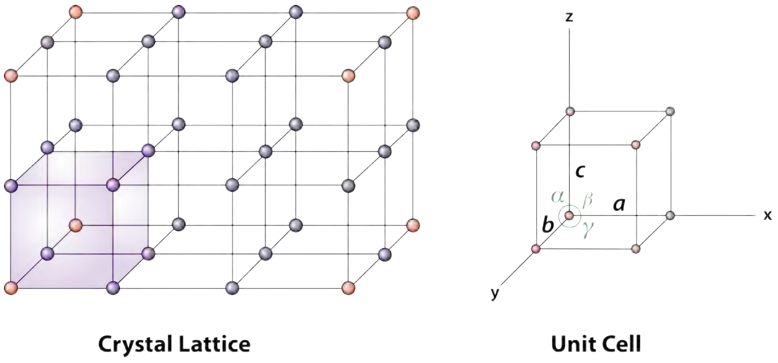


FIGURE 13.16
A unit cell is the smallest repeating portion of a crystal lattice.

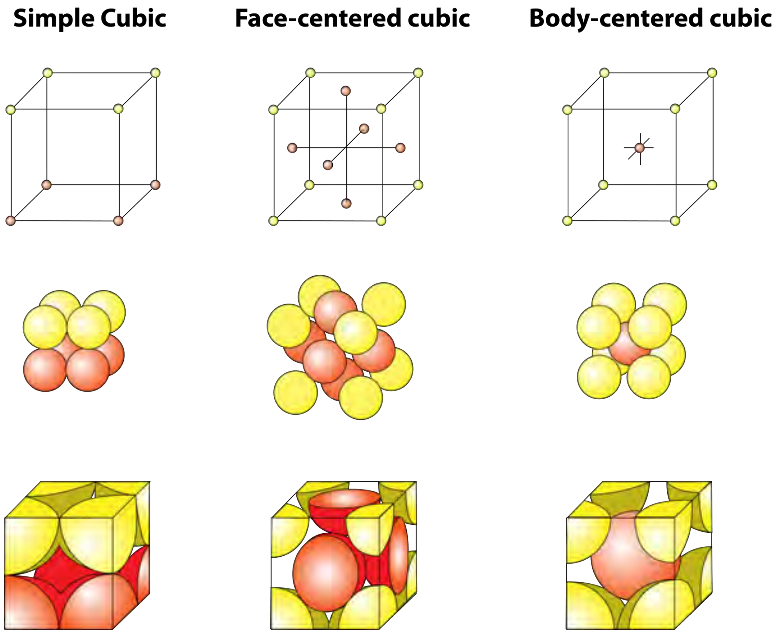


FIGURE 13.17
Three unit cells of the cubic crystal system. Each sphere represents an atom or an ion. In the simple cubic system, the atoms or ions are at the corners of the unit cell only. In the face-centered unit cell, there are also atoms or ions in the center of each of the six faces of the unit cell. In the body-centered unit cell, there is one atom or ion in the center of the unit cell in addition to the corner atoms or ions.

- rhombohedral, hexagonal, triclinic – one unique form each
- tetragonal – simple and body-centered
- monoclinic – simple and end-centered
- orthorhombic – simple, face-centered, body-centered, end-centered

Summary

- A unit cell is the smallest portion of a crystal lattice that shows the three-dimensional pattern of the entire crystal.
- There are three different types of unit cells in the cubic crystal system.

Practice

Use the link below to answer the following questions:

http://chemwiki.ucdavis.edu/Physical_Chemistry/Physical_Properties_of_Matter/Solids/Unit_Cell

1. How is a unit cell defined?
2. Opposite faces of a unit cell are __________.
3. What does the edge of a unit cell connect?

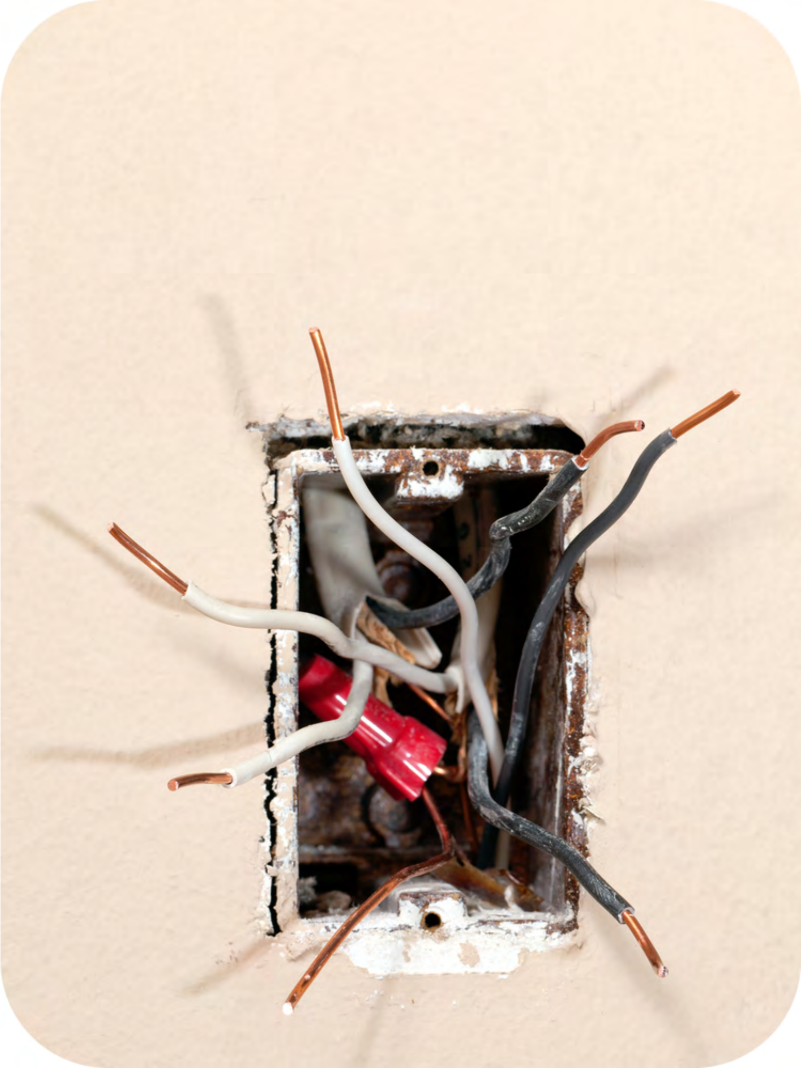
Review

1. What is a unit cell?
2. List the three cubic unit cells.
3. Does each unit cell exist as an entity by itself?

- **body-centered cubic:** There is one atom or ion in the center of the unit cell in addition to the corner atoms or ions.
- **face-centered cubic:** There are also atoms or ions in the center of each of the six faces of the unit cell.
- **simple cubic:** The atoms or ions are at the corners of the unit cell only.
- **unit cell:** The smallest portion of a crystal lattice that shows the three-dimensional pattern of the entire crystal.

13.16 Classes of Crystalline Solids

- List the four types of crystalline solids.
- Describe the properties of each type.



We often take a lot of things for granted. We just assume that we will get electric power when we connect a plug to an electrical outlet. The wire that comprises that outlet is almost always copper, a material that conducts electricity well. The unique properties of the solid copper allow electrons to flow freely through the wire and into whatever device we connect it to. Then we can enjoy music, television, work on the computer, or whatever other activity we want to undertake.

Classes of Crystalline Solids

Crystalline substances can be described by the types of particles in them and the types of chemical bonding that takes place between the particles. There are four types of crystals: (1) **ionic**, (2) **metallic**, (3) **covalent** network, and (4) **molecular**. Properties and several examples of each type are listed in the following table and are described below.

TABLE 13.5: Crystalline Solids – Melting and Boiling Points

Type of Crystalline Solid	Examples (formulas)	Melting Point (°C)	Normal Boiling Point (°C)
Ionic	NaCl	801	1413
	CaF_2	1418	2533
Metallic	Hg	-39	630
	Na	371	883
	Au	1064	2856
	W	3410	5660
Covalent network	B	2076	3927
	C (diamond)	3500	3930
	SiO_2	1600	2230
Molecular	H_2	-259	-253
	I_2	114	184
	NH_3	-78	-33
	H_2O	0	100

1. Ionic crystals – The ionic crystal structure consists of alternating positively-charged cations and negatively-charged anions. The ions may either be monatomic or polyatomic. Generally, ionic crystals form from a combination of Group 1 or 2 metals and Group 16 or 17 nonmetals or nonmetallic polyatomic ions. Ionic crystals are hard and brittle and have high melting points. Ionic compounds do not conduct electricity as solids, but do conduct when molten or in aqueous solution.

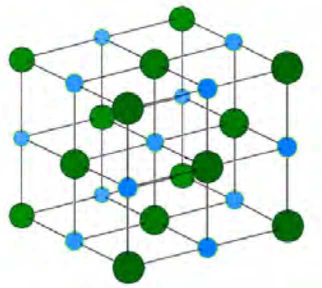


FIGURE 13.18

NaCl crystal.

2. Metallic crystals – Metallic crystals consist of metal cations surrounded by a "sea" of mobile valence electrons. These electrons, also referred to as delocalized electrons, do not belong to any one atom, but are capable of moving through the entire crystal. As a result, metals are good conductors of electricity. As seen in the **Table** 13.5, the melting points of metallic crystals display a wide range.

3. Covalent network crystals – A covalent network crystal consists of atoms at the lattice points of the crystal, with each atom being covalently bonded to its nearest neighbor atoms. The covalently bonded network is three-dimensional and contains a very large number of atoms. Network solids include diamond, quartz, many metalloids, and oxides of transition metals and metalloids. Network solids are hard and brittle, with extremely high melting and boiling points. Being composed of atoms rather than ions, they do not conduct electricity in any state.

4. Molecular crystals – Molecular crystals typically consist of molecules at the lattice points of the crystal, held together by relatively weak intermolecular forces. The intermolecular forces may be dispersion forces in the case of

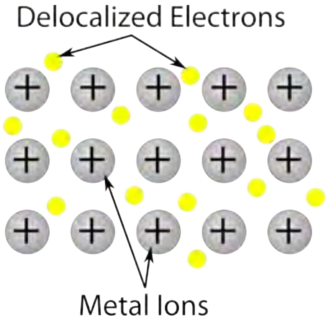


FIGURE 13.19

Metallic crystal lattice with free electrons able to move among positive metal atoms.

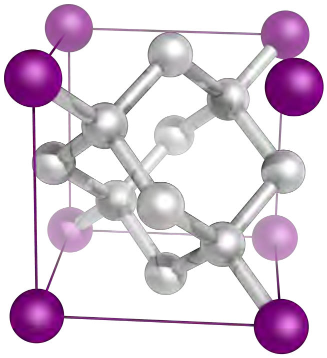


FIGURE 13.20

Diamond is a network solid and consists of carbon atoms covalently bonded to one another in a repeating three-dimensional pattern. Each carbon atom makes four single covalent bonds in a tetrahedral geometry.

nonpolar crystals, or dipole-dipole forces in the case of polar crystals. Some molecular crystals, such as ice, have molecules held together by hydrogen bonds. When one of the noble gases is cooled and solidified, the lattice points are individual atoms rather than molecules. In all cases, the intermolecular forces holding the particles together are far weaker than either ionic or covalent bonds. As a result, the melting and boiling points of molecular crystals are much lower. Lacking ions or free electrons, molecular crystals are poor electrical conductors.

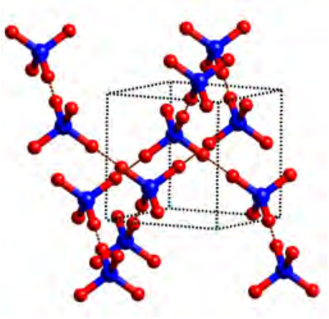


FIGURE 13.21

Ice crystal structure.

Summary

- Ionic crystals are composed of alternating positive and negative ions.
- Metallic crystals consist of metal cations surrounded by a "sea" of mobile valence electrons.
- Covalent crystals are composed of atoms which are covalently bonded to one another.
- Molecular crystals are held together by weak intermolecular forces.

Practice

Use the link below to answer the following questions:

http://www.citycollegiate.com/solid3.htm

1. What kind of three-dimensional structure do crystalline solids have?
2. Do crystalline solids have shapes?
3. Characterize the melting points and boiling points of crystalline solids.

Review

1. What is an ionic crystal?
2. What type of crystal is a diamond?
3. What forces hold molecular crystals together?
4. Which type of crystal is a good conductor of electricity?

- **covalent:** Are composed of atoms which are covalently bonded to one another.
- **ionic:** Composed of alternating positive and negative ions.
- **metallic:** Consist of metal cations surrounded by a "sea" of mobile valence electrons.
- **molecular:** Held together by weak intermolecular forces.

13.17 Amorphous Solid

- Define amorphous solid.
- List properties of amorphous solids.

When a tire goes flat, its shape changes. The tire might be flat because of a slow leak in the tire valve. It could be flat because it ran over a nail or screw and ended up with a small hole where the air can leak out over a period of time. Or it could go flat when it hits a large rock or other object while travelling at high speeds (this one is for those readers who enjoy detective movies or TV shows). What if a crystalline solid like LiBr were ever made into a tire (now there's a weird idea)? When it encountered a blow, the crystal would break into small pieces. Since rubber is an amorphous solid, it has a very different set of physical properties.

Amorphous Solids

Unlike a crystalline solid, an **amorphous** solid is a solid that lacks an ordered internal structure. Some examples of amorphous solids include rubber, plastic, and gels. Glass is a very important amorphous solid that is made by cooling a mixture of materials in such a way that it does not crystallize. Glass is sometimes referred to as a **supercooled** liquid rather than a solid. If you have ever watched a glassblower in action, you have noticed that he takes advantage of the fact that amorphous solids do not have a distinct melting point like crystalline solids do. Instead, as glass is heated, it slowly softens and can be shaped into all sorts of interesting forms. When a glass object shatters, it does so in a very irregular way, unlike crystalline solids, which always break into fragments that have the same shape as dictated by its crystal system.

Properties of amorphous solids are different in many ways from those of crystalline solids. The intermolecular force forces in amorphous solids are weaker than those in crystalline solids. Amorphous solids do not have a regular external structure and they do not have sharp melting points. Unlike crystalline solids that have regular planes of cleavage, the physical properties of amorphous solids are the same in all directions.

Plastics are used for many purposes because they are inexpensive to produce and do not shatters like glass or ceramic materials. Since they are easily disposed of, the accumulation of plastic garbage has become a serious problem in many parts of the world. Recycling programs that help reuse the plastics are growing in popularity.

FIGURE 13.22

Plastic cup.

Watch a short video in the production of glass sheets:

MEDIA

Click image to the left for more content.

http://www.youtube.com/watch?v=tDyeiePort0

Summary

- An amorphous solid is a solid that lacks an ordered internal structure.
- Examples of amorphous solids include glass, rubber, and plastics.
- The physical properties of amorphous solids differ from those of crystalline solids.

Practice

Use the link below to answer the following questions:

http://www.glassnotes.com/WindowPanes.html

1. Why would people believe that glass flows?
2. Are all glass panes in cathedrals thicker at the bottom?
3. How do we explain these findings?
4. Does the glass in Egyptian, Greek, and Roman vessels show this same phenomenon?

Review

1. What is an amorphous solid?
2. List three common examples of amorphous solids.
3. Do amorphous solids have sharp melting points?
4. What word is sometimes used to refer to glass?

- **amorphous:** A solid that lacks an ordered internal structure.
- **supercooled:** A liquid at a temperature lower than its freezing point that has not solidified.

13.18 Heating and Cooling Curves

- List the changes of state.
- Relate the change of state to a change in temperature.

During the time of Mark Twain (real name Samuel Langhorne Clemens, 1835-1910), the steamboat was a major means of transportation on the rivers and lakes of the United States. Twain himself was a steamboat pilot on the Mississippi River for a period of time and took his pen name from the measurement of water depth (twelve feet, which was a safe depth for the boats). The boats got their power from steam – liquid water converted to a gas at high temperatures. The steam would push the pistons of the engine, causing the paddle wheels to turn and propel the boat.

Heating Curves

Imagine that you have a block of ice that is at a temperature of -30°C, well below its **melting** point. The ice is in a closed container. As heat is steadily added to the ice block, the water molecules will begin to vibrate faster and faster as they absorb kinetic energy. Eventually, when the ice has warmed to 0°C, the added energy will start to break apart the hydrogen bonding that keeps the water molecules in place when it is in the **solid** form. As the ice melts, its temperature does not rise. All of the energy that is being put into the ice goes into the melting process and not into any increase in temperature. During the melting process, the two states – solid and **liquid** – are in equilibrium with one another. If the system was isolated at that point and no energy was allowed to enter or leave, the ice-water mixture at 0°C would remain. Temperature is always constant during a change of state.

Continued heating of the water after the ice has completely melted will now increase the kinetic energy of the liquid molecules and the temperature will rise. Assuming that the atmospheric pressure is standard, the temperature will rise steadily until it reaches 100°C. At this point, the added energy from the heat will cause the liquid to begin to vaporize. As with the previous state change, the temperature will remain at 100°C while the water molecules are going from the liquid to the **gas** or vapor state. Once all the liquid has completely boiled away, continued heating of the steam (remember the container is closed) will increase its temperature above 100°C.

The experiment described above can be summarized in a graph called a heating curve (**Figure** 13.23):

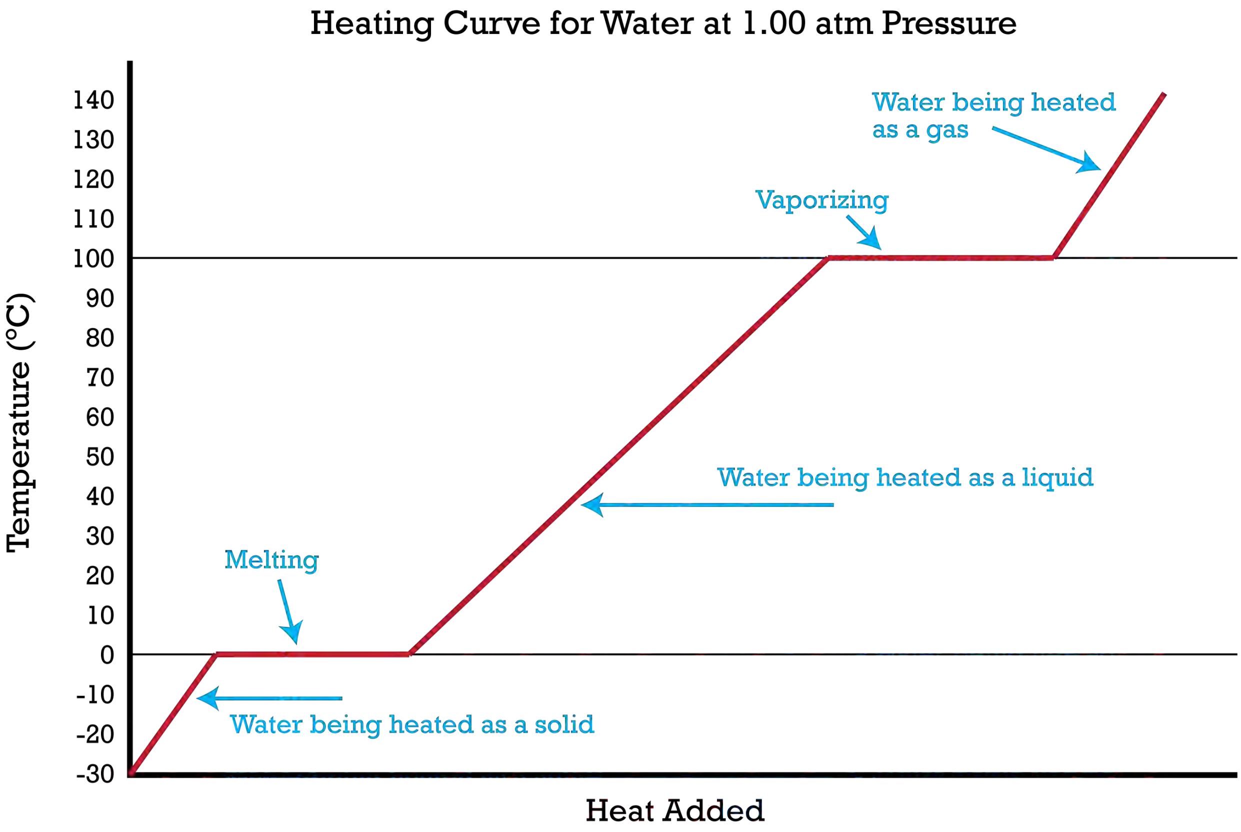


FIGURE 13.23

In the heating curve of water, the temperature is shown as heat is continually added. Changes of state occur during plateaus because the temperature is constant.

The change of state behavior of all substances can be represented with a heating curve of this type. The melting and boiling points of the substance can be determined by the horizontal lines or plateaus on the curve. Other substances would of course have melting and boiling points that are different from those of water. One exception to this exact form for a heating would be for a substance such as carbon dioxide which sublimes rather than melts at standard pressure. The heating curve for carbon dioxide would have only one plateau, at the **sublimation** temperature of CO_2.

The entire experiment could be run in reverse. Steam above 100°C could be steadily cooled down to 100°C, at which point it would condense to liquid water. The water could then be cooled to 0°C, at which point continued cooling would freeze the water to ice. The ice could then be cooled to some point below 0°C. This could be diagrammed in a cooling curve that would be the reverse of the heating curve.

Summary of State Changes

All of the changes of state that occur between solid, liquid and gas are summarized in the diagram in the figure below. **Freezing** is the opposite of melting and both represent the equilibrium between the solid and liquid states. **Evaporation** occurs when a liquid turns to a gas. **Condensation** is the opposite of vaporization and both represent the equilibrium between the liquid and gas states. **Deposition** is the opposite of sublimation and both represent the equilibrium between the solid and gas states.

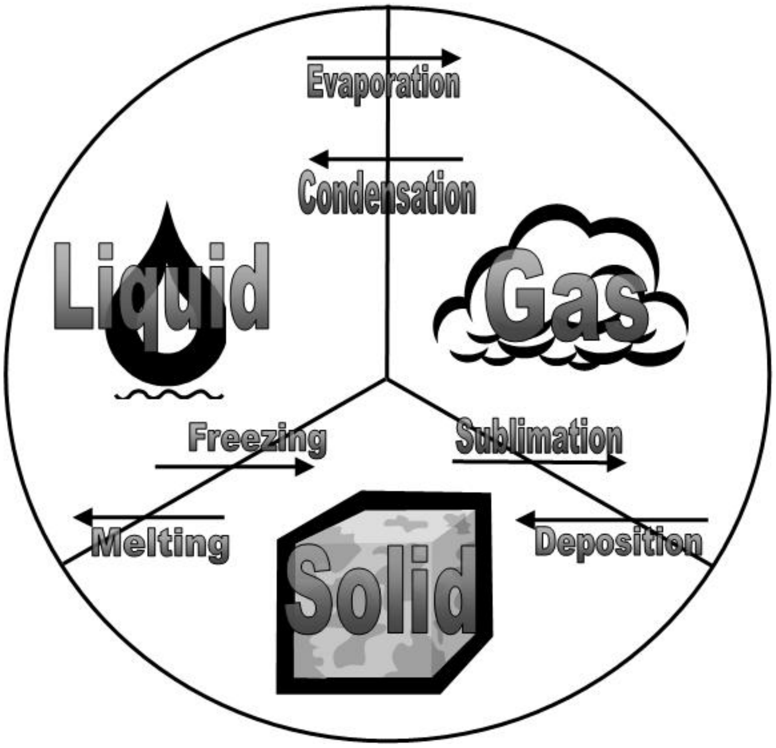


FIGURE 13.24
Solid, liquid, and gas states with the terms for each change of state that occurs between them.

Summary

- A change of state can be brought about by putting heat into a system or removing it from the system.
- The temperature of a system will not change as long as the substance is undergoing a change from solid to liquid or liquid to gas, as well as the reverse.

Practice

You can experiment with pressure, temperature and phases using this simulation

http://www.pbs.org/wgbh/nova/physics/states-of-matter.html

Change the temperature, pressure, and substance and record your observations.

Review

1. What happens when ice reaches 0°C?
2. What is sublimation?
3. What happens to steam if it is cooled to 100°C?

- **condensation:** The process of a gas turning to a liquid. The opposite of vaporization and both represent the equilibrium between the liquid and gas states.
- **deposition:** The process of a gas turning to a solid. The opposite of sublimation and both represent the equilibrium between the solid and gas states.
- **evaporation:** Occurs when a liquid turns to a gas.
- **freezing:** The process of a liquid turning to a solid. The opposite of melting and both represent the equilibrium between the solid and liquid states.
- **gas:** State of matter that fills all available space.
- **liquid:** State of matter with a definite volume and takes the shape of its container.
- **melting:** The process of a solid turning to a liquid.
- **solid:** State of matter with a definite shape and volume.
- **sublimation:** The process of a solid turning to a gas.

13.19 General Phase Diagram

- Define phase diagram.
- Define the triple point.
- Describe how to sue the phase diagram to indicate the state of a material and different temperatures and pressures.

Many rockets use a combination of kerosene and liquid oxygen for their fuel. Oxygen can be reduced to the liquid state either by cooling or by using high pressure. Since the oxygen is in a container essentially out in the open, maintaining a temperature of -183°C (the boiling point of oxygen) is not real practical. But high pressure can be used to force the oxygen into tanks and cause it to liquefy so it can then mix with the kerosene and provide a powerful ignition to move the rocket.

Phase Diagrams

The relationships among the solid, liquid, and vapor (gas) states of a substance can be shown as a function of temperature and pressure in single diagram. **A phase diagram** is a graph which the conditions of temperature and pressure under which a substance exists in the solid, liquid, and gas. Examine the general phase diagram shown in the **Figure** 13.25. In each of the three colored regions of the diagram, the substance is in a single state (or phase). The dark lines that act as the boundary between those regions represent the conditions under which the two phases are in equilibrium.

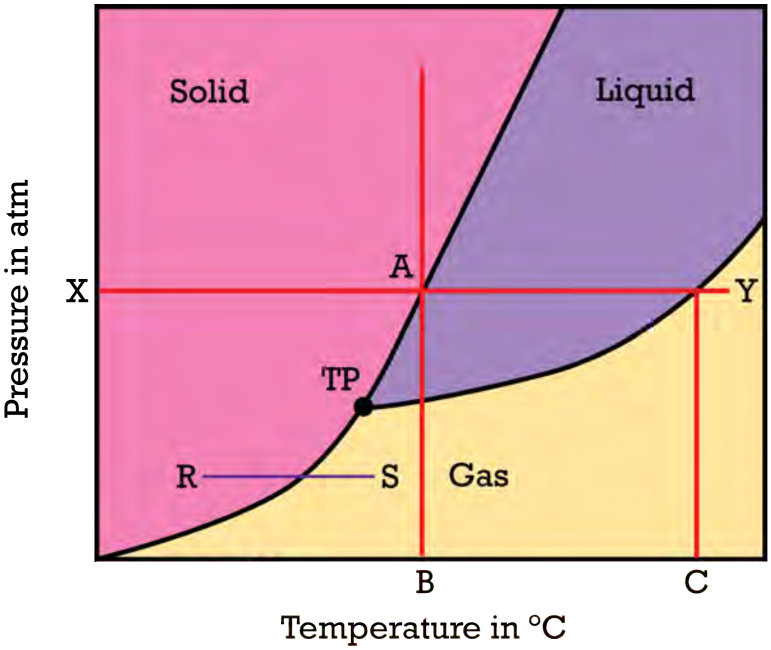


FIGURE 13.25

General phase diagram, which shows the state (phase) of a substance as a function of its temperature and pressure.

Find the X on the pressure axis and presume that the value of X is standard pressure of 1 atm. As one moves left to right across the red line, the temperature of the solid substance is being increased while the temperature remains constant. When point A is reached, the substance melts and the temperature B on the horizontal axis represents the normal melting point of the substance. Moving further to the right, the substance boils at point Y and so point C on the horizontal axis represents the normal boiling point of the substance. As the temperature increases at a constant pressure, the substance changes from solid to liquid to gas.

Start right above point B on the temperature axis and follow the red line vertically. At very low pressure, the particles of the substance are far apart from one another and the substance is in the gas state. As the pressure is increased, the particles of the substance are forced closer and closer together. Eventually the particles are pushed so close together that attractive forces cause the substance to condense into the liquid state. Continually increasing the pressure on the liquid will eventually cause the substance to solidify. For the majority of substances, the solid state is denser than the liquid state and so putting a liquid under great pressure will cause it to turn into a solid. The line segment $R-S$ represents the process of sublimation, where the substance changes directly from a solid to a gas. At a sufficiently low pressure, the liquid phase does not exist. The point labeled TP is called the **triple point**. The triple point is the one condition of temperature and pressure where the solid, liquid, and vapor states of a substance can all coexist at equilibrium.

Summary

- A phase diagram is a graph which the conditions of temperature and pressure under which a substance exists in the solid, liquid, and gas.
- The triple point is the one condition of temperature and pressure where the solid, liquid, and vapor states of a substance can all coexist at equilibrium.

Practice

Use the link below to answer the following questions:

http://chemwiki.ucdavis.edu/Physical_Chemistry/Physical_Properties_of_Matter/Phase_Transitions/Phase_Diagrams

1. What temperatures and pressures favor the formation of a solid?
2. What temperatures and pressures favor the formation of a gas?
3. What does the line *BC* represent?
4. What does the line *BD* represent?

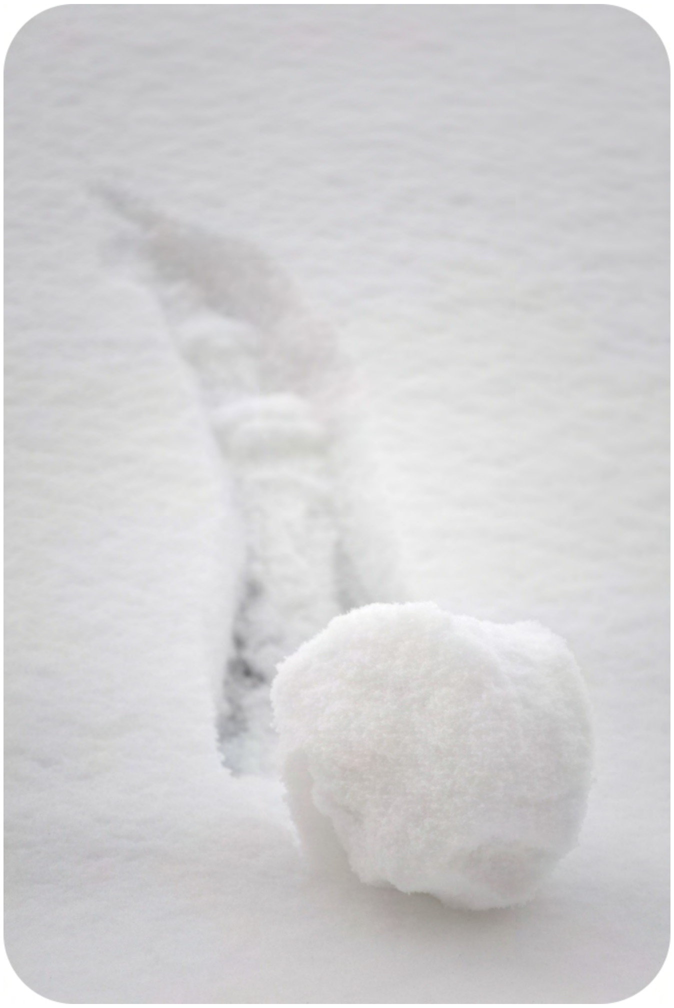
Review

1. What is a phase diagram?
2. What is the triple point?
3. What does point *C* represent?

- **phase diagram:** A graph which the conditions of temperature and pressure under which a substance exists in the solid, liquid, and gas.
- **triple point:** The one condition of temperature and pressure where the solid, liquid, and vapor states of a substance can all coexist at equilibrium.

13.20 Phase Diagram for Water

- Describe the phase diagram for water.
- Define critical temperature.
- Define critical pressure.



You need a special snow to make the best snowballs. This snow needs to be a little wet so the particles will stick together. Dry snow can be tightly pressed and will form snowballs because the higher pressure causes the snowflakes to melt somewhat. However, when you release the pressure, the snow goes back to a more solid form and the flakes no longer stick together.

Phase Diagram for Water

Water is a unique substance in many ways. One of these special properties is the fact that solid water (ice) is less dense than liquid water just above the freezing point. The phase diagram for water is shown below.

Notice one key difference between the general phase diagram and the phase diagram for water. In water's diagram, the slope of the line between the solid and liquid states is negative rather than positive. The reason is that water is

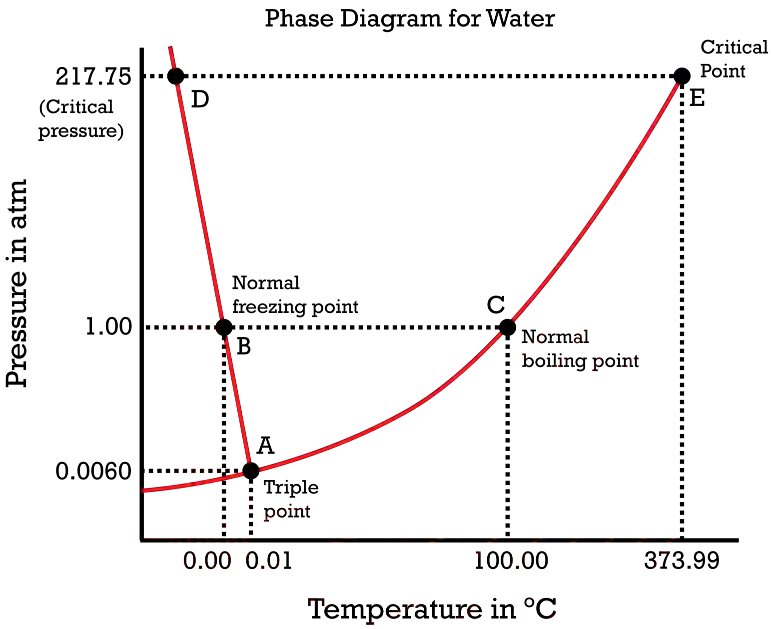


FIGURE 13.26

Phase diagram for water.

an unusual substance in that its solid state is less dense than the liquid state. Ice floats in liquid water. Therefore, a pressure change has the opposite effect on those two phases. If ice is relatively near its melting point, it can be changed into liquid water by the application of pressure. The water molecules are actually closer together in the liquid phase than they are in the solid phase.

The effect of pressure on ice can be seen when a person ice skates. The blade is on the solid ice, but the pressure of the person causes the ice directly under the blade to become more liquid. As the blade moves back off that segment of ice, it refreezes to the solid form again.

FIGURE 13.27

Ice skates designed for speed racing.

Refer again to water's phase diagram (**Figure** 13.26). Notice point E, labeled the **critical point**. What does that mean? At 373.99°C, particles of water in the gas phase are moving very, very rapidly. At any temperature higher than that, the gas phase cannot be made to liquefy, no matter how much pressure is applied to the gas. The **critical pressure** (P_c) is the pressure that must be applied to the gas at the critical temperature in order to turn it into a liquid. For water, the critical pressure is very high, 217.75 atm. The critical point is the intersection point of the **critical temperature** and the critical pressure.

Summary

- Solid water is less dense than liquid water just above the freezing point.
- The critical temperature (T_c) of a substance is the highest temperature at which the substance can possibly exist as a liquid.
- The critical pressure (P_c) is the pressure that must be applied to the gas at the critical temperature in order to turn it into a liquid.
- The critical point is the intersection point of the critical temperature and the critical pressure.

Practice

Read the section of the material at the link below that deals specifically with water:

http://www.chemguide.co.uk/physical/phaseeqia/phasediags.html

1. Why does the melting point of ice get lower at higher pressures?
2. Can you compress steam to form a liquid if the temperature is above 374°C?
3. What is the critical pressure of water?

Review

1. What happens to solid ice under high pressure near the freezing point?
2. What is the critical temperature?
3. What is the critical pressure?

- **critical point:** The intersection point of the critical temperature and the critical pressure.
- **critical pressure:** The pressure that must be applied to the gas at the critical temperature in order to turn it into a liquid.
- **critical temperature:** The highest temperature at which the substance can possibly exist as a liquid.

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CHAPTER 14 The Behavior of Gases

Chapter Outline

14.1 Compressibility

- Define compressibility.
- Give examples of the uses of compressed gases.

Will it all fit?

When we pack to go on vacation, there is always "one more" thing that we need to get in the suitcase. Maybe it's another bathing suit, pair of shoes, book – whatever the item, we need to get it in. Fortunately, we can squeeze things together somewhat. There is a little space between the folds of clothing, we can rearrange the shoes, and somehow we get that last thing in and close the suitcase.

Compressibility

Scuba diving is a form of underwater diving in which a diver carries his own breathing gas, usually in the form of a tank of compressed air. The pressure in most commonly used scuba tanks ranges from 200 to 300 atmospheres. Gases are unlike other states of matter in that a gas expands to fill the shape and volume of its container. For this reason, gases can also be compressed so that a relatively large amount of gas can be forced into a small container. If the air in a typical scuba tank were transferred to a container at the standard pressure of 1 atm, the volume of that container would need to be about 2500 liters.

Compressibility is the measure of how much a given volume of matter decreases when placed under pressure. If we put pressure on a solid or a liquid, there is essentially no change in volume. The atoms, ions, or molecules that make up the solid or liquid are very close together. There is no space between the individual particles, so they cannot pack together.

The kinetic-molecular explains why gases are more compressible than either liquids or solids. Gases are compressible because most of the volume of a gas is composed of the large amounts of empty space between the gas particles. At room temperature and standard pressure, the average distance between gas molecules is about ten times the

FIGURE 14.1

Scuba diver.

diameter of the molecules themselves. When a gas is compressed, as when the scuba tank is being filled, the gas particles are forced closer together.

Compressed gases are used in many situations. In hospitals, oxygen is often used for patients who have damaged lungs to help them breathe better. If a patient is having a major operation, the anesthesia that is administered will frequently be a compressed gas. Welding requires very hot flames produced by compresses acetylene and oxygen mixtures. Many summer barbeque grills are fueled by compressed propane.

Summary

- Gases will compress more easily that solids or liquids because here is so much space between the gas molecules.

Practice

Use the link below to answer the following questions:

http://www.cdxetextbook.com/engines/motivePower/4gasEng/engcycle.html

1. What brings the fuel-air mixture into the cylinder?
2. What is the role of the compression cycle?
3. Does the exhaust cycle compress the gases produced by ignition?

Review

1. Why is there no change in volume when pressure is applied to liquids and solids?
2. Why do gases compress more easily than liquids and solids?
3. List uses for compressed gases.

- **compressibility:** The measure of how much a given volume of matter decreases when placed under pressure.

FIGURE 14.2

Oxygen tank.

14.2 Factors Affecting Gas Pressure

- List factors that affect gas pressure.
- Explain these effects in terms of the kinetic-molecular theory of gases.

How high does a basketball bounce?

The pressure of the air in a basketball has to be adjusted so that the ball bounces to the correct height. Before a game, the officials check the ball by dropping it from shoulder height and seeing how far back up it bounces. What would the official do if the ball did not bounce up as far as it is supposed to? What would he do if it bounced too high?

The pressure inside a container is dependent on the amount of gas inside the container. If the basketball does not bounce high enough, the official could remedy the situation by using a hand pump and adding more air to the ball. Conversely, if it bounces too high, he could let some air out of the ball.

Factors Affecting Gas Pressure

Recall from the kinetic-molecular theory that gas particles move randomly and in straight lines until they elastically collide with either other gas particles or with one of the walls of the container. It is these collisions with the walls of the container that defines the pressure of the gas. Four variables are used to describe the condition of a gas. They are pressure (P), volume (V), temperature (T), and the amount of the gas as measured by the number moles (n). We will examine separately how the volume, temperature, and amount of gas each affect the pressure of an enclosed gas sample.

Amount of Gas

The **Figure** 14.3 shows what happens when air is added to a **rigid container**. A rigid container is one that is incapable of expanding or contracting. A steel canister is an example of a rigid container.

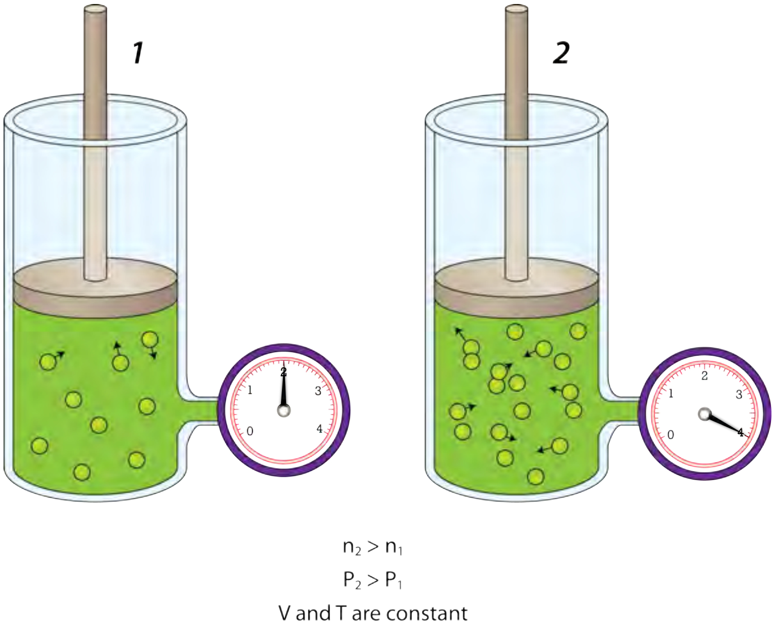


FIGURE 14.3
Increase in pressure with increase in number of gas particles.

The canister on the left contains a gas at a certain pressure. The attached air pump is then used to double the amount of gas in the canister. Since the canister cannot expand, the increased number of air molecules will strike the inside walls of the canister twice as frequently as they did before. The result is that the pressure inside the canister doubles. As you might imagine, if more and more air is continually added to a rigid container, it may eventually burst. Reducing the number of molecules in a rigid container has the opposite effect and the pressure decreases.

Volume

Pressure is also affected by the volume of the container. If the volume of a container is decreased, the gas molecules have less space in which to move around. As a result, they will strike the walls of the container more often and the pressure increases.

Figure 14.4 shows a cylinder of gas whose volume is controlled by an adjustable piston. On the left, the piston is pulled mostly out and the gauge reads a certain pressure. On the right, the piston has been pushed so that the volume of the enclosed portion of the container where the gas is located has been cut in half. The pressure of the gas doubles. Increasing the volume of the container would have the opposite effect and the pressure of the gas would decrease.

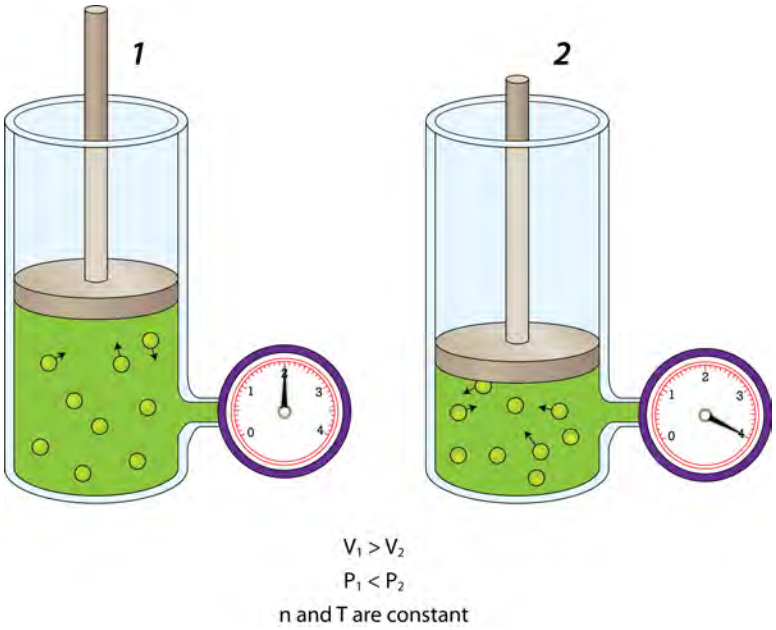


FIGURE 14.4

Decrease in gas volume produced increase in gas pressure.

Temperature

It would be very unadvisable to place a can of soup over a campfire without venting the can. As the can heats up, it may explode. The kinetic-molecular theory explains why. The air inside the rigid can of soup is given more kinetic energy by the heat coming from the campfire. The kinetic energy causes the air molecules to move faster and they impact the container walls more frequently and with more force. The increase in pressure inside may eventually exceed the strength of the can and it will explode. An additional factor is that the soup may begin boiling which will then aid even more gas and more pressure to the inside of the can.

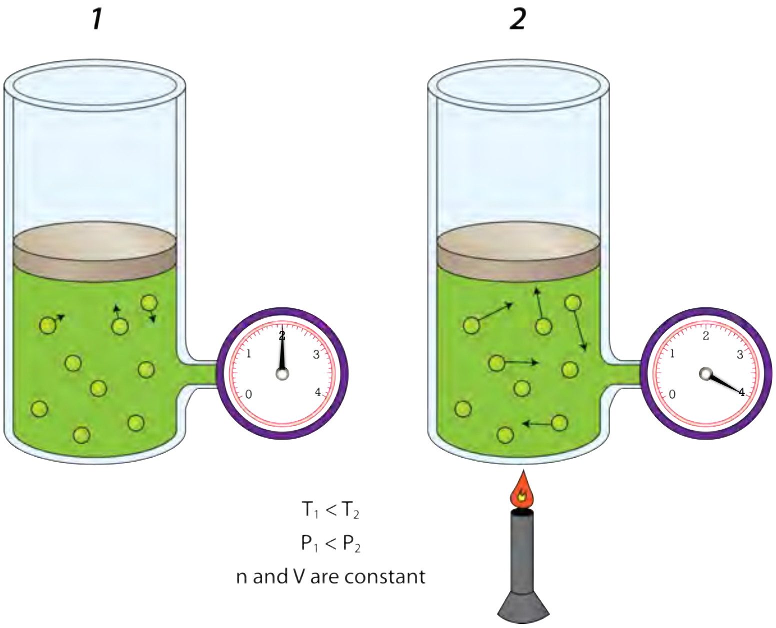


FIGURE 14.5

Increase in temperature produces increase in pressure.

Summary

- An increase in the number of gas molecules in the same volume container increases pressure.
- A decrease in container volume increases gas pressure.
- An increase in temperature of a gas in a rigid container increases the pressure.

Practice

Watch the video at the link below and answer the following questions:

MEDIA

Click image to the left for more content.

http://www.youtube.com/watch?v=0mVuWZ7nvcU

1. What causes pressure?
2. What happens when you let gas out of the container?
3. If you increase the temperature, what happens to the pressure?
4. Why does the pressure drop when you increase the volume?

Review

1. What defines the pressure of a gas?
2. Why does an increase in the number of molecules increase the pressure?
3. Why does an increase in temperature increase the pressure?

- **rigid container:** One that is incapable of expanding or contracting.

14.3 Boyle's Law

- State Boyle's Law.
- Use Boyle's Law to calculate volume-pressure relationships.

How important is it to check the weather?

Each day, hundreds of weather balloons are launched. Made of a synthetic rubber and carrying a box of instruments, the helium-filled balloon rises up into the sky. As it gains altitude, the atmospheric pressure becomes less and the balloon expands. At some point the balloon bursts due to the expansion, the instruments drop (aided by a parachute) to be retrieved and studied for information about the weather.

Boyle's Law

Robert Boyle (1627-1691), an English chemist is widely considered to be one of the founders of the modern experimental science of chemistry. He discovered that doubling the pressure of an enclosed sample of gas while keeping its temperature constant caused the volume of the gas to be reduced by half. **Boyle's law** states that the volume of a given mass of gas varies inversely with the pressure when the temperature is kept constant. An inverse relationship is described in this way. As one variable increases in value, the other variable decreases.

Physically, what is happening? The gas molecules are moving and are a certain distance apart from one another. An increase in pressure pushes the molecules closer together, reducing the volume. If the pressure is decreased, the gases are free to move about in a larger volume.

FIGURE 14.6

Robert Boyle.

Mathematically, Boyle's law can be expressed by the equation:

$$P \times V = k$$

The k is a constant for a given sample of gas and depends only on the mass of the gas and the temperature. The table below shows pressure and volume data for a set amount of gas at a constant temperature. The third column represents the value of the constant (k) for this data and is always equal to the pressure multiplied by the volume. As one of the variables changes, the other changes in such a way that the product of $P \times V$ always remains the same. In this particular case, that constant is 500 atm · ml.

TABLE 14.1: **Pressure-Volume Data**

Pressure (atm)	**Volume (mL)**	$P \times V = k(\text{atm} \cdot \text{mL})$
0.5	1000	500
0.625	800	500
1.0	500	500
2.0	250	500
5.0	100	500
8.0	62.5	500
10.0	50	500

A graph of the data in the table further illustrates the inverse relationship nature of Boyle's Law (see **Figure** 14.7). Volume is plotted on the x-axis, with the corresponding pressure on the y-axis.

Boyle's Law can be used to compare changing conditions for a gas. We use P_1 and V_1 to stand for the initial pressure and initial volume of a gas. After a change has been made, P_2 and V_2 stand for the final pressure and volume. The mathematical relationship of Boyle's Law becomes:

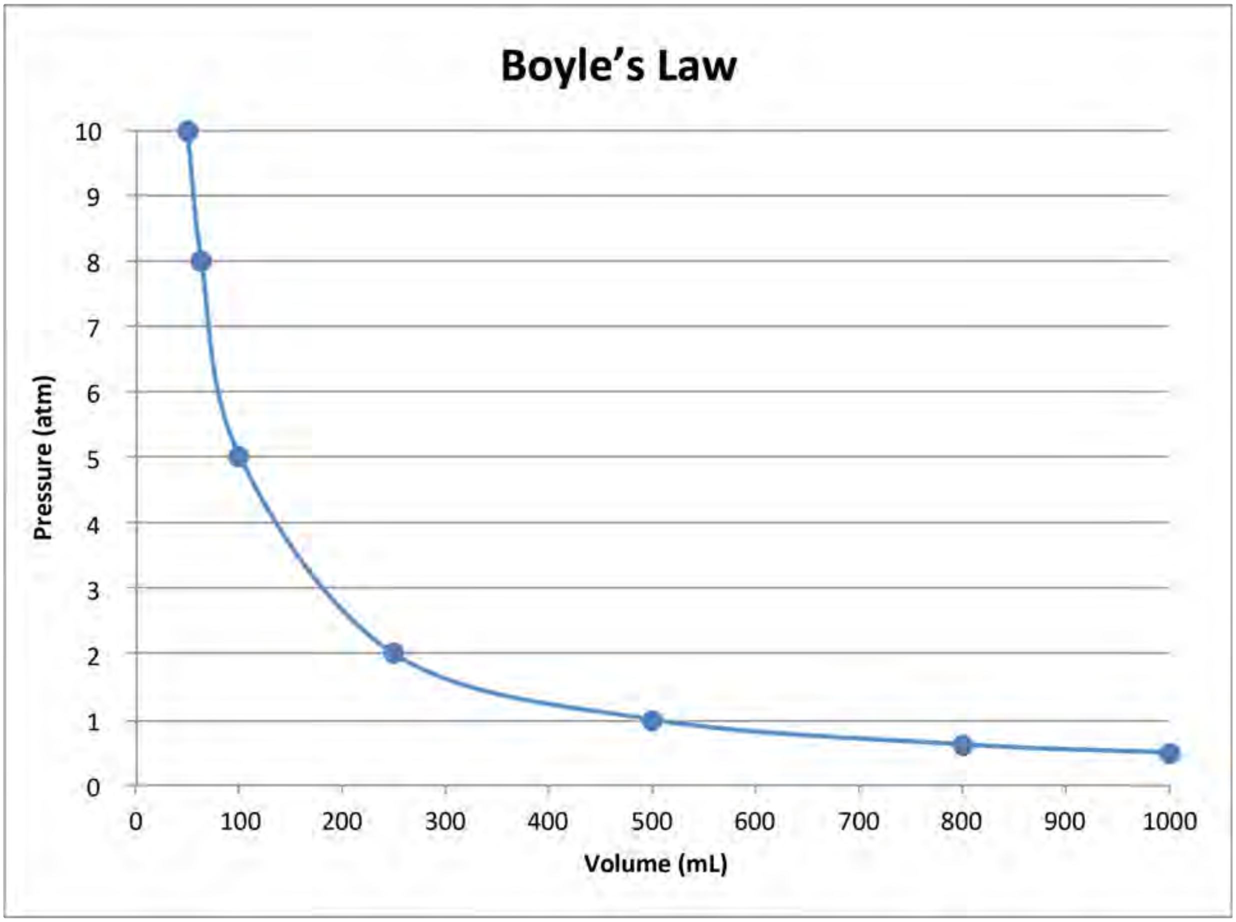


FIGURE 14.7
The pressure of a gas decreases as the volume increases, making Boyle's law an inverse relationship.

$$P_1 \times V_1 = P_2 \times V_2$$

This equation can be used to calculate any one of the four quantities if the other three are known.

Sample Problem: Boyle's Law

A sample of oxygen gas has a volume of 425 mL when the pressure is equal to 387 kPa. The gas is allowed to expand into a 1.75 L container. Calculate the new pressure of the gas.

Step 1: List the known quantities and plan the problem.

Known

- $P_1 = 387$ kPa
- $V_1 = 425$ mL
- $V_2 = 1.75$ L $= 1750$ mL

Unknown

- $P_2 = ?$ kPa

Use Boyle's Law to solve for the unknown pressure (P_2). It is important that the two volumes (V_1 and V_2) are expressed in the same units, so V_2 has been converted to mL.

Step 2: Solve.

First, rearrange the equation algebraically to solve for P_2.

$$P_2 = \frac{P_1 \times V_1}{V_2}$$

Now substitute the known quantities into the equation and solve.

$$P_2 = \frac{387 \text{ kPa} \times 425 \text{ mL}}{1750 \text{ mL}} = 94.0 \text{ kPa}$$

Step 3: Think about your result.

The volume has increased to slightly over 4 times its original value and so the pressure is decreased by about $\frac{1}{4}th$. The pressure is in kPa and the value has three significant figures. Note that any pressure or volume units can be used as long as they are consistent throughout the problem.

Summary

- The volume of a gas is inversely proportional to temperature.

Practice

Do the problems at the link below:

http://www.concord.org/ ddamelin/chemsite/g_gasses/handouts/Boyle_Problems.pdf

Review

1. What does "inversely" mean in this law?
2. Explain Boyle's law in terms of the kinetic-molecular theory of gases.
3. Does it matter what units are used?

- **Boyle's law:** The volume of a given mass of gas varies inversely with the pressure when the temperature is kept constant.

14.4 Charles's Law

- State Charles' Law.
- Use this law to perform calculations involving volume-temperature relationships.

How do you bake bread?

Everybody enjoys the smell and taste of freshly-baked bread. It is light and fluffy as a result of the action of yeast on sugar. The yeast converts the sugar to carbon dioxide, which at high temperatures causes the dough to expand. The end-result is an enjoyable treat, especially when covered with melted butter.

Charles's Law

French physicist Jacques Charles (1746-1823) studied the effect of temperature on the volume of a gas at constant pressure. **Charles's law** states that the volume of a given mass of gas varies directly with the absolute temperature of the gas when pressure is kept constant. The absolute temperature is temperature measured with the Kelvin scale. The Kelvin scale must be used because zero on the Kelvin scale corresponds to a complete stoppage of molecular motion.

Mathematically, the direct relationship of Charles's law can be represented by the following equation:

$$\frac{V}{T} = k$$

As with Boyle's law, k is constant only for a given gas sample. The **Table** 14.2 shows temperature and volume data for a set amount of gas at a constant pressure. The third column is the constant for this particular data set and is always equal to the volume divided by the Kelvin temperature.

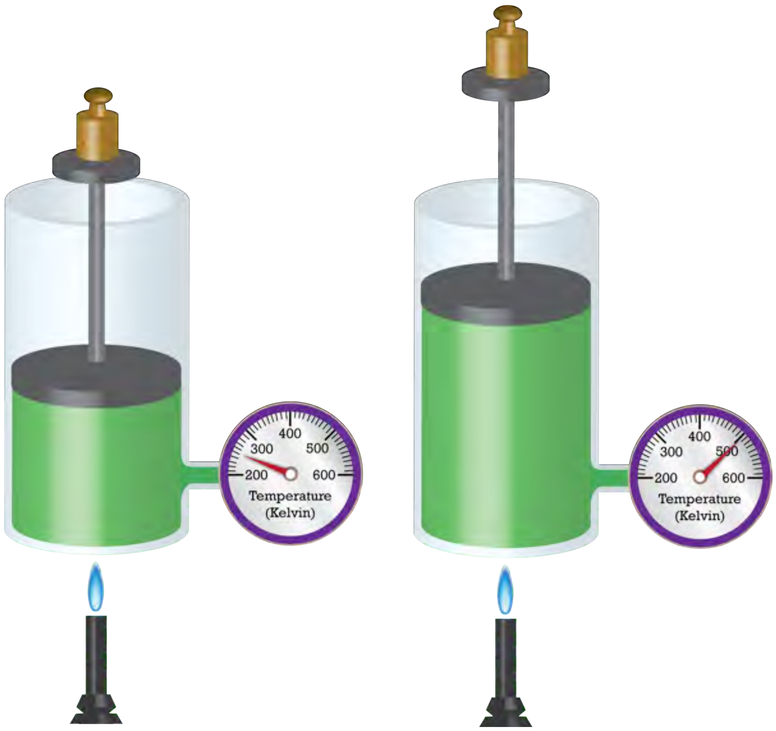


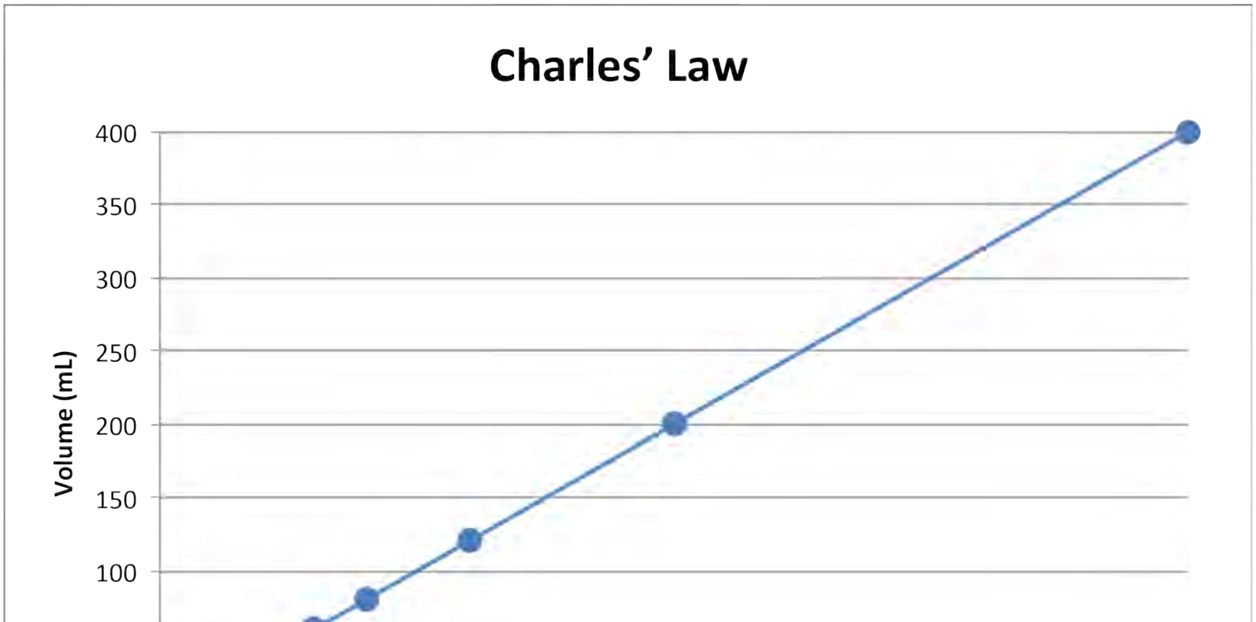
FIGURE 14.8

As a container of confined gas is heated, its molecules increase in kinetic energy and push the movable piston outward, resulting in an increase in volume.

TABLE 14.2: **Temperature-Volume Data**

Temperature (K)	**Volume (mL)**	$\frac{V}{T}=k\left(\frac{mL}{K}\right)$
50	20	0.40
100	40	0.40
150	60	0.40
200	80	0.40
300	120	0.40
500	200	0.40
1000	400	0.40

When this data is graphed, the result is a straight line, indicative of a direct relationship, shown in **Figure** 14.9.



the initial volume and temperature of a gas, while V_2 and T_2 stand for the final volume and temperature. The mathematical relationship of Charles's Law becomes:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

This equation can be used to calculate any one of the four quantities if the other three are known. The direct relationship will only hold if the temperatures are expressed in Kelvin. Temperatures in Celsius will not work. Recall the relationship that K = °C + 273.

Sample Problem: Charles's Law

A balloon is filled to a volume of 2.20 L at a temperature of 22°C. The balloon is then heated to a temperature of 71°C. Find the new volume of the balloon.

Step 1: List the known quantities and plan the problem.

Known

- $V_1 = 2.20 \text{ L}$
- $T_1 = 22^\circ\text{C} = 295 \text{ K}$
- $T_2 = 71^\circ\text{C} = 344 \text{ K}$

Unknown

- $V_2 = ?\ L$

Use Charles's law to solve for the unknown volume (V_2). The temperatures have first been converted to Kelvin.

Step 2: Solve.

First, rearrange the equation algebraically to solve for V_2.

$$V_2 = \frac{V_1 \times T_2}{T_1}$$

Now substitute the known quantities into the equation and solve.

$$V_2 = \frac{2.20 \text{ L} \times 344 \text{ K}}{295 \text{ K}} = 2.57 \text{ L}$$

Step 3: Think about your result.

The volume increases as the temperature increases. The result has three significant figures.

Summary

- Increasing the temperature of a gas at constant pressure will produce and increase in the volume.

Practice

Perform the calculations at the web site below:

http://mmsphyschem.com/chuckL.pdf

Review

1. Explain Charles' Law in terms of the kinetic molecular theory.
2. Why does the temperature need to be in Kelvin?
3. Does Charles' law hold when the gas becomes a liquid?

- **Charles's law:** The volume of a given mass of gas varies directly with the absolute temperature of the gas when pressure is kept constant.

14.5 Gay-Lussac's Law

- State Gay-Lussac's law.
- Use this law to perform calculations involving pressure-temperature relationships.

How much propane is in the tank?

Propane tanks are widely used with barbeque grills. But it's not fun to find out half-way through your grilling that you've run out of gas. You can buy gauges that measure the pressure inside the tank to see how much is left. The gauge measures pressure and will register a higher pressure on a hot day than it will on a cold day. So you need to take the air temperature into account when you decide whether or not to refill the tank before your next cook-out.

Gay-Lussac's Law

When the temperature of a sample of gas in a rigid container is increased, the pressure of the gas increases as well. The increase in kinetic energy results in the molecules of gas striking the walls of the container with more force, resulting in a greater pressure. The French chemist Joseph Gay-Lussac (1778-1850) discovered the relationship between the pressure of a gas and its absolute temperature. **Gay-Lussac's law** states that the pressure of a given mass of gas varies directly with the absolute temperature of the gas, when the volume is kept constant. Gay-Lussac's law is very similar to Charles's law, with the only difference being the type of container. Whereas the container in a Charles's law experiment is flexible, it is rigid in a Gay-Lussac's law experiment.

The mathematical expressions for Gay-Lussac's law are likewise similar to those of Charles's law:

$$\frac{P}{T} = k \quad \text{and} \quad \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

A graph of pressure vs. temperature also illustrates a direct relationship. As a gas is cooled at constant volume its pressure continually decreases until the gas condenses to a liquid.

FIGURE 14.10

Joseph Louis Gay-Lussac.

Sample Problem: Gay-Lussac's Law

The gas in an aerosol can is under a pressure of 3.00 atm at a temperature of 25°C. It is dangerous to dispose of an aerosol can by incineration. What would the pressure in the aerosol can be at a temperature of 845°C?

Step 1: List the known quantities and plan the problem.

Known

- $P_1 = 3.00 \text{ atm}$
- $T_1 = 25^\circ\text{C} = 298 \text{ K}$
- $T_2 = 845^\circ\text{C} = 1118 \text{ K}$

Unknown

- $P_2 = ?\ atm$

Use Gay-Lussac's law to solve for the unknown pressure (P_2). The temperatures have first been converted to Kelvin.

Step 2: Solve.

First, rearrange the equation algebraically to solve for V_2.

$$P_2 = \frac{P_1 \times T_2}{T_1}$$

Now substitute the known quantities into the equation and solve.

$$P_2 = \frac{3.00 \text{ atm} \times 1118 \text{ K}}{298 \text{ K}} = 11.3 \text{ atm}$$

Step 3: Think about your result.

The pressure increases dramatically due to large increase in temperature.

Summary

- Pressure and temperature at constant volume are directly proportional.

Practice

Work the problems found at the web site below:

http://www.chemteam.info/GasLaw/WS-Gay-Lussac.html

Review

1. Explain Gay-Lussac's Law in terms of the kinetic-molecular theory.
2. What would a graph of pressure vs. temperature show us?
3. What is the difference in containers in Charles' Law and Gay-Lussac's Law?

- **Gay-Lussac's law:** The pressure of a given mass of gas varies directly with the absolute temperature of the gas, when the volume is kept constant.

14.6 Combined Gas Law

- State the combined gas law.
- Use the law to calculate parameters in general gas problems.

What keeps things cold?

The modern refrigerator takes advantage of the gas laws to remove heat from a system. Compressed gas in the coils (see above) is allowed to expand. This expansion lowers the temperature of the gas and transfers heat energy from the material in the refrigerator to the gas. As the gas is pumped through the coils, the pressure on the gas compresses it and raises the gas temperature. This heat is then dissipated through the coils into the outside air. As the compressed gas is pumped through the system again, the process repeats itself.

Combined Gas Law

To this point, we have examined the relationships between any two of the variables of P, V, and T, while the third variable is held constant. However, situations arise where all three variables change. The **combined gas law** expresses the relationship between the pressure, volume, and absolute temperature of a fixed amount of gas. For a combined gas law problem, only the amount of gas is held constant.

$$\frac{P \times V}{T} = k \quad \text{and} \quad \frac{P_1 \times V_1}{T_1} = \frac{P_2 \times V_2}{T_2}$$

Sample Problem: Combined Gas Law

2.00 L of a gas at 35°C and 0.833 atm is brought to standard temperature and pressure (STP). What will be the new gas volume?

Step 1: List the known quantities and plan the problem.

Known

- $P_1 = 0.833\ atm$
- $V_1 = 2.00\ \text{L}$
- $T_1 = 35°\text{C} = 308\ \text{K}$
- $P_2 = 1.00\ \text{atm}$
- $T_2 = 0°\text{C} = 273\ \text{K}$

Unknown

- $V_2 = ?\ L$

Use the combined gas law to solve for the unknown volume (V_2). STP is 273 K and 1 atm. The temperatures have been converted to Kelvin.

Step 2: Solve

First, rearrange the equation algebraically to solve for V_2.

$$V_2 = \frac{P_1 \times V_1 \times T_2}{P_2 \times T_1}$$

Now substitute the known quantities into the equation and solve.

$$V_2 = \frac{0.833\ \text{atm} \times 2.00\ \text{L} \times 273\ \text{K}}{1.00\ \text{atm} \times 308\ \text{K}} = 1.48\ \text{L}$$

Step 3: Think about your result.

Both the increase in pressure and the decrease in temperature cause the volume of the gas sample to decrease. Since both changes are relatively small, the volume does not decrease dramatically.

It may seem challenging to remember all the different gas laws introduced so far. Fortunately, Boyle's, Charles's, and Gay-Lussac's laws can all be easily derived from the combined gas law. For example, consider a situation where a change occurs in the volume and pressure of a gas while the temperature is being held constant. In that case, it can be said that $T_1 = T_2$. Look at the combined gas law and cancel the T variable out from both sides of the equation. What is left over is Boyle's law:

$P_1 \times V_1 = P_2 \times V_2$. Likewise, if the pressure is constant, then $P_1 = P_2$ and canceling P out of the equation leaves Charles's law. If the volume is constant, then $V_1 = V_2$ and canceling V out of the equation leaves Gay-Lussac's law.

Summary

- The combined gas law shows the relationships among temperature, volume, and pressure.
- $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

Practice

Work the problems at the link below:

http://misterguch.brinkster.net/WKS001_007_146637.pdf

Review

1. What is the only thing held constant in a combined gas law problem?
2. If you want to solve for the volume of a gas (V_2) and P_1 is greater than P_2, would you expect V_2 to be larger or smaller than V_1?
3. What would be the equation for finding P_2 given all the other parameters?

- **combined gas law:** Expresses the relationship between the pressure, volume, and absolute temperature of a fixed amount of gas.

14.7 Avogadro's Law

- State Avogadro's Law.
- Use this law to perform calculations involving quantities of gases.

How much air do you put into a tire?

A flat tire is not very useful. It does not cushion the rim of the wheel and makes for a very uncomfortable ride. When air is added to the tire, the pressure increases as more molecules of gas are forced into the rigid tire. How much air should be put into a tire depends on the pressure rating for that tire. Too little pressure and the tire will not hold its shape. Too much pressure and the tire could burst.

Avogadro's Law

You have learned about Avogadro's hypothesis: equal volumes of any gas at the same temperature and pressure contain the same number of molecules. It follows that the volume of a gas is directly proportional to the number of moles of gas present in the sample. **Avogadro's law** states that the volume of a gas is directly proportional to the number of moles of gas when the temperature and pressure are held constant. The mathematical expression of Avogadro's law is

$$V = k \times n \quad \text{and} \quad \frac{V_1}{n_1} = \frac{V_2}{n_2}$$

where n is the number of moles of gas and k is a constant. Avogadro's law is in evidence whenever you blow up a balloon. The volume of the balloon increases as you add moles of gas to the balloon by blowing it up.

If the container holding the gas is rigid rather than flexible, pressure can be substituted for volume in Avogadro's law. Adding gas to a rigid container makes the pressure increase.

Sample Problem: Avogadro's Law

A balloon has been filled to a volume of 1.90 L with 0.0920 mol of helium gas. If 0.0210 mol of additional helium is added to the balloon while the temperature and pressure are held constant, what is the new volume of the balloon?

Step 1: List the known quantities and plan the problem.

Known

- $V_1 = 1.90\ L$
- $n_1 = 0.0920$ mol
- $n_2 = 0.0920 + 0.0210 = 0.1130$ mol

Unknown

- $V_2 = ?\ L$

Note that the final number of moles has to be calculated by adding the original number of moles to the moles of added helium. Use Avogadro's law to solve for the final volume.

Step 2: Solve.

First, rearrange the equation algebraically to solve for V_2.

$$V_2 = \frac{V_1 \times n_2}{n_1}$$

Now substitute the known quantities into the equation and solve.

$$V_2 = \frac{1.90 \text{ L} \times 0.1130 \text{ mol}}{0.0920 \text{ mol}} = 2.33 \text{ L}$$

Step 3: Think about your result.

Since a relatively small amount of additional helium was added to the balloon, its volume increases slightly.

Summary

- Calculations are shown for relationships between volume and number of moles of a gas.

Practice

Work the problems at the site below:

http://www.gst-d2l.com/homework/hwavogadroslaw.html

Review

1. What is held constant in the Avogadro's Law relationship?
2. What happens if you add gas to a rigid container?
3. Why does a balloon expand when you add air to it?

- **Avogadro's law:** The volume of a gas is directly proportional to the number of moles of gas when the temperature and pressure are held constant.

14.8 Ideal Gas Law

- Derive the ideal gas law from the combined gas law and Avogadro's law.
- Calculate the value of the ideal gas constant.
- Use the ideal gas law to calculate parameters for ideal gases.

What chemical reactions require ammonia?

There are a number of chemical reactions that require ammonia. In order to carry out the reaction efficiently, we need to know how much ammonia we have for stoichiometric purposes. Using gas laws, we can determine the number of moles present in the tank if we know volume, temperature, and pressure of the system.

Ideal Gas Law

The combined gas law shows that the pressure of a gas is inversely proportional to volume and directly proportional to temperature. Avogadro's law shows that volume or pressure is directly proportional to the number of moles of gas. Putting these together leaves us with the following equation:

$$\frac{P_1 \times V_1}{T_1 \times n_1} = \frac{P_2 \times V_2}{T_2 \times n_2}$$

As with the other gas laws, we can also say that $\frac{(P \times V)}{(T \times n)}$ is equal to a constant. The constant can be evaluated provided that the gas being described is considered to be ideal.

The **ideal gas law** is a single equation which relates the pressure, volume, temperature, and number of moles of an ideal gas. If we substitute in the variable R for the constant, the equation becomes:

$$\frac{P \times V}{T \times n} = R$$

The ideal gas law is conventionally rearranged to look this way, with the multiplication signs omitted:

$$PV = nRT$$

The variable R in the equation is called the **ideal gas constant**.

Evaluating the Ideal Gas Constant

The value of R, the ideal gas constant, depends on the units chosen for pressure, temperature, and volume in the ideal gas equation. It is necessary to use Kelvin for the temperature and it is conventional to use the SI unit of liters for the volume. However, pressure is commonly measured in one of three units: kPa, atm, or mmHg. Therefore, R can have three different values.

We will demonstrate how R is calculated when the pressure is measured in kPa. Recall that the volume of 1.00 mol of any gas at STP is measured to be 22.414 L. We can substitute 101.325 kPa for pressure, 22.414 L for volume, and 273.15 K for temperature into the ideal gas equation and solve for R.

$$R = \frac{PV}{nT} = \frac{101.325 \text{ kPa} \times 22.414 \text{ L}}{1.000 \text{ mol} \times 273.15 \text{ K}} = 8.314 \text{ kPa} \cdot \text{L/K} \cdot \text{mol}$$

This is the value of R that is to be used in the ideal gas equation when the pressure is given in kPa. The **Table** 14.3 shows a summary of this and the other possible values of R. It is important to choose the correct value of R to use for a given problem.

TABLE 14.3: **Values of the Ideal Gas Constant**

Unit of P	**Unit of V**	**Unit of n**	**Unit of T**	**Value and unit of R**
kPa	L	mol	K	8.314 J/K · mol
atm	L	mol	K	0.08206 L · atm/K · mol
mmHg	L	mol	K	62.36 L · mmHg/K · mol

Notice that the unit for R when the pressure is in kPa has been changed to J/K • mol. A kilopascal multiplied by a liter is equal to the SI unit for energy, a joule (J).

Sample Problem: Ideal Gas Law

What volume is occupied by 3.760 g of oxygen gas at a pressure of 88.4 kPa and a temperature of 19°C? Assume the oxygen is ideal.

Step 1: List the known quantities and plan the problem.

Known

- $P = 88.4\ kPa$
- $T = 19°\text{C} = 292\ \text{K}$
- mass $O_2 = 3.760$ g
- $O_2 = 32.00$ g/mol
- $R = 8.314\ \text{J/K} \cdot \text{mol}$

Unknown

- $V = ?\ L$

In order to use the ideal gas law, the number of moles of O_2 (n) must be found from the given mass and the molar mass. Then, use $PV = nRT$ to solve for the volume of oxygen.

Step 2: Solve.

$$3.760\ \text{g} \times \frac{1\ \text{mol}\ O_2}{32.00\ \text{g}\ O_2} = 0.1175\ \text{mol}\ O_2$$

Rearrange the ideal gas law and solve for V.

$$V = \frac{nRT}{P} = \frac{0.1175\ \text{mol} \times 8.314\ \text{J/K} \cdot \text{mol} \times 292\ \text{K}}{88.4\ \text{kPa}} = 3.23\ \text{L}\ O_2$$

Step 3: Think about your result

The number of moles of oxygen is far less than one mole, so the volume should be fairly small compared to molar volume (22.4 L/mol) since the pressure and temperature are reasonably close to standard. The result has three significant figures because of the values for T and P. Since a joule (J) = kPa • L, the units cancel correctly, leaving a volume in liters.

Summary

- The ideal gas constant is calculated.
- An example of calculations using the ideal gas law is shown.

Practice

Work the problems at the link below:

http://chemsite.lsrhs.net/gasses/handouts/Ideal_Problems.pdf

Review

1. Which value of R will you use if the pressure is given in atm?
2. You are doing a calculation where the pressure is given in mm Hg. You select 8.314 J/K • mol as your value for R. Will you get a correct answer?
3. How would you check that you have chosen the correct value of R for your problem?

- **ideal gas constant:** The variable R in the ideal gas law equation.
- **ideal gas law:** A single equation which relates the pressure, volume, temperature, and number of moles of an ideal gas.

14.9 Calculating the Molar Mass of a Gas

- Calculate the molar mass of a gas.
- Calculate the density of a gas.

What makes it float?

Helium has long been used in balloons and blimps. Since it is much less dense than air, it will float above the ground. We can buy small balloons filled with helium at stores, but large ones (such as the balloon seen above) are much more expensive and take up a lot more helium.

Calculating Molar Mass and Density of a Gas

A chemical reaction is performed that produces a gas, which is then collected and its mass and volume determined. The molar mass of the unknown gas can be found using the ideal gas law, provided the temperature and pressure of the gas are also known.

Sample Problem: Molar Mass and the Ideal Gas Law

A certain reaction occurs, producing an oxide of nitrogen as a gas. The gas has a mass of 1.211 g and occupies a volume of 677 mL. The temperature in the laboratory is 23°C and the air pressure is 0.987 atm. Calculate the molar mass of the gas and deduce its formula. Assume the gas is ideal.

Step 1: List the known quantities and plan the problem.

Known

- mass $= 1.211$ g
- $V = 677$ ml $= 0.677$ L
- $T = 23°\text{C} = 296$ K
- $P = 0.987$ atm
- $R = 0.08206\ \text{L}\cdot\text{atm/K}\cdot\text{mol}$

Unknown

- $n =?$ mol
- molar mass $=?$ g/mol

First the ideal gas law will be used to solve for the moles of unknown gas (n). Then the mass of the gas divided by the moles will give the molar mass.

Step 2: Solve.

$$n = \frac{PV}{RT} = \frac{0.987\ \text{atm} \times 0.677\ \text{L}}{0.08206\ \text{L}\cdot\text{atm/K}\cdot\text{mol} \times 296\ \text{K}} = 0.0275\ \text{mol}$$

Now divide g by mol to get the molar mass.

$$\text{molar mass} = \frac{1.211\ \text{g}}{0.0275\ \text{mol}} = 44.0\ \text{g/mol}$$

Since N has a molar mass of 14 g/mol and O has a molar mass of 16 g/mol, the formula N_2O would produce the correct molar mass.

Step 3: Think about your result

The R value that corresponds to a pressure in atm was chosen for this problem. The calculated molar mass gives a reasonable formula for dinitrogen monoxide.

Calculating Density of a Gas

The ideal gas law can be used to find the density of a gas at conditions that are not standard. For example, we will determine the density of ammonia gas (NH_3) at 0.913 atm and 20°C, assuming the ammonia is ideal. First, the molar mass of ammonia is calculated to be 17.04 g/mol. Next, assume exactly 1 mol of ammonia $(n = 1)$ and calculate the volume that such an amount would occupy at the given temperature and pressure.

$$V = \frac{nRT}{P} = \frac{1.00\ \text{mol} \times 0.08206\ \text{L}\cdot\text{atm/K}\cdot\text{mol} \times 293\ \text{K}}{0.913\ \text{atm}} = 26.3\ \text{L}$$

Now the density can be calculated by dividing the mass of one mole of ammonia by the volume above.

$$\text{density} = \frac{17.04 \text{ g}}{26.3 \text{ L}} = 0.647 \text{ g/L}$$

As a point of comparison, this density is slightly less than the density of ammonia at STP, which is equal to $\frac{(17.04 \text{ g/mol})}{(22.4 \text{ L/mol})} = 0.761$ g/L. It makes sense that the density should be lower compared to that at STP since both the increase in temperature (from 0°C to 20°C) and the decrease in pressure (from 1 atm to 0.913 atm) would cause the NH_3 molecules to spread out a bit further from one another.

Summary

- Calculations of molar mass and density of an ideal gas are described.

Practice

Answer questions and perform calculations of problems at the following link:

http://www.mybookezz.com/ebook.php?u=aHR0cDovL2dvLmhydy5jb20vcmVzb3VyY2VzL2dvX3NjL21jL0hDMlN SMTEzLlBERgpTZWN0aW9uIDM=

Review

1. Why do you need the volume, temperature, and pressure of the gas to calculate molar mass?
2. What assumption about the gas is made in all these calculations?
3. Why do you need the mass of the gas to calculate the molar mass?

14.10 Gas Stoichiometry

- Use the ideal gas law to calculate stoichiometry problems for gases.

The Haber cycle reaction of gaseous nitrogen and hydrogen to form ammonia is a critical step in the production of fertilizer from ammonia. It is important to have an excess of the starting materials so that a maximum yield of ammonia can be achieved. By knowing how much ammonia is needed for manufacture of a batch of fertilizer, the proper amounts of nitrogen and hydrogen gases can be incorporated into the process.

Gas Stoichiometry

You have learned how to use molar volume to solve stoichiometry problems for chemical reactions involving one or more gases at STP. Now, we can use the ideal gas law to expand our treatment of chemical reactions to solve stoichiometry problems for reactions that occur at any temperature and pressure.

Sample Problem: Gas Stoichiometry and the Ideal Gas Law

What volume of carbon dioxide is produced by the combustion of 25.21 g of ethanol (C_2H_5OH) at 54°C and 728 mmHg? Assume the gas is ideal.

Before using the ideal gas law, it is necessary to write and balance the chemical equation. Recall that most combustion reactions, the given substance reacts with O_2 to form CO_2 and H_2O. Here is the balanced equation for the combustion of ethanol.

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$$

Step 1: List the known quantities and solve the problem.

Known

- mass $C_2H_5OH = 25.21$ g
- molar mass $C_2H_5OH = 46.08$ g/mol
- $P = 728$ mmHg
- $T = 54°\text{C} = 327$ K

Unknown

- *Volume* $CO_2 =?$ *L*

The number of moles of carbon dioxide gas is first calculated by stoichiometry. Then the ideal gas law is used to calculate the volume of CO_2 produced.

Step 2: Solve.

$$25.21 \text{ g } C_2H_5OH \times \frac{1 \text{ mol } C_2H_5OH}{46.08 \text{ g } C_2H_5OH} \times \frac{2 \text{ mol } CO_2}{1 \text{ mol } C_2H_5OH} = 1.094 \text{ mol } C_2H_5OH$$

The moles of ethanol (n) is now substituted into $PV = nRT$ to solve for the volume.

$$V = \frac{nRT}{P} = \frac{1.094 \text{ mol} \times 62.36 \text{ L} \cdot \text{mmHg/K} \cdot \text{mol} \times 327 \text{ K}}{728 \text{ mmHg}} = 30.6 \text{ L}$$

Step 3: Think about your result.

The mass of ethanol is slightly more than one half mole, meaning that the mole ratio results in slightly more than one mole of carbon dioxide being produced. Because of the elevated temperature and reduced pressure compared to STP, the resulting volume is larger than 22.4 L.

Summary

- The ideal gas law is used to calculate stoichiometry problems for gases.

Practice

Solve the problems on the worksheet at this site:

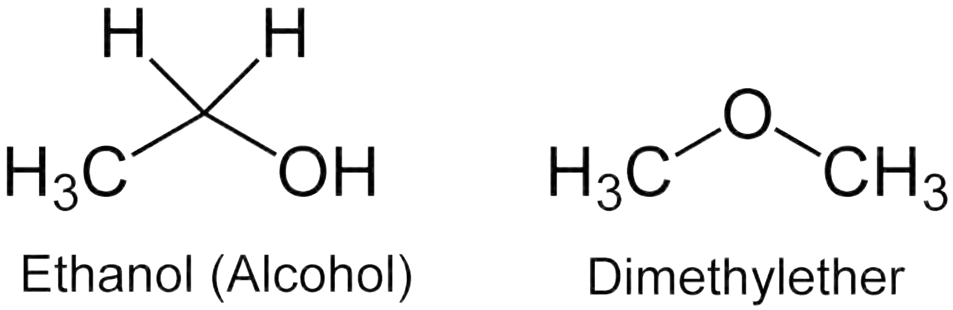
http://misterguch.brinkster.net/PRA036.pdf

Review

1. Do we need gas conditions to be at STP to calculate stoichiometry problems?
2. Why do we want to determine the stoichiometry of these reactions?
3. What assumption are we making about the gases involved?

14.11 Real and Ideal Gases

- Define a real gas.
- Describe differences between real gases and ideal gases.



Location, location, location

Behavior of molecules depends a lot on the structure. We can have two compounds with the same number of atoms and yet they act very differently. Ethanol (C_2H_5OH) is a clear liquid that has a boiling point of about 79°C. Dimethylether (CH_3OCH_3) has the same number of carbons, hydrogens, and oxygens, but boils at a much lower temperature (-25°C). The difference lies in the amount of intermolecular interaction (strong H-bonds for ethanol, weak van der Waals force for the ether).

Real and Ideal Gases

An ideal gas is one that follows the gas laws at all conditions of temperature and pressure. To do so, the gas would need to completely abide by the kinetic-molecular theory. The gas particles would need to occupy zero volume and they would need to exhibit no attractive forces what so ever toward each other. Since neither of those conditions can be true, there is no such thing as an ideal gas. A **real gas** is a gas that does not behave according to the assumptions of the kinetic-molecular theory. Fortunately, at the conditions of temperature and pressure that are normally encountered in a laboratory, real gases tend to behave very much like ideal gases.

Under what conditions then, do gases behave least ideally? When a gas is put under high pressure, its molecules are forced closer together as the empty space between the particles is diminished. A decrease in the empty space means that the assumption that the volume of the particles themselves is negligible is less valid. When a gas is cooled, the decrease in kinetic energy of the particles causes them to slow down. If the particles are moving at slower speeds, the attractive forces between them are more prominent. Another way to view it is that continued cooling the gas will eventually turn it into a liquid and a liquid is certainly not an ideal gas anymore (see liquid nitrogen in the **Figure** below). In summary, a real gas deviates most from an ideal gas at low temperatures and high pressures. Gases are most ideal at high temperature and low pressure.

The **Figure** below shows a graph of $\frac{PV}{RT}$ plotted against pressure for 1 mol of a gas at three different temperatures - 200 K, 500 K, and 1000 K. An ideal gas would have a value of 1 for that ratio at all temperatures and pressures and the graph would simply be a horizontal line. As can be seen, deviations from an ideal gas occur. As the pressure begins to rise, the attractive forces cause the volume of the gas to be less than expected and the value of $\frac{PV}{RT}$ drops under 1. Continued pressure increase results in the volume of the particles to become significant and the value of $\frac{PV}{RT}$ rises to greater than 1. Notice, that the magnitude of the deviations from ideality is greatest for the gas at 200 K and least for the gas at 1000 K.

FIGURE 14.11

Nitrogen gas that has been cooled to 77 K has turned to a liquid and must be stored in a vacuum insulated container to prevent it from rapidly vaporizing.

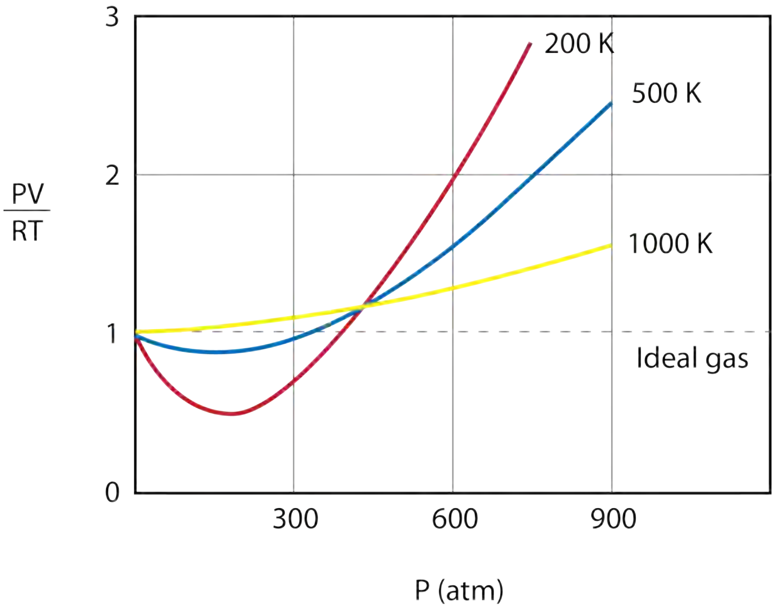


FIGURE 14.12

Real gases deviate from ideal gases at high pressures and at low temperatures.

The ideality of a gas also depends on the strength and type of intermolecular attractive forces that exist between the particles. Gases whose attractive forces are weak are more ideal than those with strong attractive forces. At the same temperature and pressure, neon is more ideal than water vapor because neon's atoms are only attracted by weak dispersion forces, while water vapor's molecules are attracted by relatively stronger hydrogen bonds. Helium is a more ideal gas than neon because its smaller number of electrons means that helium's dispersion forces are even weaker than those of neon.

Summary

- The properties of real gases and their deviations from ideality are described.

Practice

Use the link below to answer the following questions:

http://www.adichemistry.com/physical/gaseous/deviation/van-der-waals-equation.html

1. What is the compressibility factor for a perfect (ideal) gas?
2. What does it mean if $Z > 1$?
3. What does it mean if $Z < 1$?

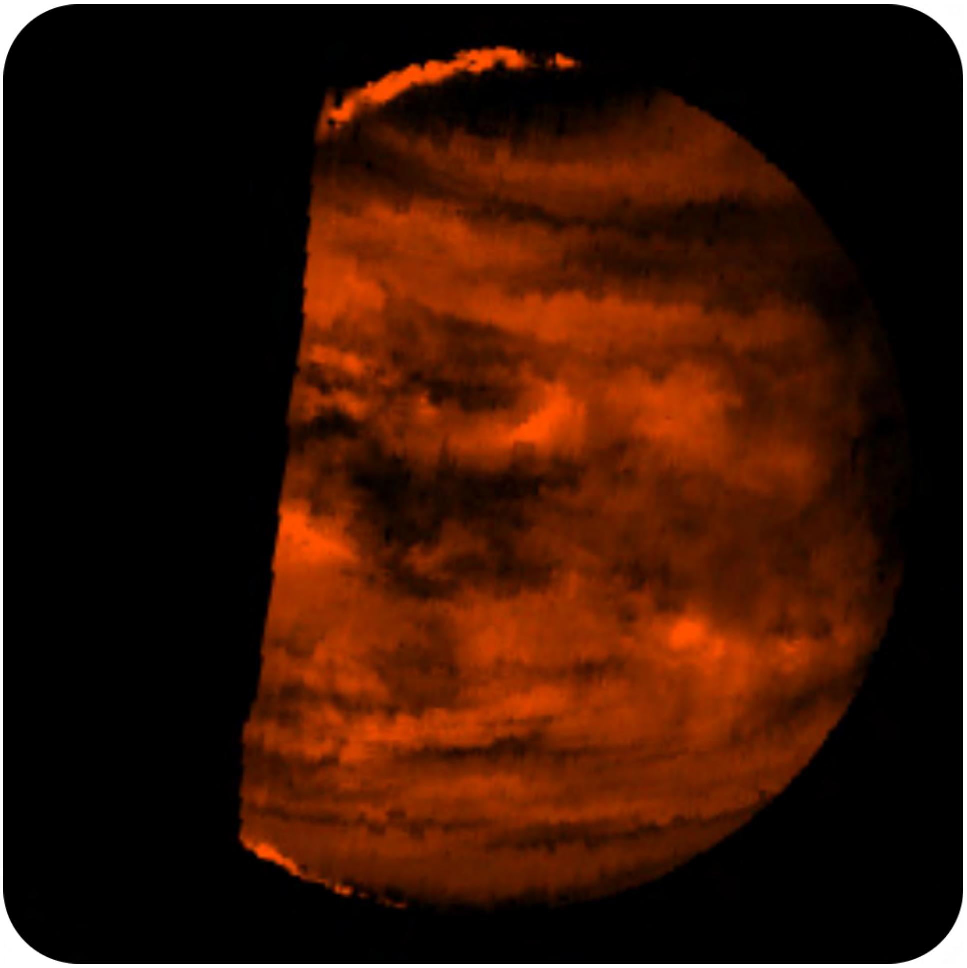
Review

1. What becomes more significant as the pressure increases?
2. Do the attractive forces between gas particles become more prominent at higher or lower temperatures?
3. Would HCl gas be more or less ideal than helium?

- **real gas:** A gas that does not behave according to the assumptions of the kinetic-molecular theory.

14.12 Dalton's Law of Partial Pressures

- Define partial pressure.
- State Dalton's law of partial pressures.
- Use this law to calculate pressures of gas mixtures.



Can we breathe on Venus?

The atmosphere of Venus is markedly different from that of Earth. The gases in the Venusian atmosphere are 96.5% carbon dioxide and 3% nitrogen. The atmospheric pressure on Venus is roughly 92 times that of Earth, so the amount of nitrogen on Venus would contribute a pressure well over 2700 mm Hg. And there is no oxygen present, so we couldn't breathe there. Not that we would want to go to Venus – the surface temperature is usually over 460°C.

Dalton's Law of Partial Pressures

Gas pressure results from collisions between gas particles and the inside walls of their container. If more gas is added to a rigid container, the gas pressure increases. The identities of the two gases do not matter. John Dalton, the English chemist who proposed the atomic theory, also studied mixtures of gases. He found that each gas in a mixture exerts a pressure independently of every other gas in the mixture. For example, our atmosphere is composed of about 78% nitrogen and 21% oxygen, with smaller amounts of several other gases making up the rest. Since nitrogen makes up 78% of the gas particles in a given sample of air, it exerts 78% of the pressure. If the overall atmospheric pressure is 1.00 atm, then the pressure of just the nitrogen in the air is 0.78 atm. The pressure of the oxygen in the air is 0.21 atm.

The **partial pressure** of a gas is the contribution that gas makes to the total pressure when the gas is part of a mixture. The partial pressure of a gas is indicated by a P with a subscript that is the symbol or formula of that gas. The partial pressure of nitrogen is represented by P_{N_2}. **Dalton's law of partial pressures** states that the total pressure of a mixture of gases is equal to the sum of all of the partial pressures of the component gases. Dalton's law can be expressed with the following equation:

$$P_{\text{total}} = P_1 + P_2 + P_3 + \ldots$$

The figure below shows two gases that are in separate, equal-sized containers at the same temperature and pressure. Each exerts a different pressure, P_1 and P_2, reflective of the number of particles in the container. On the right, the two gases are combined into the same container, with no volume change. The total pressure of the gas mixture is equal to the sum of the individual pressures. If $P_1 = 300$ mmHg and $P_2 = 500$ mmHg, then $P_{\text{Total}} = 800$ mmHg.

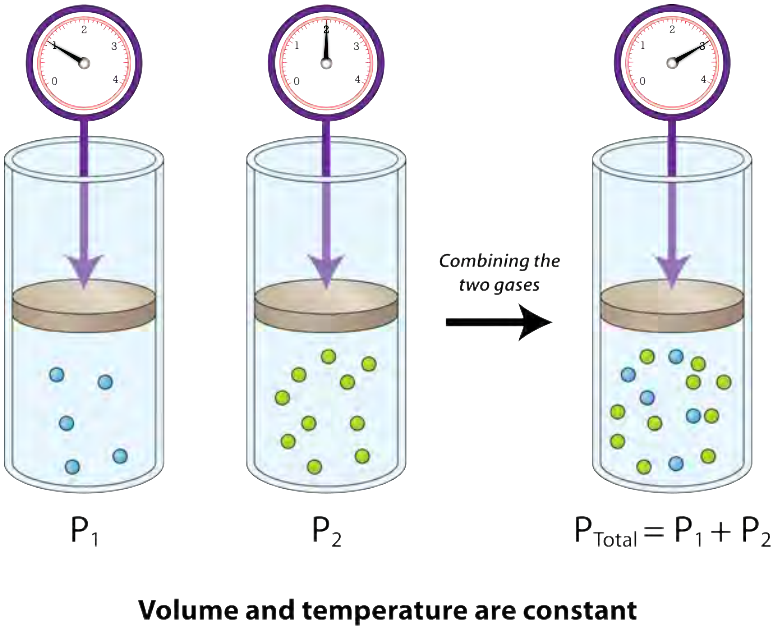


FIGURE 14.13

Dalton's law says that the pressure of a gas mixture is equal to the partial pressures of the combining gases.

Summary

- The total pressure in a system is equal to the sums of the partial pressures of the gases present.

Practice

Review the concepts at the link below and work the sample problems:

http://www.kentchemistry.com/links/GasLaws/dalton.htm

Review

1. What is the foundation for Dalton's law?
2. Argon makes up about 0.93% of our atmosphere. If the atmospheric pressure is 760 mm Hg, what is the pressure contributed by argon?
3. On a given day, the water vapor in the air is 2.5%. If the partial pressure of the vapor is 19.4 mm Hg, what is the atmospheric pressure?

- **Partial pressure:** The contribution that gas makes to the total pressure when the gas is part of a mixture.
- **Dalton's law of partial pressures:** The total pressure of a mixture of gases is equal to the sum of all of the partial pressures of the component gases.

14.13 Mole Fraction

- Define mole fraction.
- Perform calculations involving mole fractions.

The mixed blessing of sulfur dioxide

Sulfur dioxide is a by-product of many processes, both natural and human-made. Massive amounts of this gas are released during volcanic eruptions such as the one seen above on the Big Island (Hawaii). Humans produce sulfur dioxide by burning coal. The gas has a cooling effect when in the atmosphere by reflecting sunlight back away from the earth. However, sulfur dioxide is also a component of smog and acid rain, both of which are harmful to the environment. Many efforts have been made to reduce SO_2 levels to lower acid rain production. An unforeseen complication: as we lower the concentration of this gas in the atmosphere, we lower its ability to cool and then we have global warming concerns.

Mole Fraction

One way to express relative amounts of substances in a mixture is with the mole fraction. **Mole fraction** (X) is the ratio of moles of one substance in a mixture to the total number of moles of all substances. For a mixture of two substances, A and B, the mole fractions of each would be written as follows:

$$X_A = \frac{\text{mol } A}{\text{mol } A + \text{mol } B} \quad \text{and} \quad X_B = \frac{\text{mol } B}{\text{mol } A + \text{mol } B}$$

If a mixture consists of 0.50 mol A and 1.00 mol B, then the mole fraction of A would be $X_A = \frac{0.5}{1.5} = 0.33$. Similarly, the mole fraction of B would be $X_B = \frac{1.0}{1.5} = 0.67$.

Mole fraction is a useful quantity for analyzing gas mixtures in conjunction with Dalton's law of partial pressures. Consider the following situation: A 20.0 liter vessel contains 1.0 mol of hydrogen gas at a pressure of 600 mmHg. Another 20.0 liter vessel contains 3.0 mol of helium at a pressure of 1800 mmHg. These two gases are mixed together in an identical 20.0 liter vessel. Because each will exert its own pressure according to Dalton's law, we can express the partial pressures as follows:

$$P_{H_2} = X_{H_2} \times P_{\text{Total}} \quad \text{and} \quad P_{He} = X_{He} \times P_{\text{Total}}$$

The partial pressure of a gas in a mixture is equal to its mole fraction multiplied by the total pressure. For our mixture of hydrogen and helium:

$$X_{H_2} = \frac{1.0 \text{ mol}}{1.0 \text{ mol} + 3.0 \text{ mol}} = 0.25 \quad \text{and} \quad X_{He} = \frac{3.0 \text{ mol}}{1.0 \text{ mol} + 3.0 \text{ mol}} = 0.75$$

The total pressure according to Dalton's law is 600 mmHg + 1800 mmHg = 2400 mmHg. So, each partial pressure will be:

$$P_{H_2} = 0.25 \times 2400 \text{ mmHg} = 600 \text{ mmHg}$$
$$P_{He} = 0.75 \times 2400 \text{ mmHg} = 1800 \text{ mmHg}$$

The partial pressures of each gas in the mixture don't change since they were mixed into the same size vessel and the temperature was not changed.

Sample Problem: Dalton's Law

A flask contains a mixture of 1.24 moles of hydrogen gas and 2.91 moles of oxygen gas. If the total pressure is 104 kPa, what is the partial pressure of each gas?

Step 1: List the known quantities and plan the problem.

Known

- 1.24 mol H_2
- 2.91 mol O_2
- $P_{\text{Total}} = 104$ kPa

Unknown

- $P_{H_2} = ?$ kPa
- $P_{O_2} = ?$ kPa

First, the mole fraction of each gas can be determined. Then, the partial pressure can be calculated by multiplying the mole fraction by the total pressure.

Step 2: Solve.

$$X_{H_2} = \frac{1.24 \text{ mol}}{1.24 \text{ mol} + 2.91 \text{ mol}} = 0.299 \qquad X_{O_2} = \frac{2.91 \text{ mol}}{1.24 \text{ mol} + 2.91 \text{ mol}} = 0.701$$
$$P_{H_2} = 0.299 \times 104 \text{ kPa} = 31.1 \text{ kPa} \qquad P_{O_2} = 0.701 \times 104 \text{ kPa} = 72.9 \text{ kPa}$$

Step 3: Think about your result.

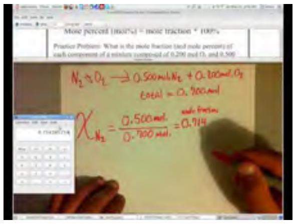
The hydrogen is slightly less than one third of the mixture, so it exerts slightly less than one third of the total pressure.

Summary

- Use of the mole fraction allows calculation to be made for mixtures of gases.

Practice

Watch the video at the link below and answer the following questions:



MEDIA

Click image to the left for more content.

http://www.youtube.com/watch?v=7BaX__s-4Ls

1. What is mole percent?
2. Do the mole fractions add up to 1.00?
3. What other way could you calculate the mole fraction of oxygen once you have the mole fraction of nitrogen?

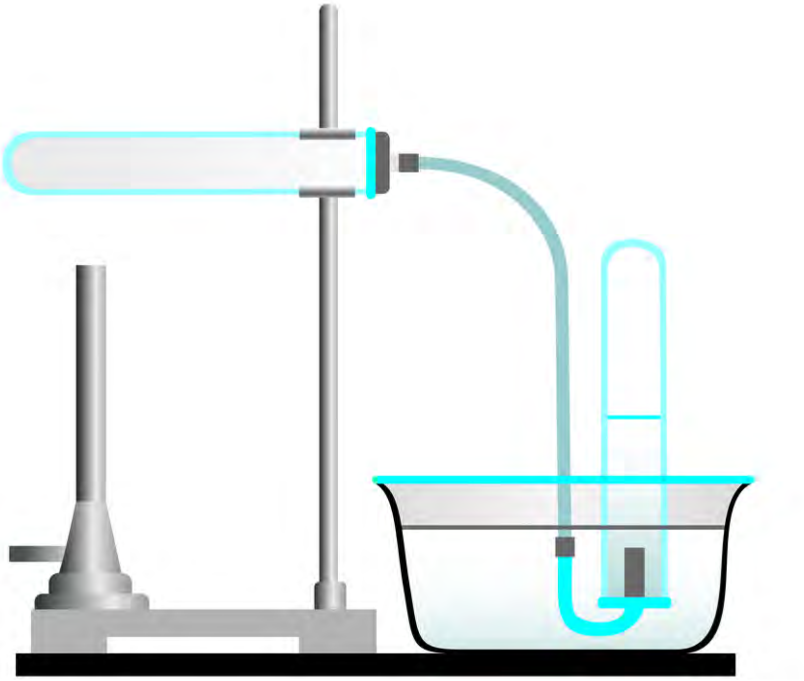
Review

1. What is mole fraction?
2. How do you determine partial pressure of a gas when given the mole fraction and the total pressure?
3. In a gas mixture containing equal numbers of moles of two gases, what can you say about the partial pressures of each gas?

- **Mole fraction** (X)**:** The ratio of moles of one substance in a mixture to the total number of moles of all substances.

14.14 Gas Collection by Water Displacement

- Calculate volumes of dry gases obtained after collecting over water.



What is the pressure?

You need to do a lab experiment where hydrogen gas is generated. In order to calculate the yield of gas, you have to know the pressure inside the tube where the gas is collected. But how can you get a barometer in there? Very simple: you don't. All you need is the atmospheric pressure in the room. As the gas pushed out the water, it is pushing against the atmosphere, so the pressure inside is equal to the pressure outside.

Gas Collection by Water Displacement

Gases that are produced in laboratory experiments are often collected by a technique called **water displacement** (see **Figure** below). A bottle is filled with water and placed upside-down in a pan of water. The reaction flask is fitted with rubber tubing which is then fed under the bottle of water. As the gas is produced in the reaction flask, it exits through the rubber tubing and displaces the water in the bottle. When the bottle is full of the gas, it can be sealed with a lid.

Because the gas is collected over water, it is not pure but is mixed with vapor from the evaporation of the water. Dalton's law can be used to calculate the amount of the desired gas by subtracting the contribution of the water vapor.

$$P_{\text{Total}} = P_g + P_{H_2O} \qquad P_g \text{ is the pressure of the desired gas}$$
$$P_g = P_{\text{Total}} - P_{H_2O}$$

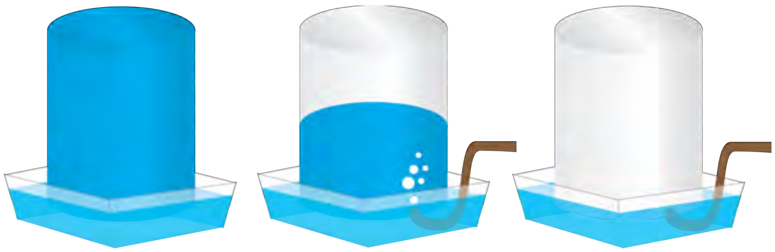


FIGURE 14.14

A gas produced in a chemical reaction can be collected by water displacement.

In order to solve a problem, it is necessary to know the vapor pressure of water at the temperature of the reaction (see **Table** 14.4). The sample problem illustrates the use of Dalton's law when a gas is collected over water.

TABLE 14.4: **Vapor Pressure of Water (mmHg) at Selected Temperatures (°C)**

0	**5**	**10**	**15**	**20**	**25**	**30**	**35**	**40**	**45**	**50**	**55**	**60**	**65**	**70**
4.58	6.54	9.21	12.79	17.54	23.76	31.82	42.18	55.32	71.88	92.51	118.04	149.38	187.54	233.7

Sample Problem: Gas Collected by Water Displacement

A certain experiment generates 2.58 L of hydrogen gas, which is collected over water. The temperature is 20°C and the atmospheric pressure is 98.60 kPa. Find the volume that the dry hydrogen would occupy at STP.

Step 1: List the known quantities and plan the problem.

Known

- $V_{\text{Total}} = 2.58\text{ L}$
- $T = 20°\text{C} = 293\text{ K}$
- $P_{\text{Total}} = 98.60\text{ kPa} = 739.7\text{ mmHg}$

Unknown

- V_{H_2} at $STP = ?$ L

The atmospheric pressure is converted from kPa to mmHg in order to match units with the table. The sum of the pressures of the hydrogen and the water vapor is equal to the atmospheric pressure. The pressure of the hydrogen is found by subtraction. Then, the volume of the gas at STP can be calculated by using the combined gas law.

Step 2: Solve.

$$P_{H_2} = P_{\text{Total}} - P_{H_2O} = 739.7\text{ mmHg} - 17.54\text{ mmHg} = 722.2\text{ mmHg}$$

Now the combined gas law is used, solving for V_2, the volume of hydrogen at STP.

$$V_2 = \frac{P_1 \times V_1 \times T_2}{P_2 \times T_1} = \frac{722.2\text{ mmHg} \times 2.58\text{ L} \times 273\text{ K}}{760\text{ mmHg} \times 293\text{ K}} = 2.28\text{ L } H_2$$

Step 3: Think about your result.

If the hydrogen gas were to be collected and STP and without the presence of the water vapor, its volume would be 2.28 L. This is less than the actual collected volume because some of that is water vapor. The conversion using STP is useful for stoichiometry purposes.

Summary

Practice

Watch the video at the link below and answer the following questions:

MEDIA

Click image to the left for more content.

http://www.youtube.com/watch?v=xmL2Pax4yUQ

1. What was the thistle tube used for?
2. How did the instructor tests for oxygen?
3. Did you observe any unsafe lab practices in the video?
4. What would have happened to the splint if carbon dioxide had been collected?

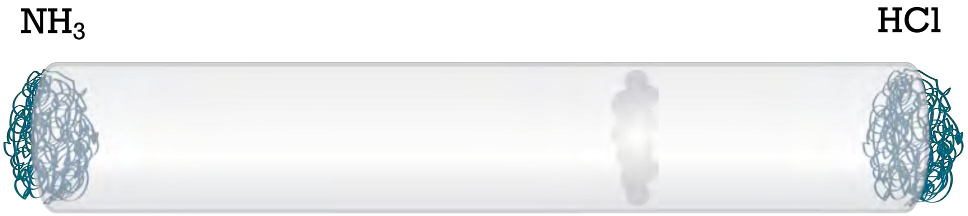
Review

1. Why is gas collected over water not pure?
2. Why would we want to correct for water vapor?
3. A student wants to collect his gas over diethyl ether (vapor pressure of 530 mm Hg at 25°C). Is this a good idea? Explain your answer.

- **water displacement:** Collection of a gas over water.

14.15 Diffusion and Effusion and Graham's Law

- Define diffusion and effusion.
- State Graham's law.
- Use Graham's law to perform calculations involving movement of gases.



How do we know how fast a gas moves?

We usually cannot see gases, so we need ways to detect their movements indirectly. The relative rates of diffusion of ammonia to hydrogen chloride can be observed in a simple experiment. Cotton balls are soaked with solutions of ammonia and hydrogen chloride (hydrochloric acid) and attached to two different rubber stoppers. These are simultaneously plugged into either end of a long glass tube. The vapors of each travel down the tube at different rates. Where the vapors meet, they react to form ammonium chloride (NH_4Cl), a white solid that appears in the glass tube as a ring.

Graham's Law

When a person opens a bottle of perfume in one corner of a large room, it doesn't take very long for the scent to spread throughout the entire room. Molecules of the perfume evaporate and the vapor spreads out to fill the entire space. **Diffusion** is the tendency of molecules to move from an area of high concentration to an area of low concentration until the concentration is uniform. While gases diffuse rather quickly, liquids diffuse much more slowly. Solids essentially do not diffuse.

Video of bromine diffusion: http://www.youtube.com/watch?v=R_xDe004oTQ

MEDIA

Click image to the left for more content.

A related process to diffusion is the 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.

Scottish chemist Thomas Graham (1805-1869) studied the rates of effusion and diffusion of gases. **Graham's law** 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. Graham's law can be understood by comparing two gases (A and B) at the same temperature, meaning the gases have the same kinetic energy. The kinetic energy of a moving object is given by the equation $KE = \frac{1}{2}mv^2$, where m is mass and v is velocity. Setting the kinetic energies of the two gases equal to one another gives:

$$\frac{1}{2}m_A v_A^2 = \frac{1}{2}m_B v_B^2$$

The equation can be rearranged to solve for the ratio of the velocity of gas A to the velocity of gas B $\left(\frac{v_A}{v_B}\right)$.

$$\frac{v_A^2}{v_B^2} = \frac{m_B}{m_A} \text{ which becomes } \frac{v_A}{v_B} = \sqrt{\frac{m_B}{m_A}}$$

For the purposes of comparing the rates of effusion or diffusion of two gases at the same temperature, the molar masses of each gas can be used in the equation for m.

Sample Problem: Graham's Law

Calculate the ratio of diffusion rates of ammonia gas (NH_3) to hydrogen chloride (HCl) at the same temperature and pressure.

Step 1: List the known quantities and plan the problem.

Known

- molar mass NH_3 = 17.04 g/mol
- molar mass HCl = 36.46 g/mol

Unknown

- velcoity ratio $\frac{v_{\mathrm{NH_3}}}{v_{\mathrm{HCl}}}$

Substitute the molar masses of the gases into Graham's law and solve for the ratio.

Step 2: Solve.

$$\frac{v_{NH_3}}{v_{HCl}} = \sqrt{\frac{36.46 \text{ g/mol}}{17.04 \text{ g/mol}}} = 1.46$$

The rate of diffusion of ammonia is 1.46 times faster than the rate of diffusion of hydrogen chloride.

Step 3: Think about your result

Since ammonia has a smaller molar mass than hydrogen chloride, the velocity of its molecules is greater and the velocity ratio is larger than 1.

Summary

- The processes of gas diffusion and effusion are described.
- Graham's law relates the molecular mass of a gas to its rate of diffusion or effusion.

Practice

Read the material on the link below and do the practice problems:

http://www.kentchemistry.com/links/GasLaws/GrahamsLaw.htm

Review

1. Why can you smell food cooking when you are in the next room?
2. Why does a helium-filled balloon gradually sink?
3. What does temperature have to do with gas kinetic energies?

- **diffusion:** The tendency of molecules to move from an area of high concentration to an area of low concentration until the concentration is uniform.
- **effusion:** The process of a confined gas escaping through a tiny hole in its container.
- **Graham's law:** The rate of effusion or diffusion of a gas is inversely proportional to the square root of the molar mass of the gas.

14.16 References

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CHAPTER 15

Water

Chapter Outline

15.1 Structure of Water

- Describe the structure of a water molecule.
- Describe the polarity of a water molecule.

How much of the Earth's surface is covered with water?

In his well-known poem "The Rime of the Ancient Mariner," Samuel Coleridge wrote "Water, water everywhere, Nor any drop to drink." He was talking about being on the ocean, but not having any water because he had killed an albatross (apparently bringing bad luck to everyone on the ship). The Earth is covered with water – about 75% of the earth's surface is water. The major constituent of the human body (over 60%) is water. This simple molecule plays important roles in all kinds of processes.

Structure of Water

Water is a simple molecule consisting of one oxygen atom bonded to two different hydrogen atoms. Because of the higher **electronegativity** of the oxygen atom, the bonds are polar covalent (**polar bonds**). The oxygen atom attracts the shared electrons of the covalent bonds to a significantly greater extent than the hydrogen atoms. As a result, the oxygen atom acquires a partial negative charge ($\delta-$), while the hydrogen atoms each acquire a partial positive charge ($\delta+$). The molecule adopts a bent structure because of the two lone pairs of electrons on the oxygen atom. The H-O-H bond angle is about 105°, slightly smaller than the ideal 109.5° of an sp^3 hybridized atomic orbital.

The bent shape of the water molecule is critical because the polar O-H bonds do not cancel one another and the molecule as a whole is polar. **Figure ??** illustrates the net polarity of the water molecule. The oxygen is the negative end of the molecule, while the area between the hydrogen atoms is the positive end of the molecule.

Polar molecules attract one another by dipole-dipole forces as the positive end of one molecule is attracted to the negative end of the nearby molecule. In the case of water, the highly polar O-H bonds results in very little electron

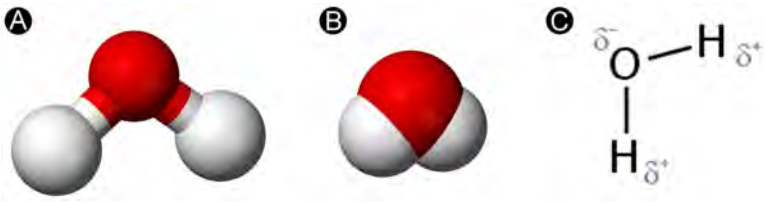


FIGURE 15.1

The water molecule, visualized three different ways: ball-and-stick model, space-filling model, and structural formula with partial charges.

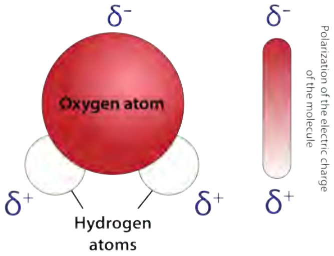


FIGURE 15.2

Water is a polar molecule, as greater electron density is found around the more electronegative oxygen atom.

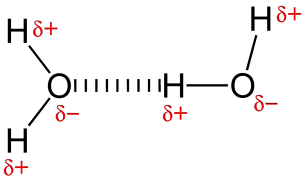


FIGURE 15.3

A hydrogen bond is the attraction between a lone pair of electrons on the oxygen atom of one molecule and the electron-deficient hydrogen atom of a nearby molecule.

density around the hydrogen atoms. Each hydrogen atom is strongly attracted to the lone-pair electrons on an adjacent oxygen atom. These are called hydrogen bonds and are stronger than conventional dipole-dipole forces.

Because each oxygen atom has two lone pairs, it can make hydrogen bonds to the hydrogen atoms of two separate other molecules. The Figure **??** shows the result – an approximately tetrahedral geometry around each oxygen atom consisting of two covalent bonds and two hydrogen bonds.

Summary

- Water is a molecular compound consisting of polar molecules that have a bent shape.
- The oxygen atom acquires a partial negative charge while the hydrogen atom acquires a partial positive charge.

Practice

Use the link below to answer the following questions:

http://www.lsbu.ac.uk/water/molecule.html

1. What is the H-O-H bond angle?
2. How far is the center of each H atom from the center of the O atom?

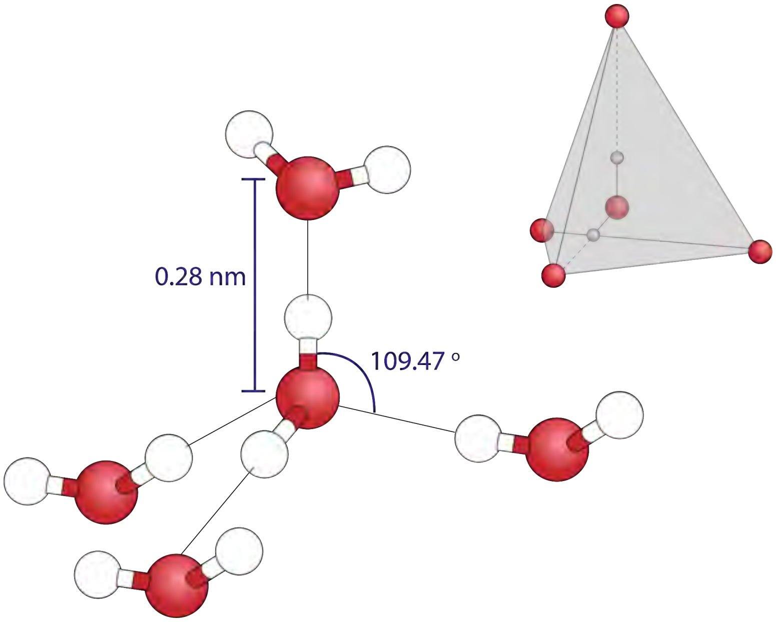


FIGURE 15.4

As a result of two covalent bonds and two hydrogen bonds, the geometry around each oxygen atom is approximately tetrahedral.

Review

1. What type of bond exists in a water molecule?
2. Which part of the molecule has a partial positive charge?
3. Which part of the molecule as a partial negative charge?
4. How do water molecules interact with one another?

- **electronegativity:** A measure of the ability of an atom to attract the electrons when the atom is part of a compound.
- **polar bond:** A covalent bond in which electrons are shared unequally between two electrons.

15.2 Structure of Ice

- Describe the structure of ice.
- Explain why ice is less dense that liquid water.

Have you ever been ice skating?

Ice is an interesting and useful material. It can be used to cool food and keep it fresh. It can provide recreation, such as ice-skating. Ice can do great damage when it freezes – roads can buckle, houses can be damaged, water pipes can burst. All this happens because of a unique property of water and ice. When water freezes, it expands in volume as ice is formed.

Structure of Ice

Liquid water is a fluid. The hydrogen bonds in liquid water constantly break and reform as the water molecules tumble past one another. As water cools, its molecular motion slows and the molecules move gradually closer to one another. The **density** of any liquid increases as its temperature decreases. For most liquids, this continues as the liquid freezes and the solid state is denser than the liquid state. However, water behaves differently. It actually reaches its highest density at about 4°C.

TABLE 15.1: **Density of Water and Ice**

Temperature (°C)	**Density (g/cm^3)**
100 (liquid)	0.9584
50	0.9881

TABLE 15.1: (continued)

25	0.9971
10	0.9997
4	1.000
0 (liquid)	0.9998
0 (solid)	0.9168

Between 4°C and 0°C the temperature gradually decreases as the hydrogen bonds begin to form a network characterized by a generally **hexagonal** structure with open spaces in the middle of the hexagons (see **Figure** 15.5).

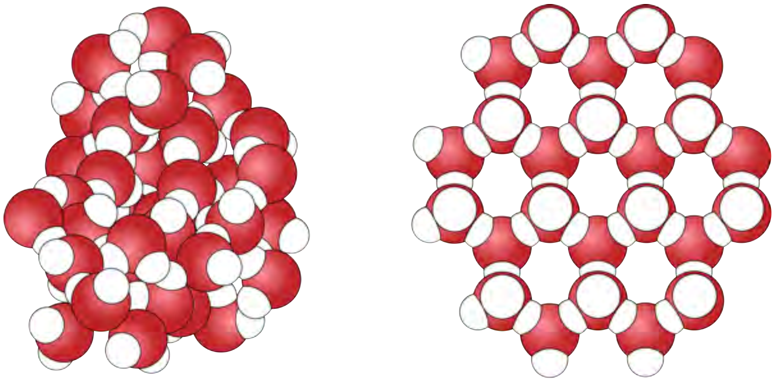


FIGURE 15.5

The structure of liquid water (left) consists of molecules connected by short-lived hydrogen bonds because water is a fluid. In ice (right), the hydrogen bonds become permanent, resulting in an interconnected hexagonally-shaped framework of molecules.

Ice is less dense than liquid water and so it floats. Ponds or lakes begin to freeze at the surface, closer to the cold air. A layer of ice forms, but does not sink as it would if water did not have this unique structure dictated by its shape, polarity, and hydrogen bonding. If the ice were to sink as it froze, entire lakes would freeze solid. Since the ice does not sink, liquid water remains under the ice all winter long. This is important, as fish and other organisms are capable of surviving through winter. Ice is one of only a very few solids that is less dense than its liquid form.

Summary

- Ice is less dense than liquid water.
- The intermolecular structure of ice has spaces that are not present in liquid water.

Practice

Use the link below to answer the following questions:

http://www.nyu.edu/pages/mathmol/textbook/info_water.html

1. What are hydrogen bonds doing in liquid water?
2. What is the structure for ice?
3. How many water molecules interact in water? In ice?

Review

1. For most liquids, what happens to density as the temperature decreases?

2. How does the density of water change at temperatures above 4°C?
3. How does the density of water change below 4°C?

- **density:** The concentration of a substance. Increases as its temperature decreases.
- **hexagonal:** Structured like a hexagon.

15.3 Physical Properties of Water

- Define surface tension.
- Define vapor pressure.
- Explain the phsyical properties of water in terms of hydrogen bonding.

What is this pan used for?

Water loss to the atmosphere is a significant problem in many parts of the world. When water supplies are low, anything that can be done to decrease water loss is important for farmers. An evaporation pan (seen above) can be used to measure how fast water evaporates in a given location. This information can be used as part of projects to develop ways to cut down on evaporation and increase the amount of usable water in a region.

Properties of Water

Compared to other molecular compounds of relatively low molar mass, ice melts at a very high temperature. A great deal of energy is required to break apart the hydrogen-bonded network of ice and return it to the liquid state. Likewise, the boiling point of water is very high. Most molecular compounds of similar molar mass are gases at room temperature.

Surface Tension

Water has a high **surface tension** (attraction between molecules at the surface of a liquid) because of its hydrogen bonding. Liquids that cannot hydrogen bond do not exhibit nearly as much surface tension. Surface tension can be seen by the curved meniscus that forms when water is in a thin column such as a graduated cylinder or a buret.

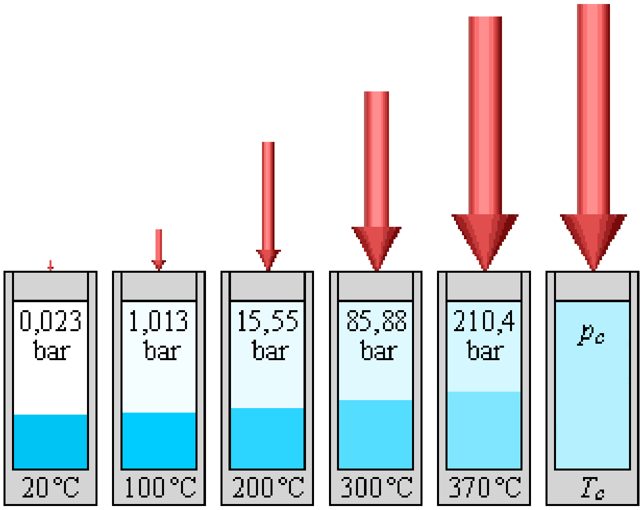
FIGURE 15.6

The meniscus of water in a graduated cylinder forms because of water's hydrogen bonding.

Vapor Pressure

The **vapor pressure** of a liquid is the pressure of the vapor produced by evaporation of a liquid or solid above the liquid or solid in a closed container. The hydrogen bonding between liquid water molecules explains water's unusually low vapor pressure. Relatively few molecules of water are capable of escaping the surface of the liquid and enter the vapor phase. Evaporation is slow and thus the vapor exerts a low pressure in a closed container. Low vapor pressure is an important physical property of water, since lakes, oceans, and other large bodies of water would all tend to evaporate much more quickly otherwise.

Vapor pressure is influenced by temperature. As the temperature increases, more molecules are released from the surface of the liquid. This increases movement above the liquid surface, increasing the pressure in the vapor stage. The **Figure ??** illustrates the effect of temperature on vapor pressure.



Summary

- Water has high surface tension because of extensive hydrogen bonding.
- The vapor pressure of water is low due to hydrogen bonding.
- Vapor pressure increases as temperature increases.

Practice

Use the link below to answer the following questions:

http://science.howstuffworks.com/environmental/earth/geophysics/h2o7.htm

1. Why does water bead up on waxy surfaces?
2. Explain capillary action.
3. Define cohesion.
4. Define adhesion.

Review

1. What is surface tension?
2. What is vapor pressure?
3. How does temperature affect vapor pressure?

- **surface tension:** The attraction between molecules at the surface of a liquid.
- **vapor pressure:** The pressure of the vapor produced by evaporation of a liquid or solid above the liquid or solid in a closed container.

15.4 Solute and Solvent

- Define solution.
- Define solute.
- Define solvent.
- Give examples of solutions.

Is snow an aqueous solution?

In the winter, the temperature often gets well below the freezing point of water. This condition can create problem in car radiators. If the water freezes, water hoses will break, the engine block can crack, and significant damage can be done to the car.

Solute and Solvent

When one substance dissolves into another, a **solution** is formed. A solution is a homogeneous mixture consisting of a **solute** dissolved into a **solvent**. The solute is the substance that is being dissolved, while the solvent is the dissolving medium. Solutions can be formed with many different types and forms of solutes and solvents.

We know of many types of solutions. Here are a few examples:

TABLE 15.2: Types of Solutions

Type	Solvent	Solute	Example
gas/gas	nitrogen	oxygen	air
gas/liquid	water	carbon dioxide	soda pop
liquid/liquid	water	ethylene glycol	antifreeze
solid/liquid	water	salts	seawater

We want to focus on solutions where the solvent is water. An aqueous solution is water that contains one or more dissolved substances. The dissolved substances in an aqueous solution may be solids, gases, or other liquids. Some examples are listed in the table above. Other examples include vinegar (acetic acid in water), alcoholic beverages (ethanol in water), and liquid cough medicines (various drugs in water).

FIGURE 15.7

Typical solution – clear and stable.

In order to be a true solution, a mixture must be stable. When sugar is fully dissolved into water, it can stand for an indefinite amount of time and the sugar will not settle out of the solution. Further, if the sugar-water solution is passed through a filter it will be unchanged. The dissolved sugar particles will pass through the filter along with the water. This is because the dissolved particles in a solution are very small, usually less than 1 nm in diameter. Solute particles can be atoms, ions, or molecules, depending on the type of substance that has been dissolved.

Summary

- A solution is a homogeneous mixture of a solute in a solvent.
- A solute is the material present in the smaller amount in the solution.
- A solvent is the material present in the larger amount in the solution.

Practice

Use the link below to answer the following questions:

http://www.chem.memphis.edu/bridson/FundChem/T13a1100.htm

1. How does sugar dissolve in water?
2. How do ionic compounds dissolve in water?

Review

1. What is a solution?
2. What is the solute?
3. What is the solvent?
4. Why is nitrogen the solvent in air?

- **solution:** A homogeneous mixture consisting of a solute dissolved into a solvent. Formed one substance dissolves into another.
- **solute:** The material present in the smaller amount in the solution.
- **solvent:** The material present in the larger amount in the solution.

15.5 Dissolving Process

- Describe how ionic compounds form solutions.
- Describe how molecular compounds form solutions.

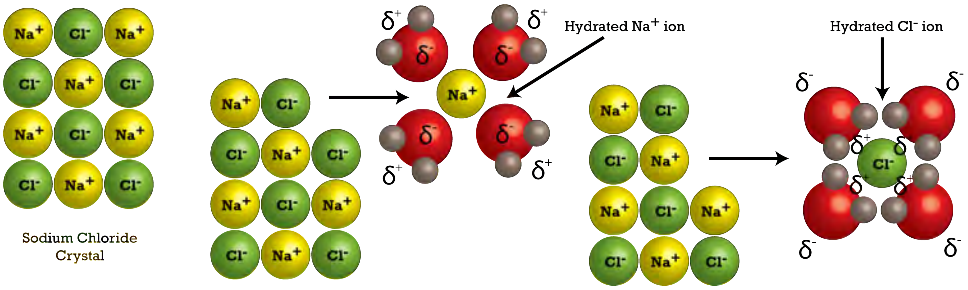
What is in this liquid that you brew at home, buy at a drive-through coffee stand, or pick up at a coffee shop or restaurant?

Many people like to start their day with a cup of coffee (others need coffee all day long in order to get anything done). The coffee you drink is a type of solution, often a very complex one. The coffee itself has been brewed so that material from the coffee bean will dissolve in hot water. Some people add sugar, while others add milk or cream. In some areas of the country, lattés are popular; so one or more special flavors might be added along with the milk. Whatever the situation, the end-result is an enjoyable solution to drink.

The Dissolving Process

Water typically dissolves many ionic compounds and polar molecules. Nonpolar molecules such as those found in grease or oil do not dissolve in water. We will first examine the process that occurs when an ionic compound such as table salt (sodium chloride) dissolves in water.

Water molecules move about continuously due to their kinetic energy. When a crystal of sodium chloride is placed into water, the water's molecules collide with the crystal lattice. Recall that the crystal lattice is composed of alternating positive and negative ions. Water is attracted to the sodium chloride crystal because water is polar and has both a positive and a negative end. The positively charged sodium ions in the crystal attract the oxygen end of the water molecules because they are partially negative. The negatively charged chloride ions in the crystal attract the hydrogen end of the water molecules because they are partially positive. The action of the polar water molecules takes the crystal lattice apart (see the figure below).



After coming apart from the crystal, the individual ions are then surrounded by solvent particles in a process called **solvation**. Note that the individual Na^+ ions are surrounded by water molecules with the oxygen atom oriented near the positive ion. Likewise, the chloride ions are surrounded by water molecules with the opposite orientation. **Hydration** is the process of solute particles being surrounded by water molecules arranged in a specific manner. Hydration helps to stabilize aqueous solutions by preventing the positive and negative ions from coming back together and forming a precipitate.

Table sugar is sucrose ($C_{12}H_{22}O_{11}$) and is an example of a molecular compound. Solid sugar consists of individual sugar molecules held together by intermolecular attractive forces. When water dissolves sugar, it separates the individual sugar molecules by disrupting the attractive forces, but does not break the covalent bonds between the carbon, hydrogen, and oxygen atoms. Dissolved sugar molecules are also hydrated, but without as distinct an orientation to the water molecules as in the case of the ions. The sugar molecule contains many -OH groups that can form hydrogen bonds with the water molecules, helping form the sucrose solution.

Summary

- Motion of water molecules helps break up interactions between solid ions or molecules.
- Solvation involves surrounding ions with solvent particles.
- Ionic solute molecules are hydrated (surrounded by solvent molecules in a specific orientation).

Practice

Use the link below to answer the following questions:

http://www.dceverest.com/srhigh/teachers/bheeren/dissolving_process.htm

1. Does the bond-breaking step require energy or release energy?
2. Does the hydration process require energy or release energy?
3. Does the distribution of solvent-solute clusters require energy or release energy?

Review

1. How does the motion of water molecules help form a solution?
2. What is solvation?
3. What is hydration?
4. How does sucrose interact with solvent water molecules?

- **hydration:** The process of solute particles being surrounded by water molecules arranged in a specific manner.
- **solvation:** Involves surrounding ions with solvent particles.

15.6 Liquid-Liquid Solutions

- Describe solubility of non-polar compounds in water.

Does oil dissolve in water?

In 2010 a major oil spill occurred when an explosion on a drilling rig in the Gulf of Mexico released millions of gallons of crude oil into the Gulf. Oil is primarily a mixture of hydrocarbons (organic compounds composed of only carbon and hydrogen atoms). Because of its composition, oil does not dissolve in water. As a result, much of the Gulf of Mexico was contaminated, as was a great deal of shoreline in the affected area.

Liquid-Liquid Solutions

Nonpolar compounds do not dissolve in water. The attractive forces that operate between the particles in a nonpolar compound are weak dispersion forces. However, the nonpolar molecules are more attracted to themselves than they are to the **polar** water molecules. When a nonpolar liquid such as oil is mixed with water, two separate layers form because the liquids will not dissolve into each other (**Figure** 15.8). When another polar liquid such as ethanol is mixed with water, they completely blend and dissolve into one another. Liquids that dissolve in one another in all proportions are said to be **miscible**. Liquids that do not dissolve in one another are called **immiscible**. The general rule for deciding if one substance is capable of dissolving another is "like dissolves like." A nonpolar solid such as iodine will dissolve in nonpolar lighter fluid, but will not dissolve in polar water.

For molecular compounds, the major factor that contributes to the material dissolving in water is the ability to form hydrogen bonds with the water solvent. Small compounds such as methanol, ethanol, acetic acid, and acetone have polar groups that can interact with the polar H of water. However, as the non-polar portion of the molecule

FIGURE 15.8

Water and oil form separate layers when they are mixed because the nonpolar oil will not dissolve into the polar. The oil forms the top layer because it is less dense than the water.

gets larger, solubility with water drops off. The non-polar portion of the molecule increasingly repels to water and eventually overrides the interaction of the polar component with water.

Summary

- Non-polar molecules are usually insoluble in water.
- A nonionized molecule must be relatively polar to interact with water molecules.

Practice

Use the link below to answer the following question:

http://chemistry.about.com/od/factsstructures/ig/Chemical-Structures—E/Ethylene-Glycol.htm

1. Explain why ethylene glycol will dissolve in water.

Review

1. What are the main forces that operate between nonpolar molecules?
2. What part of a molecule is needed for that molecule to dissolve in water?
3. List some organic molecules that will dissolve well in water.

- **immiscible:** Liquids that do not dissolve in one another.
- **miscible:** Liquids that dissolve in one another in all proportions.
- **polar:** Molecule that has partial negative and positive charges.

15.7 Electrolytes and Nonelectrolytes

- Define electrolyte.
- Define nonelectrolyte.
- List common electrolyets and nonelectrolytes.

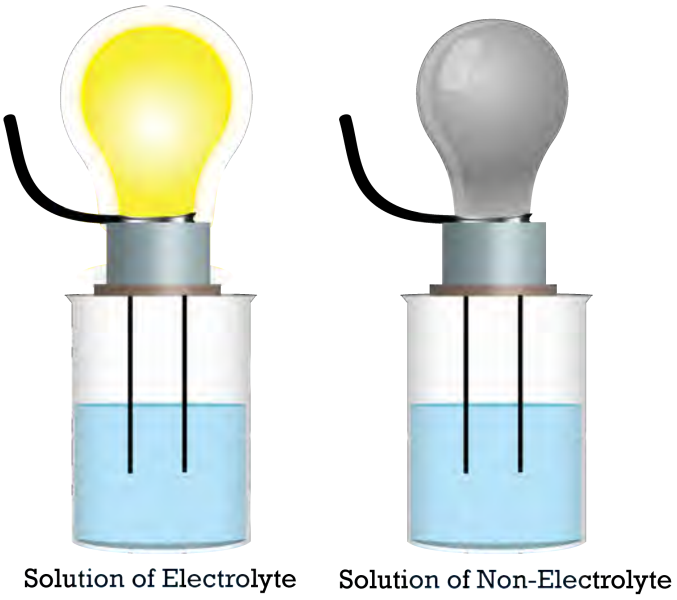
Why do runners worry about losing electrolytes?

Millions of people in the world jog for exercise. For the most part, jogging can be a healthy way to stay fit. However, problems can also develop for those who jog in the heat. Excessive sweating can lead to electrolyte loss that could be life-threatening. Early symptoms of electrolyte deficiency can include nausea, fatugue, and dizziness. If not treated, individuals can experience muscle weakness and increased heart rate (which could lead to a heart attack). Many sports drinks can be consumed to restore electrolytes quickly in the body.

Electrolytes and Nonelectrolytes

An **electrolyte** is a compound that conducts an electric current when it is in an aqueous solution or melted. In order to conduct a current, a substance must contain mobile ions that can move from one electrode to the other. All ionic compounds are electrolytes. When ionic compounds dissolve, they break apart into ions which are then able to conduct a current (**conductivity**). Even insoluble ionic compounds such as $CaCO_3$ are electrolytes because they can conduct a current in the molten (melted) state.

A **nonelectrolyte** is a compound that does not conduct an electric current in either aqueous solution or in the molten state. Many molecular compounds, such as sugar or ethanol, are nonelectrolytes. When these compounds dissolve in water, they do not produce ions. The **Figure** 15.9 illustrates the difference between an electrolyte and a nonelectrolyte.



A conductivity apparatus is an incomplete electrical circuit that contains a source of electricity and a light bulb or meter that will show when current is flowing through the circuit. The ends of the incomplete circuit are prongs that can be lowered into a solution. If the prongs are lowered into a solution containing a sufficient number of ions, the circuit will be completed by the solution, current will flow, and the light bulb will light up. If the prongs are lowered into a solution with no ions or an insufficient number of ions, not enough current will flow to light the bulb.

FIGURE 15.9

Conductivity apparatus.

Roles of Electrolytes in the Body

Several electrolytes play important roles in the body. Here are a few significant electrolytes:

1. calcium – in bone and teeth. Also important for muscle contraction, blood clotting, and nerve function.
2. sodium – found outside the cell. Mainly involved in water balance as well as nerve signaling.
3. potassium – major cation inside the cell. Important for proper functioning of heart, muscles, kidneys, and nerves.
4. magnesium – in bone and cells. Involved in muscle, bone, nervous system, and takes part in many biochemical reactions.

Summary

- Electrolytes conduct electric current when in solution or melted.
- Nonelectrolytes do not conduct electric current when in solution or melted.
- Some electrolytes play important roles in the body.

Practice

Use the link below to answer the following questions:

http://www.youtube.com/watch?v=Pxegf2KKiuc

1. How did the instructor test for the presence of electrolytes?
2. Is distilled water an electrolyte?
3. Is a solution of salt an electrolyte

4. Is sugar an electrolyte?
5. Is vinegar an electrolyte?

Review

1. What is an electrolyte?
2. What is a nonelectrolyte?
3. Give two examples of electrolytes.
4. Give two examples of nonelectrolytes.

- **electrolyte:** A compound that conducts an electric current when it is in an aqueous solution or melted.
- **nonelectrolyte:** A compound that does not conduct an electric current in either aqueous solution or in the molten state.
- **conductivity:** The ability to form an electric current.

15.8 Dissociation

- Define dissociation.
- Be able to write equations for dissociation of ionic compounds.

Have you ever seen trucks pour salt on icy roads?

In many areas, ice on the streets and sidewalks represent a serious walking and driving hazard. One common approach to melting the ice is to put some form of deicing salt on the surface. Materials such as sodium chloride or calcium chloride are frequently employed for this purpose. In order to be effective, the solid material must first dissolve and break up into the ions that make up the compound.

Dissociation

An ionic crystal lattice breaks apart when it is dissolved in water. **Dissociation** is the separation of ions that occurs when a solid ionic compound dissolves. It is important to be able to write dissociation equations. Simply undo the crisscross method that you learned when writing chemical formulas of ionic compounds. The subscripts for the ions in the chemical formulas become the coefficients of the respective ions on the product side of the equation. Shown below are dissociation equations for NaF, $Ca(NO_3)_2$, and $(NH_4)_3PO_4$.

$$NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$$

$$Ca(NO_3)_2(aq) \rightarrow Ca2+(aq) + 2NO_3{}^-(aq)$$

$$(NH_4)_3PO_4(s) \rightarrow 3NH_4{}^+(aq) + PO_4{}^{3-}(aq)$$

The formula unit of sodium chloride dissociates into one sodium ion and one chloride ion. The calcium nitrate formula unit dissociates into one calcium ion and two nitrate ions. This is because of the 2+ charge of the calcium ion. Two nitrate ions, each with a 1− charge are required to make the equation balance electrically. The ammonium phosphate formula unit dissociates into three ammonium ions and one phosphate ion. Note that the polyatomic ions themselves do not dissociate further, but remain intact.

Do not confuse the subscripts of the atoms within the polyatomic ion for the subscripts that result from the crisscrossing of the charges that make the original compound neutral. The 3 subscript of the nitrate ion and the 4 subscript of the ammonium ion are part of the polyatomic ion and simply remain as part of its formula after the compound dissociates. Notice that the compounds are solids (s) which then become ions in aqueous solution (aq).

FIGURE 15.10

Calcium nitrate is a typical ionic compound. In an aqueous solution it dissociates into calcium ions and nitrate ions.

Nonelectrolytes do not dissociate when forming an aqueous solution. An equation can still be written that simply shows the solid going into solution. For the dissolving of sucrose:

$$C_{12}H_{22}O_{11}(s) \rightarrow C_{12}H_{22}O_{11}(aq)$$

Summary

- Dissociation is the separation of ions that occurs when a solid ionic compound dissolves.
- Nonionic compounds do not dissociate in water.

Practice

Use the link below to answer the following questions:

http://www.chemistrylecturenotes.com/html/dissociation_of_ionic_compound.html

1. What does silver nitrate form upon dissociation in water?
2. How would HCl dissociate in water?
3. Is HF primarily dissociated or undissociated in water?
4. Do alcohols dissociate in water?

Review

1. Define dissociation.
2. Do polyatomic ions dissociate when dissolved in water?
3. Write the equation for the dissociation of KBr in water.
4. Write the equation for the dissociation of NH_4Cl in water.

- **dissociation:** The separation of ions that occurs when a solid ionic compound dissolves.

15.9 Strong and Weak Electrolytes

- Define strong electrolyte.
- Define weak electrolyte.
- Explain how to write equations for a weak electrolyte in solution.

Can car batteries be hazardous?

Car batteries, like the one shown above, are used around the world to provide the power to start car engines. One essential component of car batteries is the strong electrolyte sulfuric acid. In the battery, this material dissociates into hydrogen ions and sulfate ions. As the battery is used, the concentrations of these ions decrease. Older batteries had openings in the top where new sulfuric acid could be added to replenish the supply. Today, batteries are sealed to prevent leakage of the hazardous sulfuric acid.

Strong and Weak Electrolytes

Some polar molecular compounds are nonelectrolytes when they are in their pure state, but become electrolytes when they are dissolved in water. Hydrogen chloride (HCl) is a gas in its pure molecular state and is a nonelectrolyte. However, when HCl is dissolved in water, it conducts a current well because the HCl molecule ionizes into hydrogen and chloride ions.

$$\text{HCl}(g) \rightarrow \text{H}^+(aq) + \text{Cl}^-(aq)$$

When HCl is dissolved into water, it is called hydrochloric acid. Ionic compounds and polar compounds are completely broken apart into ions and thus conduct a current very well. A **strong electrolyte** is a solution in which a large fraction of the dissolved solute exists as ions.

Some other polar molecular compounds become electrolytes upon being dissolved into water, but do not ionize to very great extent. Gaseous nitrous acid ionizes in solution into hydrogen ions and nitrite ions, but does so very weakly. Aqueous nitrous acid is composed of only about 5% ions and 95% intact nitrous acid molecules. A **weak electrolyte** is a solution in which only a small fraction of the dissolved solute exists as ions. The equation showing the ionization of a weak electrolyte utilizes a double arrow indicating an equilibrium between the reactants and products.

$$\mathrm{HNO_2}(g) \rightleftarrows \mathrm{H^+}(aq) + \mathrm{NO_2^-}(aq)$$

Summary

- A strong electrolyte exists mainly as ions in solution.
- A weak electrolyte has only a small amount of ionization in solution.

Practice

Use the link below to answer the following questions:

http://www.stolaf.edu/depts/chemistry/courses/toolkits/121/js/naming/elec.htm

1. What is the principal species for a strong electrolyte?
2. What is the principle species for a weak electrolyte?
3. Is KOH a strong electrolyte or a weak electrolyte?
4. How would you classify $CaCl_2$?

Review

1. Is gaseous HCl an electrolyte or a nonelectrolyte?
2. What happens to gaseous HCl when it dissolves in water?
3. What is a strong electrolyte?
4. What is a weak electrolyte?
5. Is HNO_3 a strong electrolyte or a weak electrolyte?

- **strong electrolyte:** A solution in which a large fraction of the dissolved solute exists as ions.
- **weak electrolyte:** A solution in which only a small fraction of the dissolved solute exists as ions.

15.10 Suspensions

- Define suspension.
- Describe the properties and behavior of some typical suspensions.

Why is the sea clear on some days, but not on others?

On a calm day, the Caribbean Sea is clear and smooth. You can see deep into the water, seeing fish and underwater plant life without obstruction. The situation changes markedly when a storm blows up. The sand on the bottom of the sea is stirred up, the water becomes turbid, and you can't see anything below the surface. The sand forms a suspension in the water that slowly clears up again after the storm blows over.

Suspensions

Take a glass of water and throw in a handful of sand or dirt. Stir it and stir it and stir it. The water may become **turbid**, or unclear. Have you made a solution? Sand and dirt do not dissolve in water and though it may look homogeneous for a few moments, the sand or dirt gradually sinks to the bottom of the glass.

FIGURE 15.11

A suspension of dirt in water.

A **suspension** is a heterogeneous mixture in which some of the particles settle out of the mixture upon standing. The particles in a suspension are far larger than those of a solution and thus gravity is able to pull them down out of the **dispersion medium** (water). The typical diameter for the dispersed particles (the sand) of a suspension is about 1000 times greater than those of a solution (less than approximately two nanometers for particles in solution, compared to greater than 1000 nanometers for particles in suspension). Unlike in a solution, the dispersed particles can be separated from the dispersion medium by filtering. Suspensions are heterogeneous because at least two different substances in the mixture can be identified.

Some Typical Aqueous Suspensions

a. milk

Milk is a complex mixture of water, proteins, fats, carbohydrates, and minerals. While the minerals and carbohydrates are water-soluble, the fats and some of the proteins do not dissolve but are held in suspension.

b. paint

Paint can either be water-based or use an organic solvent. For our discussion, we will limit ourselves to water-based paints. The materials will contain binders (organic polymers that help hold the paint to the surface of the material being painted). In addition, pigments are included to provide the desired color. Both the binders and the pigments are not water-soluble, so the paint must be stirred every time it is used. Paint that is allowed to sit for a long period of time will slowly begin to separate as the suspension of binders and pigments settles out.

Summary

- Suspensions are heterogeneous mixtures.
- Some of the material in a suspension will settle out on standing.
- Solid material in a suspension can be removed by filtration.

Practice

Use the link below to answer the following questions:

http://www.chemistrylearning.com/colloidal-solution-true-solution-and-suspension/

1. How large are particles in solution?
2. How large are particles in suspension?
3. Describe the appearance of a solution.
4. Describe the appearance of a suspension.

Review

1. Is a suspension a heterogeneous or a homogeneous mixture?
2. How can the solid material in a suspension be separated from the liquid?
3. Which part of milk is in suspension?

- **dispersion medium:** The material in which the particles are distributed.
- **suspension:** A heterogeneous mixture in which some of the particles settle out of the mixture upon standing.
- **turbid:** Unclear, thick, or cloudy.

15.11 Colloids

- Define colloid.
- List differences between colloids, solutions, and suspensions.
- Give examples of colloids.

What type of mixture is a smoke flare?

Imagine you are sailing on your yacht (I guess you first have to imagine you have a yacht). The engine suddenly breaks down and you are stranded in the middle of the ocean. You call the Coast Guard on your radio, but cannot give them an exact location because your GPS isn't working (you really need to take better care of your equipment). Fortunately, you have a smoke flare, which you fire off. The dense colored smoke shows the Coast Guard where you are so they can rescue you. In using the flare, you are taking advantage of a type of mixture called a colloid.

Colloids

A **colloid** is a heterogeneous mixture whose particle size is intermediate between those of a solution and a suspension. The dispersed particles are spread evenly throughout the **dispersion medium**, which can be a solid, liquid, or gas. Because the dispersed particles of a colloid are not as large as those of a suspension, they do not settle out upon standing. Table below summarizes the properties and distinctions between solutions, colloids, and suspensions.

TABLE 15.3: **Properties of Solutions, Colloids, and Suspensions**

Solutions	Colloids	Suspensions
Homogeneous	Heterogeneous	Heterogeneous
Particle size: 0.01-1 nm; atoms, ions, or molecules	Particle size: 1-1000 nm, dispersed; large molecules or aggregates	Particle size: over 1000 nm, suspended; large particles or aggregates
Do not separate on standing	Do not separate on standing	Particles settle out
Cannot be separated by filtration	Cannot be separated by filtration	Can be separated by filtration

TABLE 15.3: (continued)

Do not scatter light	Scatter light (Tyndall effect)	May either scatter light or be opaque

Colloids are unlike solutions because their dispersed particles are much larger than those of a solution. The dispersed particles of a colloid cannot be separated by filtration, but they scatter light, a phenomenon called the **Tyndall effect**.

Tyndall Effect

When light is passed through a true solution, the dissolved particles are too small to deflect the light. However, the dispersed particles of a colloid, being larger, do deflect light. The Tyndall effect is the scattering of visible light by colloidal particles. You have undoubtedly "seen" a light beam as it passes through fog, smoke, or a scattering of dust particles suspended in air. All three are examples of colloids. Suspensions may scatter light, but if the number of suspended particles is sufficiently large, the suspension may simply be opaque and the light scattering will not occur.

FIGURE 15.12

The Tyndall effect allows sunlight to be seen as it passes through a fine mist.

Examples of Colloids

The table below lists examples of colloidal systems, most of which are very familiar. The dispersed phase describes the particles, while the dispersion medium is the material in which the particles are distributed.

TABLE 15.4: **Classes of Colloids**

Class of Colloid	Dispersed Phase	Dispersion Medium	Examples
Sol and gel	solid	liquid	paint, jellies, blood, gelation, mud
Solid aerosol	solid	gas	smoke, dust in air
Solid emulsion	liquid	solid	cheese, butter
Liquid emulsion	liquid	liquid	milk, mayonnaise
Liquid aerosol	liquid	gas	fog, mist, clouds, aerosol spray
Foam	gas	solid	marshmallow

TABLE 15.4: (continued)

Foam	gas	liquid	whipped cream, shaving cream

Another property of a colloidal system is the observed when the colloids are studied under a light microscope. The colloids scintillate, reflecting brief flashes of light because the colloidal particles move in a rapid and random fashion. This phenomenon, called Brownian motion, is caused by collisions between the small colloidal particles and the molecules of the dispersion medium.

Emulsions

Butter and mayonnaise are examples of a class of colloids called **emulsions**. An emulsion is a colloidal dispersion of a liquid in either a liquid or a solid. A stable emulsion requires an emulsifying agent to be present. Mayonnaise is made in part of oil and vinegar. Since oil is nonpolar and vinegar is an aqueous solution and polar, the two do not mix and would quickly separate into layers. However, the addition of egg yolk causes the mixture to become stable and not separate. Egg yolk is capable of interacting with both the polar vinegar and the nonpolar oil. The egg yolk is called the emulsifying agent. Soap acts as an emulsifying agent between grease and water. Grease cannot be simply rinsed off your hands or another surface because it is insoluble. However, the soap stabilizes a grease-water mixture because one end of a soap molecule is polar and the other end is nonpolar. This allows the grease to be removed from your hands or your clothing by washing with soapy water.

Summary

- A colloid is a heterogeneous mixture whose particle size is intermediate between those of a solution and a suspension.
- The Tyndall effect is the scattering of visible light by colloidal particles.
- An emulsion is a colloidal dispersion of a liquid in either a liquid or a solid.

Practice

Use the link below to answer the following questions:

http://www.infoplease.com/encyclopedia/science/colloid-properties-colloids.html

1. What is one property of colloids that distinguishes them from true solutions?
2. What is Brownian movement?
3. Do colloid particles acquire an electrical charge?

Review

1. What is a colloid?
2. What is the Tyndall effect?
3. What is the dispersion medium in blood?
4. What is an emulsion?

- **colloid:** A heterogeneous mixture whose particle size is intermediate between those of a solution and a suspension.
- **Tyndall effect:** Phenomenon in which the dispersed particles of a colloid cannot be separated by filtration, but they scatter light.

- **emulsion:** A colloidal dispersion of a liquid in either a liquid or a solid.
- **dispersion medium:** The material in which the particles are distributed.

15.12 References

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CHAPTER 16 Solutions

Chapter Outline

16.1 Solute-Solvent Combinations

- Describe different types of solutions and give an example of each.

A unique sound.

Dixieland music arose in New Orleans in the early 1900s. This driving style of music emphasized improvisation on the basic musical theme. Much of the sound quality associated with this music is due to the brass instruments (including the trumpet, trombone, and tuba). New Orleans is still the home of Dixieland, and the French Quarter echoes nightly to the sounds of this exciting music.

Solute-Solvent Combinations

The focus in the last chapter was on water and its role in the formation of aqueous solutions. We examined the primary characteristics of a solution, how water is able to dissolve solid solutes, and we differentiated between a solution, a suspension, and a colloid. There are many examples of solutions that do not involve water at all, or that involve solutes that are not solids. The **Table** 16.1 summarizes the possible combinations of solute-solvent states, along with examples of each.

TABLE 16.1: Solute-Solvent Combinations

Solute State	Solvent State	Example
liquid	gas	water in air
gas	gas	oxygen in nitrogen (gas mixture)
solid	liquid	salt in water
liquid	liquid	alcohol in water
gas	liquid	carbon dioxide in water
solid	solid	zinc in copper (brass alloy)
liquid	solid	mercury in silver and tin (dental amalgam)

Gas-Gas Solutions

Our air is a homogeneous mixture of many different gases and therefore qualifies as a solution. Approximately 78% of the atmosphere is nitrogen, making it the solvent for this solution. The next major constituent is oxygen (about 21%), followed by the inert gas argon (0.9%), carbon dioxide (0.03%) and trace amounts of neon, methane, helium, and other gases.

Solid-Solid Solutions

Solid-solid solutions such as brass, bronze, and sterling silver are called alloys. Bronze (composed mainly of copper with added tine) was widely used in making weapons in times past dating back to at least 2400 B.C. This metal alloy was hard and tough, but was eventually replaced by iron.

Liquid-Solid Solutions

Perhaps the most familiar liquid-solid solution is dental amalgam, used to fill teeth when there is a cavity. Approximately 50% of the amalgam material is liquid mercury to which a powdered alloy of silver, tin and copper is added. Mercury is used because it binds well with the solid metal alloy. There appears to be no toxic issues associated with the use of mercury for this purpose.

Summary

- Solutions may be composed of a variety of solid, liquid, or gaseous materials.

Practice

Read the material and answer questions 1-3 on the following website:

http://www.science.uwaterloo.ca/ cchieh/cact/c120/solution.html

Review

1. Does a solution have to have water as the solvent?
2. Is there an example of a solution where water is the solute?
3. When we mix ethylene glycol with the water in our car radiator to prevent freezing, which is the solvent and which is the solute?

16.2 Rate of Dissolving

- List and describe factors that affect the rate of dissolving.

How sweet do you like your tea?

Many people enjoy a cold glass of iced tea on a hot summer day. Some like it unsweetened, while others like to put sugar in it. How fast the sugar dissolved depends on several factors: how much sugar was put in the tea and how cold it is? You usually have to stir the tea for a while to get all the sugar dissolved.

Rate of Dissolving

We know that the dissolving of a solid by water depends upon the collisions that occur between the solvent molecules and the particles in the solid crystal. Anything that can be done to increase the frequency of those collisions and/or to give those collisions more energy will increase the rate of dissolving. Imagine that you were trying to dissolve some sugar in a glassful of tea. A packet of granulated sugar would dissolve faster than a cube of sugar. The rate of dissolving would be increased by stirring, or agitating the solution. Finally, the sugar would dissolve faster in hot tea than it would in cold tea.

Surface Area

The rate at which a solute dissolves depends upon the size of the solute particles. Dissolving is a surface phenomenon since it depends on solvent molecules colliding with the outer surface of the solute. A given quantity of solute dissolves faster when it is ground into small particles than if it is in the form of a large chunk because more **surface area** is exposed. The packet of granulated sugar exposes far more surface area to the solvent and dissolves more quickly than the sugar cube.

Agitation of the Solution

Dissolving sugar in water will occur more quickly if the water is stirred. The stirring allows fresh solvent molecules to continually be in contact with the solute. If it is not stirred, then the water right at the surface of the solute becomes saturated with dissolved sugar molecules, meaning that it is more difficult for additional solute to dissolve. The sugar cube would eventually dissolve because random motions of the water molecules would bring enough fresh solvent into contact with the sugar, but the process would take much longer. It is important to realize that neither stirring nor breaking up a solute affect the overall amount of solute that dissolves. It only affects the rate of dissolving.

Temperature

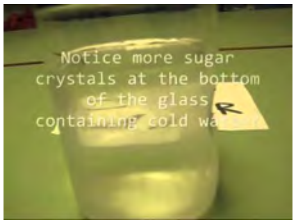
Heating up the solvent gives the molecules more kinetic energy. The more rapid motion means that the solvent molecules collide with the solute with greater frequency and the collisions occur with more force. Both factors increase the rate at which the solute dissolves. As we will see in the next section, a temperature change not only affects the rate of dissolving, but also affects the amount of solute that dissolves.

Summary

- The rate of dissolving is influenced by surface area, stirring, and temperature.

Practice

Watch the video at the link below and answer the following questions:



MEDIA

Click image to the left for more content.

http://www.youtube.com/watch?v=TO42FOay7rg

1. Did the sugar dissolve faster in the hot water or the cold water?
2. What would be another experiment similar to this one that would examine the effect of particle size on the rate of dissolving?
3. What experiment could you perform that would test all three factors?

Review

1. What is the relationship between surface area and rate of dissolving?
2. How does stirring influence the rate of dissolving?
3. How does temperature influence the rate of dissolving?

- **surface area:** The amount of solid surface exposed to the solvent.

16.3 Saturated and Unsaturated Solutions

- Define saturated solution.
- Define unsaturated solution.
- Define solution equilibrium.

How do you make sure a compound is pure?

When compounds are synthesized, they often have contaminating materials mixed in with them. The process of recrystallization can be used to remove these impurities. The crystals are dissolved in a hot solvent, forming a solution. When the solvent is cooled the compound is no longer as soluble and will precipitate out of solution, leaving other materials still dissolved.

Saturated and Unsaturated Solutions

Table salt (NaCl) readily dissolves in water. Suppose that you have a beaker of water to which you add some salt, stirring until it dissolves. So you add more and that dissolves. You keep adding more and more salt, eventually reaching a point that no more of the salt will dissolve no matter how long or how vigorously you stir it. Why? On the molecular level, we know that action of the water causes the individual ions to break apart from the salt crystal and enter the solution, where they remain hydrated by water molecules. What also happens is that some of the dissolved ions collide back again with the crystal and remain there. **Recrystallization** is the process of dissolved solute returning to the solid state. At some point the rate at which the solid salt is dissolving becomes equal to the rate at which the dissolved solute is recrystallizing. When that point is reached, the total amount of dissolved salt remains unchanged. **Solution equilibrium** is the physical state described by the opposing processes of dissolution and recrystallization occurring at the same rate. The solution equilibrium for the dissolving of sodium chloride can be represented by one of two equations.

$$\text{NaCl}(s) \rightleftarrows \text{NaCl}(aq)$$

While this shows the change of state back and forth between solid and aqueous solution, the preferred equation also shows the dissociation that occurs as an ionic solid dissolves.

$$\text{NaCl}(s) \rightleftarrows \text{Na}^+(aq) + \text{Cl}^-(aq)$$

When the solution equilibrium point is reached and no more solute will dissolve, the solution is said to be saturated. A **saturated solution** is a solution that contains the maximum amount of solute that is capable of being dissolved. At 20°C, the maximum amount of NaCl that will dissolve in 100. g of water is 36.0 g. If any more NaCl is added past that point, it will not dissolve because the solution is saturated. What if more water is added to the solution instead? Now more NaCl would be capable of dissolving in the additional solvent. An **unsaturated solution** is a solution that contains less than the maximum amount of solute that is capable of being dissolved. **Figure** 16.1 illustrates the above process and shows the distinction between unsaturated and saturated.

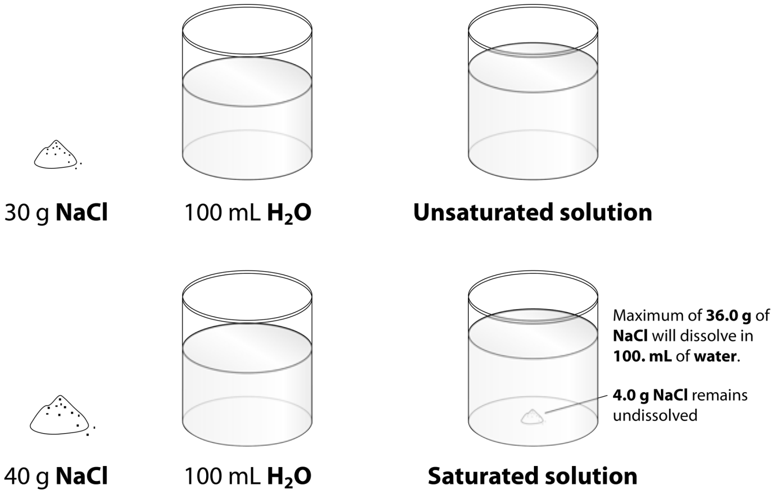


FIGURE 16.1

When 30.0 g of NaCl is added to 100 ml of water, it all dissolves, forming an unsaturated solution. When 40.0 g is added, 36.0 g dissolves and 4.0 g remains undissolved, forming a saturated solution.

How can you tell if a solution is saturated or unsaturated? If more solute is added and it does not dissolve, then the original solution was saturated. If the added solute dissolves, then the original solution was unsaturated. A solution that has been allowed to reach equilibrium but which has extra undissolved solute at the bottom of the container must be saturated.

Summary

- Saturated and unsaturated solutions are defined.
- Solution equilibrium exists when the rate of dissolving equals the rate of recrystallization.

Practice

Watch the video at the link below and answer the following questions:

MEDIA

Click image to the left for more content.

http://www.youtube.com/watch?v=gawS3sBHMQw

1. What is the initial solution used?
2. What is the heat source for evaporation?
3. Why does the salt precipitate out of solution?

Review

1. Why is the preferred equation for solution equilibrium of NaCl an equilibrium between solid NaCl and the ions.
2. If I add water to a saturated sucrose solution, what will happen?
3. If I heat a solution and remove water, I see crystals at the bottom of the container. What happened?

- **recrystallization:** The process of dissolved solute returning to the solid state.
- **saturated solution:** A solution that contains the maximum amount of solute that is capable of being dissolved.
- **solution equilibrium:** The physical state described by the opposing processes of dissolution and recrystallization occurring at the same rate.
- **unsaturated solution:** A solution that contains less than the maximum amount of solute that is capable of being dissolved.

16.4 How Temperature Influences Solubility

- Describe the influence of temperature on the solubility of solids in water.
- Describe the influence of temperature on the solubility of gases in water.

What happens to the fish in the water next to a nuclear power plant?

Nuclear power plants require large amounts of water to generate steam for the turbines and to cool the equipment. They will usually be situated near bodies of water to use that water as a coolant, returning the warmer water back to the lake or river. This increases the overall temperature of the water, which lowers the quantity of dissolved oxygen, affecting the survival of fish and other organisms.

How Temperature Influences Solubility

The **solubility** of a substance is the amount of that substance that is required to form a saturated solution in a given amount of solvent at a specified temperature. Solubility is often measured as the grams of solute per 100 g of solvent. The solubility of sodium chloride in water is 36.0 g per 100 g water at 20°C. The temperature must be specified because solubility varies with temperature. For gases, the pressure must also be specified. Solubility is specific for a particular solvent. We will consider solubility of material in water as solvent.

The solubility of the majority of solid substances increases as the temperature increases. However, the effect is difficult to predict and varies widely from one solute to another. The temperature dependence of solubility can be visualized with the help of a **solubility curve**, a graph of the solubility vs. temperature (see **Figure** 16.2).

Notice how the temperature dependence of NaCl is fairly flat, meaning that an increase in temperature has relatively little effect on the solubility of NaCl. The curve for KNO_3, on the other hand, is very steep and so an increase in temperature dramatically increases the solubility of KNO_3.

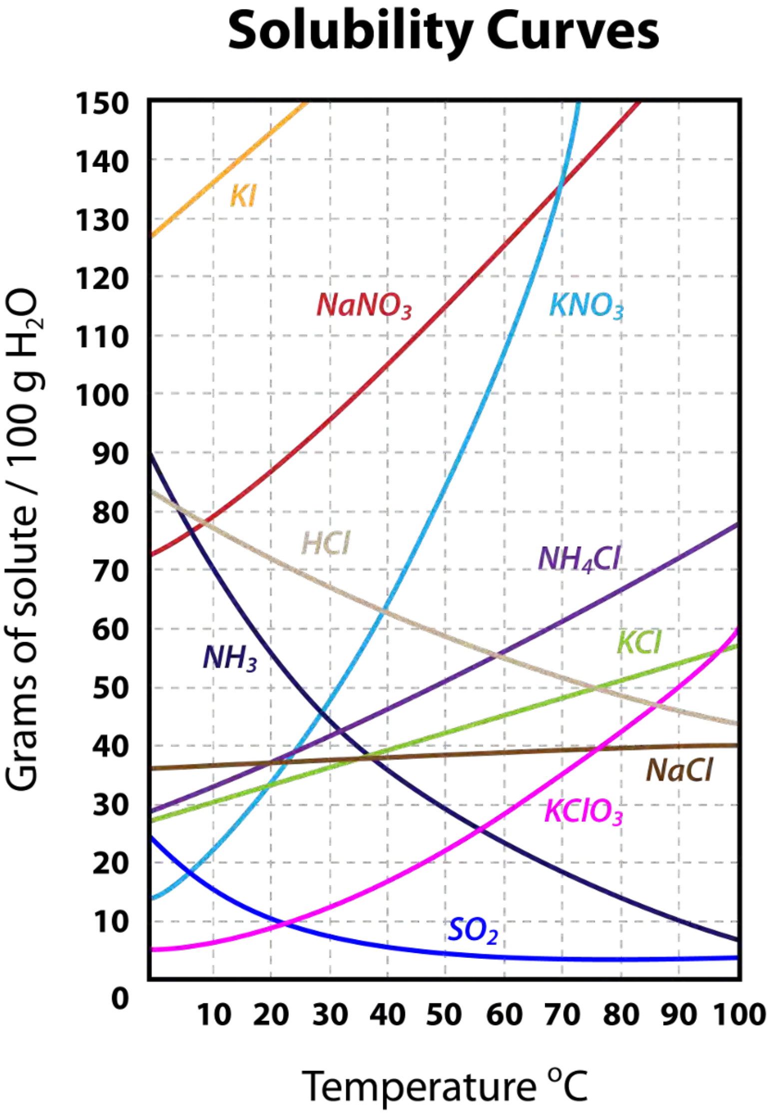


FIGURE 16.2
Solubility curves for several compounds.

Several substances – HCl, NH_3, and SO_2 – have solubility that decreases as temperature decreases. They are all gases at standard pressure. When a solvent with a gas dissolved in it is heated, the kinetic energy of both the solvent and solute increases. As the kinetic energy of the gaseous solute increases, its molecules have a greater tendency to escape the attraction of the solvent molecules and return to the gas phase. Therefore, the solubility of a gas decreases as the temperature increases.

Solubility curves can be used to determine if a given solution is saturated or unsaturated. Suppose that 80 g of KNO_3 is added to 100 g of water at 30°C. According to the solubility curve, approximately 48 g of KNO_3 will dissolve at 30°C. This means that the solution will be saturated since 48 g is less than 80 g. We can also determine that there will be 80 - 48 = 32 g of undissolved KNO_3 remaining at the bottom of the container. Now suppose that this saturated solution is heated to 60°C. According to the curve, the solubility of KNO_3 at 60°C is about 107 g. Now the solution is unsaturated since it contains only the original 80 g of dissolved solute. Now suppose the solution is cooled all the way down to 0°C. The solubility at 0°C is about 14 g, meaning that 80 - 14 = 66 g of the KNO_3 will recrystallize.

Summary

- The solubility of a solid in water increases with an increase in temperature.

- Gas solubility decreases as the temperature increases.

Practice

Read the material at the link below and answer the questions. Try not to look at the answers until you do your own work:

http://chemwiki.ucdavis.edu/Physical_Chemistry/Physical_Properties_of_Matter/Solutions/SOLUBILITY/Temperature_Effects_On_The_Solubility_Of_Gases

Review

1. Why does the solubility of a gas decrease as the temperature increases?
2. Is the solubility of NaCl affected by solvent?
3. What is the solubility of KNO_3 at 50°C?

- **solubility:** The amount of a substance that is required to form a saturated solution in a given amount of solvent at a specified temperature.
- **solubility curve:** A graph of the solubility of substances as a function of temperature.

16.5 Supersaturated Solutions

- Describe the process of supersaturation.

How does a hot or a cold pack work?

In the picture above, a thermal pack is applied to the back. Small packs can be used either for heating or cooling, depending on the material used. A heat pack contains a supersaturated solution of material such as sodium acetate. The solution is clear until a small metal trigger is activated. The sodium acetate then crystallizes out of solution and generates heat in the process.

Supersaturated Solutions

Watch a video:

MEDIA

Click image to the left for more content.

http://www.youtube.com/watch?v=_NsX6EkqmsQ

Some solutes, such as sodium acetate, do not recrystallize easily. Suppose an exactly saturated solution of sodium acetate is prepared at 50°C. As it cools back to room temperature, no crystals appear in the solution, even though the solubility of sodium acetate is lower at room temperature. A **supersaturated solution** is a solution that contains more than the maximum amount of solute that is capable of being dissolved at a given temperature. The recrystallization of the excess dissolved solute in a supersaturated solution can be initiated by the addition of a tiny crystal of solute, called a seed crystal. The seed crystal provides a nucleation site on which the excess dissolved crystals can begin to grow. Recrystallization from a supersaturated solution is typically very fast.

Summary

- A supersaturated solution can recrystallize when a seed crystal is added to the solution.

Practice

Read the materials and watch the video at the link below, then answer the questions:

http://commons.wikimedia.org/wiki/File:Handwarmer-crystallisation.ogv

1. Name a compound that can form supersaturated solutions.
2. Is the recrystallization process fast or slow?
3. What else happened when recrystallization took place?

Review

1. How do we know a solution is supersaturated?
2. How can we cause recrystallization of a supersaturated solution?
3. What does the seed crystal do?

- **supersaturated solution:** A solution that contains more than the maximum amount of solute that is capable of being dissolved at a given temperature.

16.6 Henry's Law

- State Henry's Law.
- Perform calculations involving Henry's Law.

How is sipping soda in outer space different then on Earth?

Having a soft drink in outer space poses some special problems. Under microgravity, the carbonation could quickly dissipate if not kept under pressure. You can't open the can or you will lose carbonation. So a special pressurized container has been developed to get around the problem of gas loss at low gravity.

Henry's Law

Pressure has very little effect on the solubility of solids or liquids, but has a significant effect on the solubility of gases. Gas solubility increases as the partial pressure of a gas above the liquid increases. Suppose a certain volume of water is in a closed container with the space above it occupied by carbon dioxide gas at standard pressure. Some of the CO_2 molecules come into contact with the surface of the water and dissolve into the liquid. Now suppose that more CO_2 is added to the space above the container, causing a pressure increase. More CO_2 molecules are now in contact with the water and so more of them dissolve. Thus the solubility increases as the pressure increases. As with a solid, the CO_2 that is undissolved reaches an equilibrium with the dissolved CO_2, represented by the following equation.

$$CO_2(g) \rightleftarrows CO_2(aq)$$

At equilibrium, the rate of gaseous CO_2 dissolving is equal to the rate of dissolved CO_2 coming out of the solution.

When carbonated beverages are packaged, they are done so under high CO_2 pressure so that a large amount of carbon dioxide dissolves in the liquid. When the bottle is open, the equilibrium is disrupted because the CO_2 pressure above the liquid decreases. Immediately, bubbles of CO_2 rapidly exit the solution and escape out of the top of the open bottle. The amount of dissolve CO_2 decreases. If the bottle is left open for an extended period of time, the beverage becomes "flat" as more and more CO_2 comes out of the liquid.

The relationship of gas solubility to pressure is described by Henry's law, named after English chemist William Henry (1774-1836). **Henry's Law** states that the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas above the liquid. Henry's law can be written as follows:

$$\frac{S_1}{P_1} = \frac{S_2}{P_2}$$

S_1 and P_1 are the solubility and the pressure at an initial set of conditions; S_2 and P_2 are the solubility and pressure at another changed set of conditions. Solubilities of gases are typically reported in g/L, as seen in sample problem 16.1.

Sample Problem:

The solubility of a certain gas in water is 0.745 g/L at standard pressure. What is its solubility when the pressure above the solution is raised to 4.50 atm? The temperature is constant at 20°C.

Step 1: List the known quantities and plan the problem.

Known

- $S_1 = 0.745\ g/L$
- $P_1 = 1.00$ atm
- $P_2 = 4.50$ atm

Unknown

- $S_2 = ?\ g/L$

Substitute into Henry's law and solve for S_2.

Step 2: Solve.

$$S_2 = \frac{S_1 \times P_2}{P_1} = \frac{0.745 \text{ g/L} \times 4.50 \text{ atm}}{1.00 \text{ atm}} = 3.35 \text{ g/L}$$

Step 3: Think about your result.

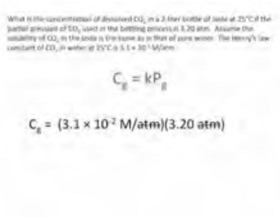
The solubility is increased to 4.5 times its original value according to the direct relationship.

Summary

- The pressure above a liquid affects the solubility of a gas in the liquid.

Practice

Watch the video at the link below and answer the questions:



$C_g = kP_g$

$C_g = (3.1 \times 10^{-2}\ M/atm)(3.20\ atm)$

MEDIA

Click image to the left for more content.

http://www.youtube.com/watch?v=eM56JYel1aM

1. What affects the Henry's law constant?
2. What do you need to be careful of in the way of units?
3. If we know the atmospheric pressure and the mole fraction of the gas, how do we calculate the partial pressure of the gas?

Review

1. Does pressure affect the solubility of liquids and solids?
2. If you increase the pressure of a gas above the liquid, how does that affect the amount of gas dissolved in the liquid?
3. What equilibrium is eventually reached?

- **Henry's Law:** The solubility of a gas in a liquid is directly proportional to the partial pressure of the gas above the liquid.

16.7 Percent Solutions

- Define concentration.
- Perform calculations involving mass percent and volume percent solutions.

How many?

There are cultures that have no numbers above three. Anything greater than that is simply referred to as "much" or "many". We recognize how limited this form of calculation is, but we do some of the same thing. There are several ways to express the amount of solute in a solution in a quantitative manner. The **concentration** of a solution is a measure of the amount of solute that has been dissolved in a given amount of solvent or solution. A **concentrated** solution is one that has a relatively large amount of dissolved solute. A **dilute** solution is one that has a relatively small amount of dissolved solute. However, those terms are vague and we need to be able to express concentration with numbers.

Percent Solutions

One way to describe the concentration of a solution is by the percent of a solute in the solvent. The percent can further be determined in one of two ways: (1) the ratio of the mass of the solute divided by the mass of the solution or (2) the ratio of the volume of the solute divided by the volume of the solution.

Mass Percent

When the solute in a solution is a solid, a convenient way to express the concentration is a mass percent $\left(\frac{\text{mass}}{\text{mass}}\right)$, which is the grams of solute per 100 g of solution.

$$\text{Percent by mass} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\%$$

Suppose that a solution was prepared by dissolving 25.0 g of sugar into 100 g of water. The percent by mass would be calculated by:

$$\text{Percent by mass} = \frac{25 \text{ g sugar}}{125 \text{ g solution}} \times 100\% = 20\% \text{ sugar}$$

Sometimes you may want to make up a particular mass of solution of a given percent by mass and need to calculate what mass of the solvent to use. For example, you need to make 3000 g of a 5% solution of sodium chloride. You can rearrange and solve for the mass of solute.

$$\text{mass of solute} = \frac{\text{percent by mass}}{100\%} \times \text{mass of solution} = \frac{5\%}{100\%} \times 3000 \text{ g} = 150 \text{ g NaCl}$$

You would need to weigh out 150 g of NaCl and add it to 2850 g of water. Notice that it was necessary to subtract the mass of the NaCl (150 g) from the mass of solution (3000 g) to calculate the mass of the water that would need to be added.

Volume Percent

The percentage of solute in a solution can more easily be determined by volume when the solute and solvent are both liquids. The volume of the solute divided by the volume of solution expressed as a percent yields the percent by volume $\left(\frac{\text{volume}}{\text{volume}}\right)$ of the solution. If a solution is made by adding 40 mL of ethanol to 20 mL of water, the percent by volume is:

$$\begin{aligned}\text{Percent by volume} &= \frac{\text{volume of solute}}{\text{volume of solution}} \times 100\% \\ &= \frac{40 \text{ mL ethanol}}{240 \text{ mL solution}} \times 100\% \\ &= 16.7\% \text{ ethanol}\end{aligned}$$

Frequently, ingredient labels on food products and medicines have amounts listed as percentages

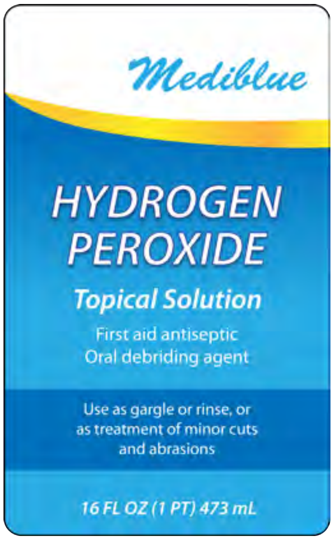


FIGURE 16.3
Hydrogen peroxide is commonly sold as a 3% by volume solution for use as a disinfectant.

Summary

- Techniques for calculation percent mass and percent volume solution concentrations are described.

Practice

Read pages 1-3 of the material on the link below and do the problems associated with that section. Work the problems before checking the answers.

http://go.hrw.com/resources/go_sc/mc/HUGPS163.PDF

Review

1. Why are the terms "concentrated" and "dilute" not very helpful?
2. When would you use volume percent calculations?
3. Why do you subtract the mass of the solute from the total mass desired when making mass percent calculations?

- **concentrated:** A solution that has a relatively large amount of dissolved solute.
- **concentration:** A measure of the amount of solute that has been dissolved in a given amount of solvent or solution.
- **dilute:** A solution that has a relatively small amount of dissolved solute.

16.8 Molarity

- Define molarity.
- Perform calculations involving molarity.

How many molecules?

Chemists deal with amounts of molecules every day. Our reactions are described as so many molecules of compound A reacting with so many molecules of compound B to form so many molecules of compound C. When we determine how much reagent to use, we need to know the number of molecules in a given volume of the reagent. Percent solutions only tell us the number of grams, not molecules. A 100 mL solution of 2% NaCl will have a very different number of molecules than a 2% solution of CsCl. So we need another way to talk about numbers of molecules.

Molarity

Chemists primarily need the concentration of solutions to be expressed in a way that accounts for the number of particles that react according to a particular chemical equation. Since percentage measurements are based on either mass or volume, they are generally not useful for chemical reactions. A concentration unit based on moles is preferable. The **molarity (M)** of a solution is the number of moles of solute dissolved in one liter of solution. To calculate the molarity of a solution, you divide the moles of solute by the volume of the solution expressed in liters.

$$\text{Molarity (M)} = \frac{\text{moles of solute}}{\text{liters of solution}} = \frac{\text{mol}}{\text{L}}$$

Note that the volume is in liters of solution and not liters of solvent. When a molarity is reported, the unit is the symbol M and is read as "molar". For example a solution labeled as 1.5 M NH_3 is read as "1.5 molar ammonia solution".

Sample Problem: Calculating Molarity

A solution is prepared by dissolving 42.23 g of NH_4Cl into enough water to make 500.0 mL of solution. Calculate its molarity.

Step 1: List the known quantities and plan the problem.

Known	Unknown
mass $= 42.23$ g NH_4Cl	molarity = ? M
molar mass $NH_4Cl = 53.50$ g/mol	
volume solution $= 500.0$ mL $= 0.5000$ L	

The mass of the ammonium chloride is first converted to moles. Then the molarity is calculated by dividing by liters. Note the given volume has been converted to liters.

Step 2: Solve.

$$42.23 \text{ g } NH_4Cl \times \frac{1 \text{ mol } NH_4Cl}{53.50 \text{ g } NH_4Cl} = 0.7893 \text{ mol } NH_4Cl$$

$$\frac{0.7893 \text{ mol } NH_4Cl}{0.5000 \text{ L}} = 1.579 \text{ M}$$

Step 3: Think about your result.

The molarity is 1.579 M, meaning that a liter of the solution would contain 1.579 mol NH_4Cl. Four significant figures are appropriate.

In a laboratory situation, a chemist must frequently prepare a given volume of solutions of a known molarity. The task is to calculate the mass of the solute that is necessary. The molarity equation can be rearranged to solve for moles, which can then be converted to grams. See sample problem 16.3.

Sample Problem:

A chemist needs to prepare 3.00 L of a 0.250 M solution of potassium permanganate ($KMnO_4$). What mass of $KMnO_4$ does she need to make the solution?

Step 1: List the known quantities and plan the problem.

Known

- molarity = 0.250 M
- volume = 3.00 L
- molar mass $KMnO_4$ = 103.10 g/mol

Unknown

- mass $KMnO_4$ = ? g

Moles of solute is calculated by multiplying molarity by liters. Then, moles is converted to grams.

Step 2: Solve.

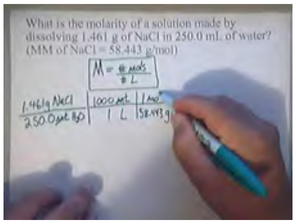
$$\text{mol KMnO}_4 = 0.250 \text{ M KMnO}_4 \times 3.00 \text{ L} = 0.750 \text{ mol KMnO}_4$$

$$0.750 \text{ mol KMnO}_4 \times \frac{103.10 \text{ g KMnO}_4}{1 \text{ mol KMnO}_4} = 77.3 \text{ g KMnO}_4$$

Step 3: Think about your result.

When 77.3 g of potassium permanganate is dissolved into water to make 3.00 L of solution, the molarity is 0.250 M.

Watch a video of molarity calculations:



What is the molarity of a solution made by dissolving 1.461 g of NaCl in 250.0 mL of water? (MM of NaCl = 58.443 g/mol)

MEDIA

Click image to the left for more content.

http://www.youtube.com/watch?v=8oTqwBAvbnY

Summary

- Calculations using the concept of molarity are described.

Practice

Read the material and work the problems at the site below:

http://www.occc.edu/kmbailey/Chem1115Tutorials/Molarity.htm

Review

1. What does M stand for?
2. What does molarity tell us that percent solution information does not tell us?
3. What do we need to know about a molecule in order to carry out molarity calculations?

- **molarity (M):** The number of moles of solute dissolved in one liter of solution.

16.9 Preparing Solutions

- Describe the process for preparing solutions.

How much water do I add?

Back in the "good old days" (whenever that really was), many cooks didn't bother with careful measurements. They "just knew" how much flour to use or how much water to add. Most of us need somewhat more precise ways to measure when we cook. Chemists are very careful when they prepare solutions since the results of their experiments need to be quantitative. "Just knowing" is not accurate enough for scientific purposes.

Preparing Solutions

If you are attempting to prepare 1.00 L of a 1.00 solution of NaCl, you would obtain 58.44 g of sodium chloride. However you cannot simply add the sodium chloride to 1.00 L of water. After the solute dissolves, the volume of the solution will be slightly greater than a liter because the hydrated sodium and chloride ions take up space in the solution. Instead, a **volumetric flask** needs to be used. Volumetric flasks come in a variety of sizes (see **Figure** below) and are designed to allow a chemist to prepare a solution only of one specific volume.

FIGURE 16.4

Volumetric flasks.

In other words, you cannot use a 1-liter volumetric flask to make 500 ml of a solution. It can only be used to prepare 1 liter of a solution. The steps to follow when preparing a solution with a 1-liter volumetric flask are outlined below and shown in the **Figure** 16.5.

1. The appropriate mass of solute is weighed out and added to volumetric flask that has been about half-filled with distilled water.
2. The solution is swirled until all of the solute dissolves.
3. More distilled water is carefully added up to the line etched on the neck of the flask.
4. The flask is capped and inverted several times to completely mix.

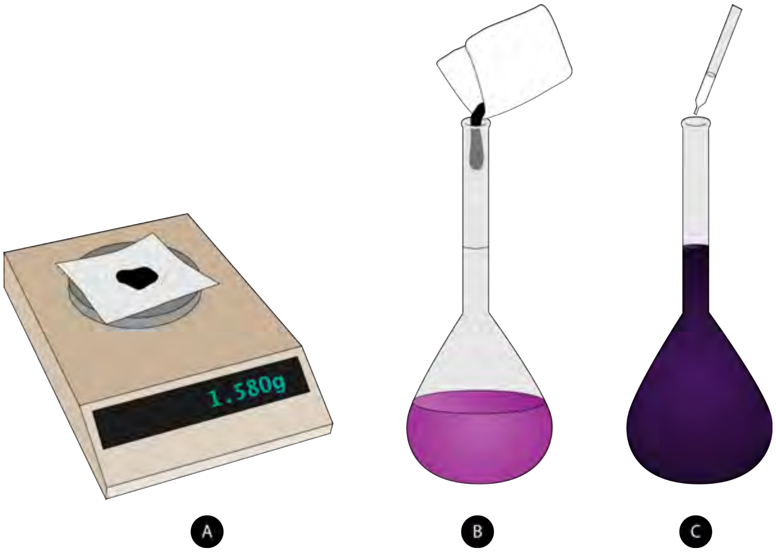


FIGURE 16.5

Steps to follow in preparing a solution of known molarity: (A) weigh out correct mass of solute, (B) dissolve into solvent in a volumetric flask, and (C) add solvent to the fill line on the flask and mix.

Summary

- Steps for the preparation of a solution are outlined.

Practice

Watch the video at the link below and answer the following questions:

MEDIA

Click image to the left for more content.

http://www.youtube.com/watch?v=A2YyIo8vSCA

1. What is a solution?
2. What is the solute?
3. What is the solvent?
4. What safety precautions need to be taken?

Review

1. Why do you add the solute to the flask only partially filled with solvent?
2. How much solvent do you add at the end?
3. Why do you invert the flask a few times after diluting to the mark?

- **volumetric flask:** A calibrated long-necked flask design for the accurate preparation of solutions.

16.10 Dilution

- Perform calculations involving dilutions.

How do you clean concrete?

Muriatic acid (another name for HCl) is widely used for cleaning concrete and masonry surfaces. The acid must be diluted before use to get it down to a safer strength. Commercially available at concentrations of about 18%, this compound can be used to remove scales and deposits (usually composed of basic materials).

Dilutions

When additional water is added to an aqueous solution, the concentration of that solution decreases. This is because the number of moles of the solute does not change, while the volume of the solution increases. We can set up an equality between the moles of the solute before the dilution (1) and the moles of the solute after the dilution (2).

$$\text{mol}_1 = \text{mol}_2$$

Since the moles of solute in a solution is equal to the molarity multiplied by the liters, we can set those equal.

$$M_1 \times L_1 = M_2 \times L_2$$

Finally, because the two sides of the equation are set equal to one another, the volume can be in any units we choose, as long as that unit is the same on both sides. Our equation for calculating the molarity of a diluted solution becomes:

$$M_1 \times V_1 = M_2 \times V_2$$

Suppose that you have 100. mL of a 2.0 M solution of HCl. You dilute the solution by adding enough water to make the solution volume 500. mL. The new molarity can easily be calculated by using the above equation and solving for M_2.

$$M_2 = \frac{M_1 \times V_1}{V_2} = \frac{2.0 \text{ M} \times 100. \text{ mL}}{500. \text{ mL}} = 0.40 \text{ M } HCl$$

The solution has been diluted by one-fifth since the new volume is five times as great as the original volume. Consequently, the molarity is one-fifth of its original value.

Another common dilution problem involves deciding how much of a highly concentrated solution is requires to make a desired quantity of solution of lesser concentration. The highly concentrated solution is typically referred to as the stock solution.

Sample Problem: Dilution of a Stock Solution

Nitric acid (HNO_3) is a powerful and corrosive acid. When ordered from a chemical supply company, its molarity is 16 M. How much of the stock solution of nitric acid needs to be used to make 8.00 L of a 0.50 M solution?

Step 1: List the known quantities and plan the problem.

Known

- stock HNO_3 = 16 M
- $V_2 = 8.00$ L
- $M_2 = 0.50$ M

Unknown

- volume stock HNO_3 $(V_1) =?$ L

The unknown in the equation is V_1, the volume of the concentrated stock solution.

Step 2: Solve.

$$V_1 = \frac{M_2 \times V_2}{M_1} = \frac{0.50 \text{ M} \times 8.00 \text{ L}}{16 \text{ M}} = 0.25 \text{ L} = 250 \text{ mL}$$

Step 3: Think about your result.

250 mL of the stock HNO_3 needs to be diluted with water to a final volume of 8.00 L. The dilution is by a factor of 32 to go from 16 M to 0.5 M.

Dilutions can be performed in the laboratory with various tools, depending on the volumes required and the desired accuracy. The following images illustrate the use of two different types of pipettes. **Figure** 16.6 illustrates the use of two different types of pipettes. In the first figure, a glass **pipette** is being used to transfer a portion of a solution to a graduated cylinder. Use of a pipette rather than a graduated cylinder for the transfer improves accuracy. In the second **Figure** 16.7, the student is using a **micropipette**, which is designed to quickly and accurately dispense small volumes. Micropipettes are adjustable and come in a variety of sizes.

FIGURE 16.6

Volumetric pipette.

FIGURE 16.7

Micropipette.

Summary

- A process is described for calculations of dilutions.

Practice

Read the material and work the problems at the link below:

http://dl.clackamas.edu/ch105-04/dilution.htm

Review

1. What does not change when additional water is added to a solution?
2. What is a stock solution?
3. How is a stock solution used?

- **micropipette:** A pipette designed to transfer very small amounts of fluid.
- **pipette:** A calibrated glass tube for the accurate transfer of liquids.

16.11 Molality

- Define molality.
- Perform calculations involving molality.

How do you measuring physical parameters of solutions?

For many purposes, the use of molarity is very convenient. However, when we want to know the concentration of solute present in situations where there are temperature changes, molarity won't work. The volume of the solution will change somewhat with temperature, enough to make accurate data observations and calculations in error. Another parameter is needed, one not affected by the temperature of the material we are studying.

Molality

A final way to express the concentration of a solution is by its molality. The **molality (*m*)** of a solution is the moles of solute divided by the kilograms of solvent. A solution that contains 1.0 mol of NaCl dissolved into 1.0 kg of water is a "one-molal" solution of sodium chloride. The symbol for molality is a lower-case m written in italics.

$$\text{Molality } (m) = \frac{\text{moles of solute}}{\text{kilograms of solvent}} = \frac{\text{mol}}{\text{kg}}$$

Molality differs from molarity only in the denominator. While molarity is based on the liters of solution, molality is based on the kilograms of solvent. Concentrations expressed in molality are used when studying properties of solutions related to vapor pressure and temperature changes. Molality is used because its value does not change with changes in temperature. The volume of a solution, on the other hand, is slightly dependent upon temperature.

Sample Problem: Calculating Molality

Determine the molality of a solution prepared by dissolving 28.60 g of glucose ($C_6H_{12}O_6$) into 250. g of water.

Step 1: List the known quantities and plan the problem.

Known

- mass solute= 28.60 g $C_6H_{12}O_6$
- mass solvent = 250. g = 0.250 kg
- molar mass $C_6H_{12}O_6$ = 180.18 g/mol

Unknown

- molality = ? *m*

Convert grams of glucose to moles and divide by the mass of the water in kilograms.

Step 2: Solve.

$$28.60 \text{ g } C_6H_{12}O_6 \times \frac{1 \text{ mol } C_6H_{12}O_6}{180.18 \text{ g } C_6H_{12}O_6} = 0.1587 \text{ mol } C_6H_{12}O_6$$

$$\frac{0.1587 \text{ mol } C_6H_{12}O_6}{0.250 \text{ kg } H_2O} = 0.635\ m\ C_6H_{12}O_6$$

Step 3: Think about your result.

The answer represents the moles of glucose per kilogram of water and has three significant figures.

Molality and molarity are closely related in value for dilute aqueous solutions because the density of those solutions is relatively close to 1.0 g/mL. This means that 1.0 L of solution has nearly a mass of 1.0 kg. As the solution becomes more concentrated, its density will not be as close to 1.0 g/ml and the molality value will be different than the molarity. For solutions with solvents other than water, the molality will be very different than the molarity. Make sure that you are paying attention to which quantity is being used in a given problem.

Summary

- The calculation of molality is described.

Practice

Read the material at the link below and do the practice problems:

http://www.chemteam.info/Solutions/Molality.html

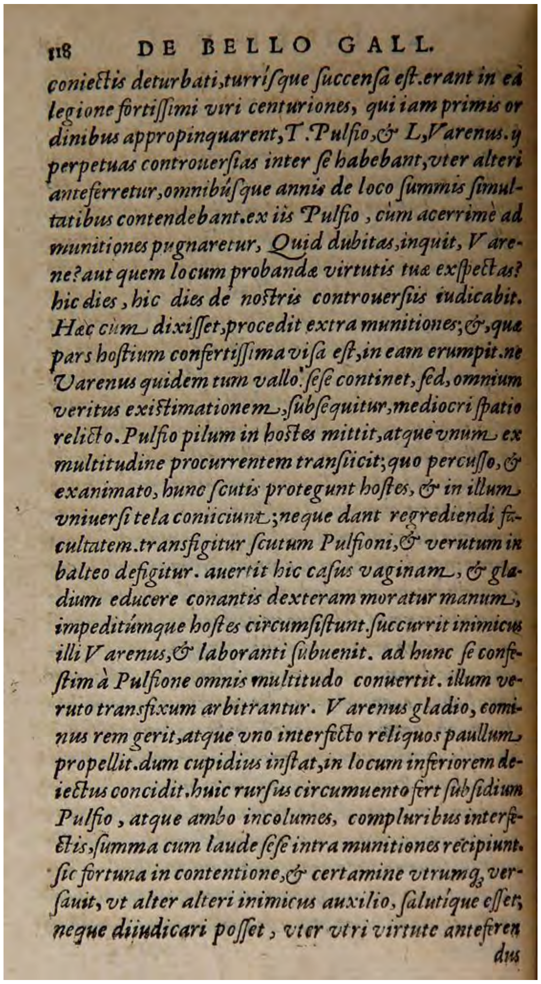
Review

1. What is the difference between molarity and molality?
2. Is molality affected by changes in temperature?
3. Do you dilute the solute to a given final volume when making molal solutions?

- **molality (*m*):** Moles of solute divided by the kilograms of solvent.

16.12 Vapor Pressure Lowering

- Define colligative property.
- Define vapor pressure.
- Use vapor pressure to explain colligative properties of solutions.



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dus

What did Caesar say?

Latin is an interesting and useful language, even if you don't want to read Julius Caesar's writings. A knowledge of Latin helps us understand our own language better. Take the "colligative". Where did that come from? If you know a little Latin, you know that it comes from two Latin words meaning "to tie together". This helps you better understand some of the science terminology we use every day.

Vapor Pressure Lowering

A **colligative property** is a property of a solution that depends only on the number of solute particles dissolved in the solution and not on their identity. Recall that the vapor pressure of a liquid is determined by how easily its molecules are able to escape the surface of the liquid and enter the gaseous phase. When a liquid evaporates easily, it will have a relatively large number of its molecules in the gas phase and thus will have a high vapor pressure.

Liquids that do not evaporate easily have a lower vapor pressure. The **Figure** 16.8 shows the surface of a pure solvent compared to a solution. In the picture on the left, the surface is entirely occupied by liquid molecules, some of which will evaporate and form a vapor pressure. On the right, a nonvolatile solute has been dissolved into the solvent. **Nonvolatile** means that the solute itself has little tendency to evaporate. Because some of the surface is now occupied by solute particles, there is less room for solvent molecules. This results in less solvent being able to evaporate. The addition of a nonvolatile solute results in a lowering of the vapor pressure of the solvent.

Pure Solvent

Solution

FIGURE 16.8

The solution on the right left has had some of its solvent particles replaced by solute particles. Since the solute particles do not evaporate, the vapor pressure of the solution is lower than that of the pure solvent.

The lowering of the vapor pressure depends on the number of solute particles that have been dissolved. The chemical nature of the solute is not important because the vapor pressure is merely a physical property of the solvent. The only requirement is that the solute only dissolved and does not undergo a chemical reaction with the solvent.

While the chemical nature of the solute is not a factor, it is necessary to take into account whether the solute is an electrolyte or a nonelectrolyte. Recall that ionic compounds are strong electrolytes and thus dissociate into ions when they dissolve. This results in a larger number of dissolved particles. For example, consider two different solutions of equal concentration. One is made from the ionic compound sodium chloride, while the other is made from the molecular compound glucose. The following equations show what happens when these solutes dissolve.

$$\begin{aligned} &\text{NaCl}(s) \rightarrow \text{Na}^+(aq) + \text{Cl}^-(aq) && \text{2 dissolved particles} \\ &\text{C}_6\text{H}_{12}\text{O}_6(s) \rightarrow \text{C}_6\text{H}_{12}\text{O}_6(aq) && \text{1 dissolved particle} \end{aligned}$$

The sodium chloride dissociates into two ions, while the glucose does not dissociate. Therefore, equal concentrations of each solution will result in twice as many dissolved particles in the case of the sodium chloride. The vapor pressure of the sodium chloride solution will be lowered twice the amount as the glucose solution.

Summary

- Addition of a nonvolatile solute to a solution lowers the vapor pressure of the solution.

Practice

Watch the video at the link given and answer the following questions:

MEDIA

Click image to the left for more content.

http://www.youtube.com/watch?v=0ZwknpcwTyQ

1. What happens between the water molecules and the solute molecules?
2. How does this affect vapor pressure?
3. What is a non-volatile material?

Review

1. The boiling point of diethyl ether is 34.6°C. Would this compound be considered non-volatile?
2. How does the number of particles influence vapor pressure?
3. Silver chloride is a non-volatile material, but does not dissolve in water. What effect will it have on the vapor pressure of water?

- **colligative property:** A property of a solution that depends only on the number of solute particles dissolved in the solution and not on their identity.
- **non-volatile:** Does not evaporate easily.

16.13 Freezing Point Depression

- Define freezing point depression.
- Calculate the freezing point of a solution when given the molal freezing-point depression constant.

Why salt the roads?

Colligative properties have practical applications, such as the salting of roads in cold-weather climates. By applying salt to an icy road, the melting point of the ice is decreased, and the ice will melt more quickly, making driving safer. Sodium chloride ($NaCl$) and either calcium chloride ($CaCl_2$) or magnesium chloride ($MgCl_2$) are used most frequently, either alone or in a mixture. Sodium chloride is the least expensive option, but is less effective because it only dissociates into two ions instead of three.

Freezing Point Depression

The **Figure** 16.9 shows the phase diagram for a pure solvent and how it changes when a solute is added to it. The solute lowers the vapor pressure of the solvent resulting in a lowering of the freezing point of the solution compared to the solvent. The **freezing point depression** is the difference in temperature between the freezing point of the pure solvent and that of the solution. On the graph, the freezing point depression is represented by ΔT_f.

When a pure solvent freezes, its particles become more ordered as the intermolecular forces that operate between the molecules become permanent. In the case of water, the hydrogen bonds make the hexagonally-shaped network of molecules that characterizes the structure of ice. By dissolving a solute into the liquid solvent, this ordering process is disrupted. As a result, more energy must be removed from the solution in order to freeze it, and the freezing point of the solution is lower than that of the pure solvent.

The magnitude of the freezing point depression is directly proportional to the molality of the solution. The equation is:

$$\Delta T_f = K_f \times m$$

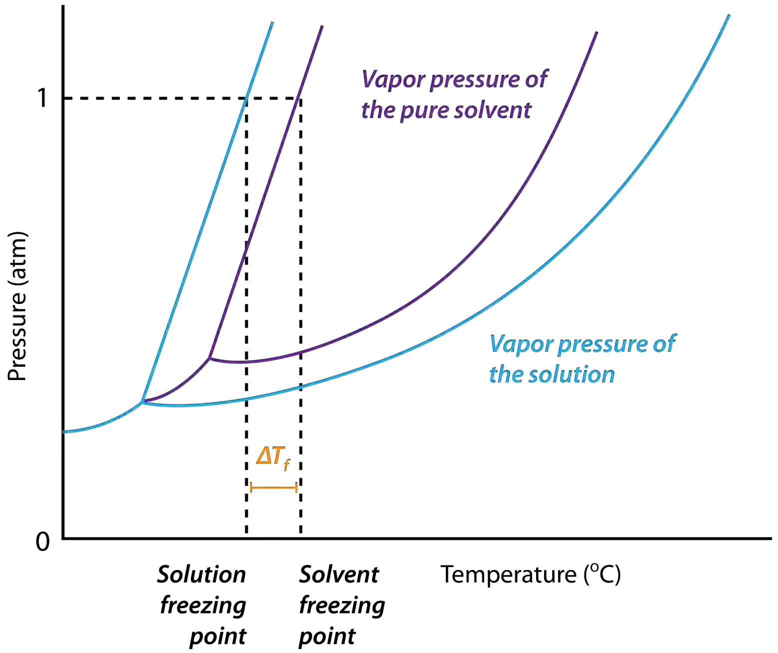


FIGURE 16.9

The vapor pressure of a solution (blue) is lower than the vapor pressure of a pure solvent (pink). As a result, the freezing point of a solvent decreases when any solute is dissolved into it.

The proportionality constant, K_f, is called the **molal freezing-point depression constant**. It is a constant that is equal to the change in the freezing point for a 1-molal solution of a nonvolatile molecular solute. For water, the value of K_f is -1.86°C/ m. So the freezing temperature of a 1-molal aqueous solution of any nonvolatile molecular solute is -1.86°C. Every solvent has a unique molal freezing-point depression constant. These are shown in **Table** 16.2, along with a related value for the boiling point called K_b.

TABLE 16.2: Molal Freezing-Point and Boiling-Point Constants

Solvent	**Normal freezing point (°C)**	**Molal freezing-point depression constant, K_f (°C/*m*)**	**Normal boiling point (°C)**	**Molal boiling-point elevation constant, Kb (°C/*m*)**
Acetic acid	16.6	-3.90	117.9	3.07
Camphor	178.8	-39.7	207.4	5.61
Naphthalene	80.2	-6.94	217.7	5.80
Phenol	40.9	-7.40	181.8	3.60
Water	0.00	-1.86	100.00	0.512

Sample Problem: Freezing Point of a Nonelectrolyte

Ethylene glycol ($C_2H_6O_2$) is a molecular compound that is used in many commercial anti-freezes. A water solution of ethylene glycol is used in vehicle radiators to lower its freezing point and thus prevent the water in the radiator from freezing. Calculate the freezing point of a solution of 400. g of ethylene glycol in 500. g of water.

Step 1: List the known quantities and plan the problem.

Known

- mass $C_2H_6O_2$ = 400. g
- molar mass $C_2H_6O_2$ = 62.08 g/mol
- mass H_2O = 500.0 g = 0.500 kg

- mass $H_2O = 500.0 \text{ g} = 0.500 \text{ kg}$

- $K_f(H_2O) = -1.86°C/m$

Step 3: Think about your result.

The freezing point of the water decreases by a large amount, protecting the radiator from damage due to the expansion of water when it freezes. There are three significant figures in the result.

Summary

- Freezing point depression is defined.
- Calculations involving freezing point depression are described.

Practice

Solve the problems at the site below:

http://home.comcast.net/ cochranjim/PDFS3/COLIGWS1A.pdf

Review

1. How does a solute affect the freezing of water?
2. How many moles of glucose would be needed to lower the freezing point of one kg of water 3.72°C?
3. How many moles of NaCl would be needed to produce the same amount of lowering of temperature?

- **freezing point depression:** The difference in temperature between the freezing point of the pure solvent and that of the solution.
- **molal freezing-point depression constant:** A constant that is equal to the change in the freezing point for a 1-molal solution of a nonvolatile molecular solute.

16.14 Boiling Point Elevation

- Define boiling point elevation.
- Calculate the boiling point of a solution when given the molal boiling-point elevation constant.

Does adding salt help water boil?

Salt is often added to boiling water when preparing spaghetti or other pasta. One reason is to add flavor to the food. Some people believe that the addition of salt increases the boiling point of the water. Technically, they are correct, but the increase is rather small. You would need to add over 100 grams of NaCl to a liter of water to increase the boiling point a couple of degrees, which is just not healthy.

Boiling Point Elevation

The **Figure** 16.10 shows the phase diagram of a solution and the effect that the lowered vapor pressure has on the boiling point of the solution compared to the solvent. In this case, the solution has a higher boiling point than the pure solvent. Since the vapor pressure of the solution is lower, more heat must be supplied to the solution to bring its vapor pressure up to the pressure of the external atmosphere. The **boiling point elevation** is the difference in temperature between the boiling point of the pure solvent and that of the solution. On the graph, the boiling point elevation is represented by ΔT_b.

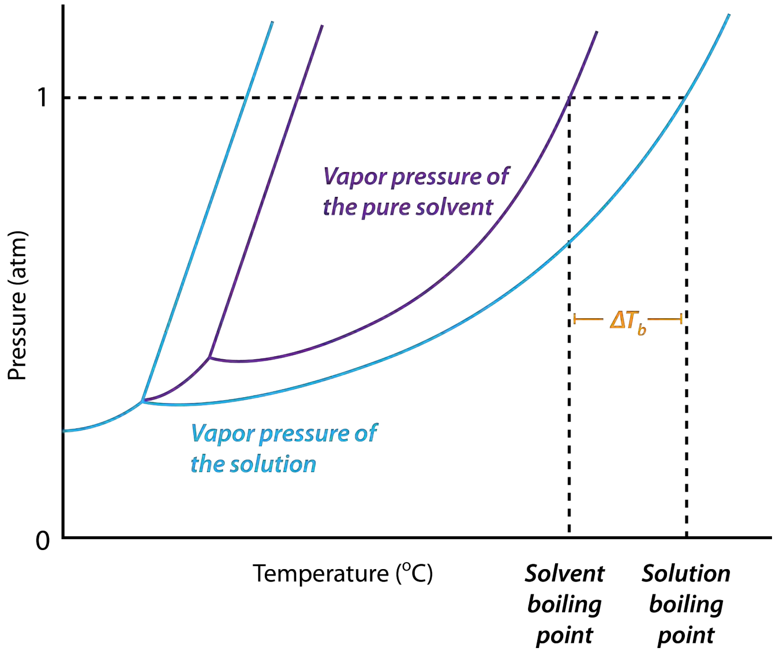


FIGURE 16.10
The lowering of the vapor pressure in a solution causes the boiling point of the solution to be higher than that of the pure solvent.

The magnitude of the boiling point elevation is also directly proportional to the molality of the solution. The equation is:

$$\Delta T_b = K_b \times m$$

The proportionality constant, K_b, is called the **molal boiling-point elevation constant.** It is a constant that is equal to the change in the boiling point for a 1-molal solution of a nonvolatile molecular solute. For water, the value of K_b is 0.512°C/ m. So the boiling temperature of a 1-molal aqueous solution of any nonvolatile molecular solute is 100.512°C.

Summary

- Boiling point elevation is defined.
- Calculations involving the molal boiling point elevation constant are outlined.

Practice

Solve the problems at the link below:

http://home.comcast.net/ cochranjim/PDFS3/COLIGWS2A.pdf

Review

1. Why does addition of a solute to water increase the boiling point?
2. What does the molal boiling point elevation constant tell us?

3. Addition of KCl raises the boiling point of 1.0 kg water by 1.014°C. How many moles of KCl were added?

- **boiling point elevation:** The difference in temperature between the boiling point of the pure solvent and that of the solution.
- **molal boiling-point elevation constant:** A constant that is equal to the change in the boiling point for a 1-molal solution of a nonvolatile molecular solute.

16.15 Electrolytes and Colligative Properties

- Perform calculations involving the effects of electrolytes on colligative properties.

What effect do ions have?

The addition of ions creates significant changes in properties of solutions. Water molecules surround the ions and are somewhat tightly bound to them. Colligative properties are affected because the solvent properties are no longer the same as those in the pure solvent.

Electrolytes and Colligative Properties

Ionic compounds are electrolytes and dissociate into two or more ions as they dissolve. This must be taken into account when calculating the freezing and boiling points of electrolyte solutions. The sample problem below demonstrates how to calculate the freezing point and boiling point of a solution of calcium chloride. Calcium chloride dissociates into three ions according to the equation:

$$\text{CaCl}_2(s) \rightarrow \text{Ca}^{2+}(aq) + 2\text{Cl}^-(aq)$$

The values of the freezing point depression and the boiling point elevation for a solution of CaCl_2 will be three times greater than they would be for an equal molality of a nonelectrolyte.

Sample Problem: Freezing and Boiling Point of an Electrolyte

Determine the freezing and boiling point of a solution prepared by dissolving 82.20 g of calcium chloride into 400.g of water.

Step 1: List the known quantities and plan the problem.

Known

- mass $CaCl_2$ = 82.20 g
- molar mass $CaCl_2$ = 110.98 g/mol
- mass H_2O = 400. g = 0.400 kg
- $K_f(H_2O) = -1.86^\circ\ C/m$
- $K_b(H_2O) = 0.512^\circ\ C/m$
- $CaCl_2$ dissociates into 3 ions

Unknown

- $T_f = ?\ ^\circ C$
- $T_b = ?\ ^\circ C$

The moles of $CaCl_2$ is first calculated, followed by the molality of the solution. The freezing and boiling points are then determined, including multiplying by 3 for the three ions.

Step 2: Solve.

$$82.20 \text{ g CaCl}_2 \times \frac{1 \text{ mol CaCl}_2}{110.98 \text{ g CaCl}_2} = 0.7407 \text{ mol CaCl}_2$$

$$\frac{0.7407 \text{ mol CaCl}_2}{0.400 \text{ kg H}_2\text{O}} = 1.85\ m \text{ CaCl}_2$$

$$\Delta T_f = K_f \times m \times 3 = -1.86^\circ\text{C}/m \times 1.85\ m \times 3 = -10.3^\circ\text{C} \qquad T_f = -10.3^\circ\text{C}$$

$$\Delta T_b = K_b \times m \times 3 = 0.512^\circ\text{C}/m \times 1.85\ m \times 3 = 2.84^\circ\text{C} \qquad T_b = 102.84^\circ\text{C}$$

Step 3: Think about your result.

Since the normal boiling point of water is 100.00°C, the calculated result for ΔT_b must be added to 100.00 to find the new boiling point.

Summary

- The effect of ionization on colligative properties is described.

Practice

Do the practice and homework problems dealing with ionic solutions toward the end of the section on the link below:

http://avon-chemistry.com/solution_lec_p2.html

Review

1. Why do ionic materials change the colligative properties of a solution?
2. Would HCl be expected to alter colligative properties?
3. Calcium carbonate is ionic, but insoluble in water. What effect would it have on the boiling point of water?

16.16 Calculating Molar Mass

- Perform calculations for the determination of molar mass from changes in boiling or freezing points.

How much antifreeze is needed?

We know that we can put antifreeze into a radiator and keep an engine from freezing up. By knowing how cold it will get and how much water is in the radiator, we can determine how much antifreeze to add to achieve our desired freezing point depression. We can do this because we know what the antifreeze is. Can we switch things around and get some information about the properties of the antifreeze (such as its molecular weight) from the freezing point decrease? It turns out that we can do this fairly easily and accurately.

Calculating Molar Mass

In the laboratory, freezing point or boiling point data can be used to determine the molar mass of an unknown solute. Since we know the relationship between a decrease in freezing point and the concentration of solute, if we dissolve a known mass of our unknown solute into a known amount of solvent, we can calculate the molar mass of the solute. The K_f or K_b of the solvent must be known. We also need to know if the solute is an electrolyte or a nonelectrolyte. If the solvent is an electrolyte, you would need to know the number of ions is produced when it dissociates.

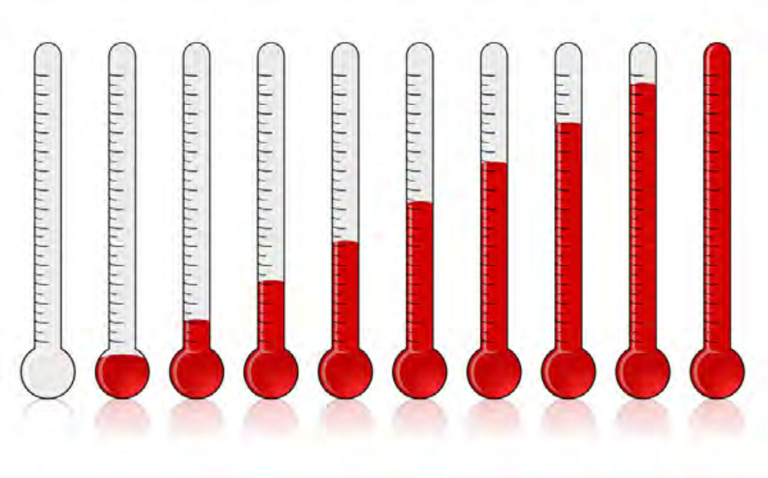


FIGURE 16.11

Changes in temperature.

Sample Problem: Molar Mass from Freezing Point Depression

38.7 g of a nonelectrolyte is dissolved into 218 g of water. The freezing point of the solution is measured to be -5.53°C. Calculate the molar mass of the solute.

Step 1: List the known quantities and plan the problem.

Known

- $\Delta T_f = -5.53^\circ\ C$
- mass H_2O 218 g = 0.218 kg
- mass solute = 38.7 g
- $K_f(\text{H}_2\text{O}) = -1.86^\circ\ \text{C}/m$

Unknown

- molar mass solute = ? g/mol

Use the freeing point depression (ΔT_f) to calculate the molality of the solution. Then use the molality equation to calculate the moles of solute. Then divide the grams of solute by the moles to determine the molar mass.

Step 2: Solve.

$$m = \frac{\Delta T_f}{K_f} = \frac{-5.53^\circ\text{C}}{-1.86^\circ\text{C}/m} = 2.97\ m$$

$$\text{mol solute} = m \times \text{kg H}_2\text{O} = 2.97\ m \times 0.218\ \text{kg} = 0.648\ \text{mol}$$

$$\frac{38.7\ \text{g}}{0.648\ \text{mol}} = 59.7\ \text{g/mol}$$

Step 3: Think about your result.

The molar mass of the unknown solute is 59.7 g/mol. Knowing the molar mass is an important step in determining the identity of an unknown. A similar problem could be done with the change in boiling point.

Summary

- Determination of molar mass by measuring freezing point depression is described.

Practice

Work the problems at the link below:

http://www.gst-d2l.com/homework/fpdepression.html

Review

1. What do we need to know about the solvent to use this technique?
2. Will it work with ionizable compounds?
3. Can we use boiling point elevation to determine molar mass?

16.17 Molecular and Ionic Equations

- Define molecular and ionic equations.
- Give examples of molecular and ionic equations.

"Just a little rain..."

One of the unfortunate by-products of our industrialized society is acid rain. Sulfur dioxide from burning coal and nitric oxides from vehicle emissions both form acids. When these acids react with limestone (calcium carbonate), reactions occur that dissolve the limestone and release water and carbon dioxide. Over a period of time, serious damage is caused to the structures.

Molecular and Ionic Equations

When ionic compounds are dissolved into water, the polar water molecules break apart the solid crystal lattice, resulting in the hydrated ions being evenly distributed through the water. This process is called dissociation and is the reason that all ionic compounds are strong electrolytes. When two different ionic compounds that have been dissolved in water are mixed, a chemical reaction may occur between certain pairs of the hydrated ions.

Consider the double-replacement reaction that occurs when a solution of sodium chloride is mixed with a solution of silver nitrate.

$$\text{NaCl}(aq) + \text{AgNO}_3(aq) \rightarrow \text{NaNO}_3(aq) + \text{AgCl}(s)$$

The driving force behind this reaction is the formation of the silver chloride precipitate (see below)

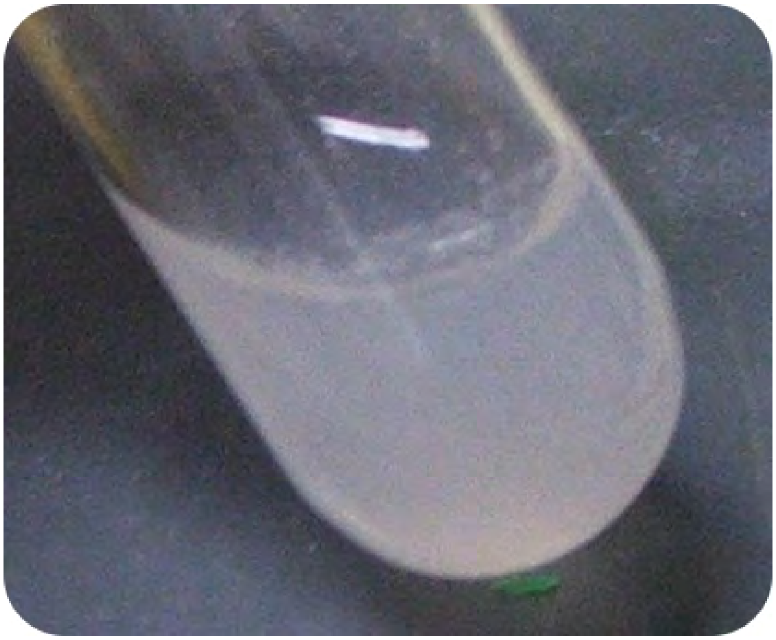


FIGURE 16.12

The white silver chloride precipitate instantly forms when a solution of silver nitrate is added to a solution of sodium chloride.

This is called a molecular equation. A **molecular equation** is an equation in which the formulas of the compounds are written as though all substances exist as molecules. However, there is a better way to show what is happening in this reaction. All of the aqueous compounds should be written as ions because they are present in the water as separated ions because of their dissociation.

$$\text{Na}^+(aq) + \text{Cl}^-(aq) + \text{Ag}^+(aq) + \text{NO}_3^-(aq) \rightarrow \text{Na}^+(aq) + \text{NO}_3^-(aq) + \text{AgCl}(s)$$

This equation is called an **ionic equation**, an equation in which dissolved ionic compounds are shown as free ions.

Some other double-replacement reactions do not produce a precipitate as one of the products. The production of a gas and/or a molecular compound such as water may also drive the reaction. For example, consider the reaction of a solution of sodium carbonate with a solution of hydrochloric acid (HCl). The products of the reaction are aqueous sodium chloride, carbon dioxide, and water. The balanced molecular equation is:

$$\text{Na}_2\text{CO}_3(aq) + 2\text{HCl}(aq) \rightarrow 2\text{NaCl}(aq) + \text{CO}_2(g) + \text{H}_2\text{O}(l)$$

The ionic equation is:

$$2\text{Na}^+(aq) + \text{CO}_3^{2-}(aq) + 2\text{H}^+(aq) + 2\text{Cl}^-(aq) \rightarrow 2\text{Na}^+(aq) + 2\text{Cl}^-(aq) + \text{CO}_2(g) + \text{H}_2\text{O}(l)$$

A single-replacement reaction is one in which an element replaces another element in a compound. An element is in either the solid, liquid, or gas state and is not an ion. The example below shows the reaction of solid magnesium metal with aqueous silver nitrate to form aqueous magnesium nitrate and silver metal.

Balanced molecular equation:

$$\text{Mg}(s) + 2\text{AgNO}_3(aq) \rightarrow \text{Mg(NO}_3)_2(aq) + 2\text{Ag}(s)$$

Ionic equation:

$$\text{Mg}(s) + 2\text{Ag}^+(aq) + 2\text{NO}_3^-(aq) \rightarrow \text{Mg}^{2+}(aq) + 2\text{NO}_3^-(aq) + 2\text{Ag}(s)$$

This type of single-replacement reaction is called a metal replacement. Other common categories of single-replacement reactions are hydrogen replacement and halogen replacement.

Summary

- Examples of molecular and ionic equations are shown.

Practice

Read the material at the link below and solve the practice equations:

www.chemteam.info/Equations/DoubleReplacement.html

Review

1. What do the small letters after the compounds indicate?
2. Why is it important to show the state of each compound?
3. What do ionic equations tell us?

- **ionic equation:** An equation in which dissolved ionic compounds are shown as free ions.
- **molecular equation:** An equation in which the formulas of the compounds are written as though all substances exist as molecules

16.18 Net Ionic Equations

- Define spectator ion.
- Define net ionic equation.
- Write and balance net ionic equations.

Yes, we need the crowd.

At sports events around the world, we see a few athletes on the field competing hard. They get tired, they get dirty, sometimes they get hurt as they try to win the game. Surrounding them are thousands of spectators watching and cheering. Would the game be different without the spectators? Yes, it definitely would. They provide encouragement to the team and generate enthusiasm. The spectators are not really playing the game. but they are certainly a part of the process.

Net Ionic Equations

We can write a molecular equation for the formation of silver chloride precipitate:

$\text{NaCl} + \text{AgNO}_3 \rightarrow \text{NaNO}_3 + \text{AgCl}$

The corresponding ionic equation is:

$\text{Na}^+(aq) + \text{Cl}^-(aq) + \text{Ag}^+(aq) + \text{NO}_3^-(aq) \rightarrow \text{Na}^+(aq) + \text{NO}_3^-(aq) + \text{AgCl}(s)$

If you look carefully at the ionic equation, you will notice that the sodium ion and the nitrate ion appear unchanged on both sides of the equation. When the two solutions are mixed, neither the Na^+ nor the $\text{NO}_3{}^-$ ions participate in the reaction. They can be eliminated from the reaction.

$$\cancel{\text{Na}^+(aq)} + \text{Cl}^-(aq) + \text{Ag}^+(aq) + \cancel{\text{NO}_3^-(aq)} \rightarrow \cancel{\text{Na}^+(aq)} + \cancel{\text{NO}_3^-(aq)} + \text{AgCl}(s)$$

A **spectator ion** is an ion that does not take part in the chemical reaction and is found in solution both before and after the reaction. In the above reaction, the sodium ion and the nitrate ion are both spectator ions. The equation can now be written without the spectator ions.

$$\text{Ag}^+(aq) + \text{Cl}^-(aq) \rightarrow \text{AgCl}(s)$$

The **net ionic equation** is the chemical equation that shows only those elements, compounds, and ions that are directly involved in the chemical reaction. Notice that in writing the net ionic equation, the positively-charged silver cation was written first on the reactant side, followed by the negatively-charged chloride anion. This is somewhat customary because that is the order in which the ions must be written in the silver chloride product. However, it is not absolutely necessary to order the reactants in this way.

Net ionic equations must be balanced by both mass and charge. Balancing by mass means making sure that there are equal numbers of each element. Balancing by charge means making sure that the overall charge is the same on both sides of the equation. In the above equation, the overall charge is zero, or neutral, on both sides of the equation. As a general rule, if you balance the molecular equation properly, the net ionic equation will end up being balanced by both mass and charge.

Sample Problem: Writing and Balancing Net Ionic Equations

When aqueous solutions of copper(II) chloride and potassium phosphate are mixed, a precipitate of copper(II) phosphate is formed. Write a balanced net ionic equation for this reaction.

Step 1: Plan the problem.

Write and balance the molecular equation first, making sure that all formulas are correct. Then write the ionic equation, showing all aqueous substances as ions. Carry through any coefficients. Finally, eliminate spectator ions and write the net ionic equation.

Step 2: Solve.

Molecular equation:

$$3\text{CuCl}_2(aq) + 2\text{K}_3\text{PO}_4(aq) \rightarrow 6\text{KCl}(aq) + \text{Cu}_3(\text{PO}_4)_2(s)$$

Ionic equation:

$$3\text{Cu}^{2+}(aq) + 6\text{Cl}^-(aq) + 6\text{K}^+(aq) + 2\text{PO}_4^{3-}(aq) \rightarrow 6\text{K}^+(aq) + 6\text{Cl}^-(aq) + \text{Cu}_3(\text{PO}_4)_2(s)$$

Notice that the balancing is carried through when writing the dissociated ions. For example, there are six chloride ions on the reactant side because the coefficient of 3 is multiplied by the subscript of 2 in the copper(II) chloride formula. The spectator ions are K^+ and Cl^- and can be eliminated.

Net ionic equation:

$$3\text{Cu}^{2+}(aq) + 2\text{PO}_4^{3-}(aq) \rightarrow \text{Cu}_3(\text{PO}_4)_2(s)$$

Step 3: Think about your result

For a precipitation reaction, the net ionic equation always shows the two ions that come together to form the precipitate. The equation is balanced by mass and charge.

Summary

- Net ionic equations are described and an example of writing a net ionic equation is given.

Practice

Do the practice equations at the web site below:

http://www.files.chem.vt.edu/RVGS/ACT/notes/net_ionic_rxns/net_ionic_rxns.html

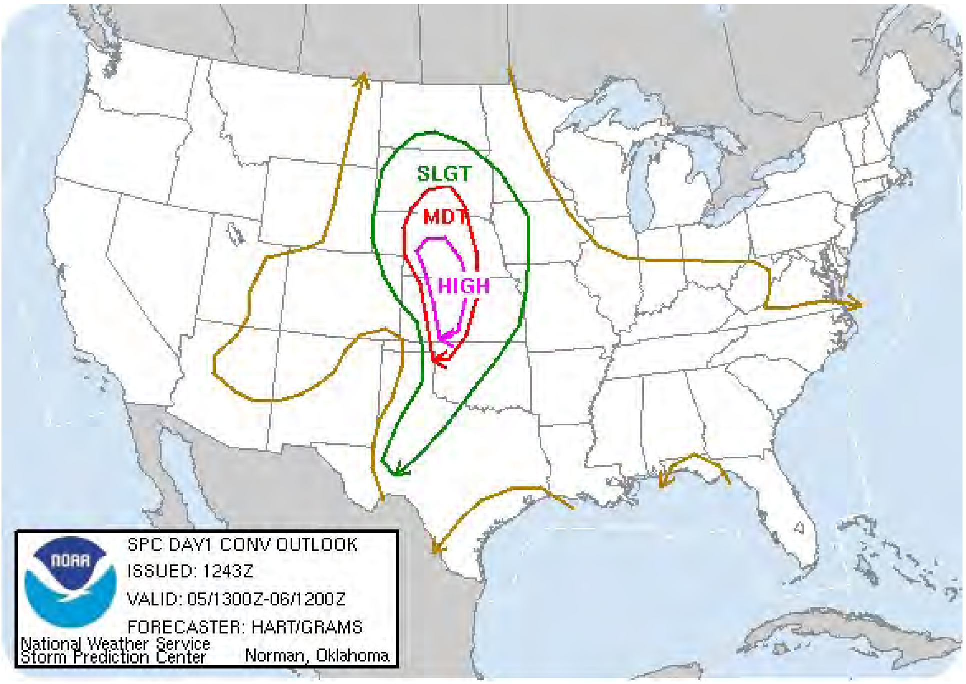
Review

1. What does the name "spectator ion" mean?
2. Is there a reaction if no precipitate or gas is formed in an ionic equation?
3. What do we need to balance in net ionic equations?

- **net ionic equation:** The chemical equation that shows only those elements, compounds, and ions that are directly involved in the chemical reaction.
- **spectator ion:** An ion that does not take part in the chemical reaction and is found in solution both before and after the reaction.

16.19 Predicting Precipitates Using Solubility Rules

- Use solubility rules to predict when a product will precipitate.



Will it rain?

Predicting the weather is tricky business. A lot of study goes into making the daily forecast. Wind patterns, historical data, barometric pressure – these and many other data are fed into computers that then use a set of rules to predict what will happen based on past history.

Predicting Precipitates Using Solubility Rules

Some combinations of aqueous reactants result in the formation of a solid precipitate as a product. However, some combinations will not produce such a product. If solutions of sodium nitrate and ammonium chloride are mixed, no reaction occurs. One could write a molecular equation showing a double-replacement reaction, but both products, sodium chloride and ammonium nitrate, are soluble and would remain in the solution as ions. Every ion is a spectator ion and there is not net ionic equation at all.

It is useful to be able to predict when a precipitate will occur in a reaction. To do so, you can use a set of guidelines called the **solubility rules** (see **Table** 16.3).

TABLE 16.3: **Solubility Rules for Ionic Compounds in Water**

Soluble	Compounds containing the alkali metal ions (Li^+, Na^+, K^+, Rb^+, Cs^+) and ammonium ion ($NH_4{}^+$)
Soluble	Compounds containing the nitrate ion ($NO_3{}^-$), acetate ion (CH_3COO^-), chlorate ion ($ClO_3{}^-$), and bicarbonate ion ($HCO_3{}^-$)

TABLE 16.3: (continued)

Mostly soluble	Compounds containing the chloride ion (Cl^-), bromide ion (Br^-), and iodide ion (I^-) – Exceptions are those of silver (Ag^+), mercury(I) ($Hg_2{}^{2+}$), and lead(II) (Pb^{2+})
Mostly soluble	Compounds containing the sulfate ion ($SO_4{}^{2-}$) – Exceptions are those of silver (Ag^+), calcium (Ca^{2+}), strontium (Sr^{2+}), barium (Ba^{2+}), mercury(I) ($Hg_2{}^{2+}$), and lead(II) (Pb^{2+})
Mostly insoluble	Compounds containing the carbonate ion ($CO_3{}^{2-}$), phosphate ion ($PO_4{}^{3-}$), chromate ion ($CrO_4{}^{2-}$), sulfide ion (S^{2-}), and silicate ion ($SiO_3{}^{2-}$) – Exceptions are those of the alkali metals and ammonium
Mostly insoluble	Compounds containing the hydroxide ion (OH^-) – Exceptions are those of the alkali metals and the barium ion (Ba^{2+})

As an example on how to use the solubility rules, predict if a precipitate will form when solutions of cesium bromide and lead(II) nitrate are mixed.

$$\mathrm{Cs}^+(aq) + \mathrm{Br}^-(aq) + \mathrm{Pb}^{2+}(aq) + 2\mathrm{NO}_3^-(aq) \rightarrow ?$$

The potential precipitates from a double-replacement reaction are cesium nitrate and lead(II) bromide. According to the solubility rules table, cesium nitrate is soluble because all compounds containing the nitrate ion, as well as all compounds containing the alkali metal ions, are soluble. Most compounds containing the bromide ion are soluble, but lead(II) is an exception. Therefore, the cesium and nitrate ions are spectator ions and the lead(II) bromide is a precipitate. The balanced net ionic reaction is:

$$\mathrm{Pb}^{2+}(aq) + 2\mathrm{Br}^-(aq) \rightarrow \mathrm{PbBr}_2(s)$$

Summary

- Solubility rules allow prediction of what products will be insoluble in water.

Practice

Work the problems at the link below:

http://chemwiki.ucdavis.edu/Inorganic_Chemistry/Reactions_in_Aqueous_Solutions/Precipitation_Reactions#Practice_Problems

Review

1. Are all alkali metal salts soluble?
2. What chloride salts are not soluble?
3. Would you expect sodium silicate to dissolve?
4. Is lead(II) sulfate soluble?

- **solubility rules:** A set of guidelines for predicting insoluble products of reactions.

16.20 References

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CHAPTER 17 Thermochemistry

Chapter Outline

17.1 Chemical Potential Energy

- Define chemical potential energy.
- Give examples of chemical potential energy.

Where did gunpowder come from?

Gun powder was originally developed by the Chinese in the ninth century AD, primarily for rockets. This material is composed of charcoal, sulfur, and saltpeter (potassium nitrate). The reaction involves the conversion of the charcoal to carbon dioxide with the potassium nitrate providing the extra oxygen needed for a rapid reaction. Sulfur was included to stabilize the product, but gunpowder is still highly explosive.

Types of Energy

Two basic types of energy exist: potential energy and kinetic energy. **Potential energy** is stored energy. It has not yet been released, but is ready to go. **Kinetic energy** is energy of motion. It causes work to be done by moving something.

Chemical Potential Energy

Energy is the capacity for doing work or supplying heat. When you fill your car with gasoline, you are providing it with potential energy. **Chemical potential energy** is the energy stored in the chemical bonds of a substance. The various chemicals that make up gasoline contain a large amount of chemical potential energy that is released when the gasoline is burned in a controlled way in the engine of the car. The release of that energy does two things. Some of the potential energy is transformed into work, which is used to move the car. At the same time, some of the potential energy is converted to heat, making the car's engine very hot. The energy changes of a system occur as either heat or work, or some combination of both.

FIGURE 17.1

A dragster is able to accelerate because of the chemical potential energy of its fuel. The burning of the fuel also produces large amounts of heat.

Dynamite is another example of chemical potential energy. The major component of dynamite is nitroglycerin, a very unstable material. By mixing it with diatomaceous earth, the stability is increased and it is less likely to explode if it receives a physical shock. When ignited, the nitroglycerin explodes rapidly, releasing large amounts of nitrogen and other gases along with a massive amount of heat.

FIGURE 17.2

Dynamite explosion.

Summary

- Chemical potential energy is energy available in the chemical bonds of a compound.

Practice

Read the material at the link below and answer the questions:

http://www.brighthubeducation.com/science-homework-help/118803-what-is-chemical-potential-energy/

1. How is chemical potential energy released?

2. Give examples of chemical potential energy.
3. What is chemical potential energy dependent upon?

Review

1. What is chemical potential energy?
2. How is gasoline used as kinetic energy?
3. How is dynamite used as kinetic energy?

- **chemical potential energy:** The energy stored in the chemical bonds of a substance.
- **kinetic energy:** Energy of motion.
- **potential energy:** Stored energy.

17.2 Heat

- Define heat.
- Define thermochemistry.

"Under the spreading chestnut tree ..."

Iron is a rigid, solid metal. At room temperature, it is extremely difficult to bend iron. However, when heated to a high enough temperature, iron can be easily worked. The heat energy in the forge is transferred to the metal, making the iron atoms vibrate more and move around more readily.

Heat

Heat is energy that is transferred from one object or substance to another because of a difference in temperature between them. Heat always flows from an object at a higher temperature to an object a lower temperature (see **Figure** 17.3). The flow of heat will continue until the two objects are at the same temperature.

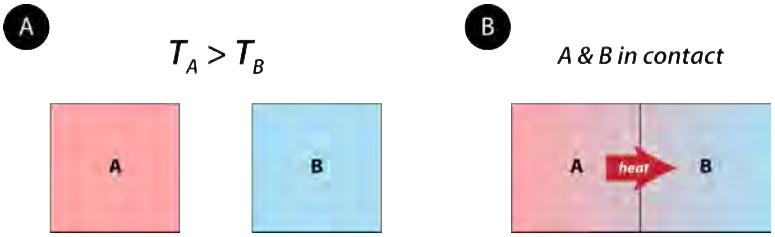


FIGURE 17.3

Object A starts with a higher temperature than object B. No heat flows when the objects are isolated from each other. When brought into contact, heat flows from A to B until the temperatures of the two objects are the same.

Thermochemistry is the study of energy changes that occur during chemical reactions and during changes of state. When chemical reactions occur, some chemical bonds are broken, while new chemical bonds form. As a result of the rearrangement of atoms, the total chemical potential energy of the system either increases or decreases.

Summary

- Heat is transferred energy from a site of higher energy to a site of lower energy.

Practice

Use the link below to answer the following questions:

http://hyperphysics.phy-astr.gsu.edu/hbase/thermo/heat.html

1. What is the correct term for the "heat" an object possesses?
2. How do we increase the internal energy of an object?
3. What is the internal energy a result of?

Review

1. What is heat?
2. In which direction does heat flow?
3. What does thermochemistry involve?

- **heat:** Energy that is transferred from one object or substance to another because of a difference in temperature between them.
- **thermochemistry:** The study of energy changes that occur during chemical reactions and during changes of state.

17.3 Exothermic and Endothermic Processes

- State the law of conservation of energy.
- Define and endothermic process.
- Define an exothermic process.
- Make conversions involving heat units.

How to keep warm?

A camp fire is an example of basic thermochemistry. The reaction is initiated by the application of heat from a match. The reaction converting wood to carbon dioxide and water (among other things) continues, releasing heat energy in the process. This heat energy can then be used to cook food, roast marshmallows, or just keep warm when it's cold outside.

Exothermic and Endothermic Processes

When physical or chemical changes occur, they are generally accompanied by a transfer of energy. The **law of conservation of energy** states that in any physical or chemical process, energy is neither created nor destroyed. In other words, the entire energy in the universe is conserved. In order to better understand the energy changes taking place during a reaction, we need to define two parts of the universe, called the system and the surroundings. The **system** is the specific portion of matter in a given space that is being studied during an experiment or an observation. The **surroundings** is everything in the universe that is not part of the system. In practical terms for a laboratory chemist, the system is the particular chemicals being reacted, while the surroundings is the immediate vicinity within the room. During most processes, energy is exchanged between the system and the surroundings. If the system loses a certain amount of energy, that same amount of energy is gained by the surroundings. If the system gains a certain amount of energy, that energy is supplied by the surroundings.

In the study of thermochemical processes, things are viewed from the point of view of the system. A chemical reaction or physical change is **endothermic** if heat is absorbed by the system from the surroundings. In the course of an endothermic process, the system gains heat from the surroundings and so the temperature of the surroundings decreases. The quantity of heat for a process is represented by the letter q. The sign of q for an endothermic process is positive because the system is gaining heat. A chemical reaction or physical change is **exothermic** if heat is released by the system into the surroundings. Because the surroundings is gaining heat from the system, the temperature of the surroundings increases. The sign of q for an exothermic process is negative because the system is losing heat.

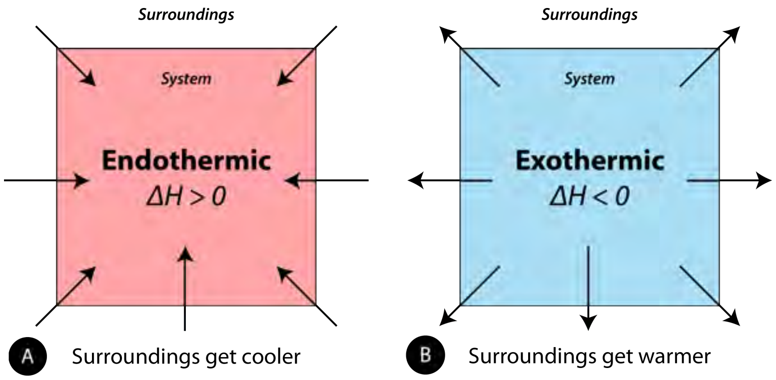


FIGURE 17.4

(A) Endothermic reaction. (B) Exothermic reaction.

Units of Heat

Heat flow is measured in one of two common units: the calorie and the joule. The joule (J) is the SI unit of energy. The calorie is familiar because it is commonly used when referring to the amount of energy contained within food. A **calorie (cal)** is the quantity of heat required to raise the temperature of 1 gram of water by 1°C. For example, raising the temperature of 100 g of water from 20°C to 22°C would require 100 × 2 = 200 cal.

Calories contained within food are actually kilocalories (kcal). In other words, if a certain snack contains 85 food calories, it actually contains 85 kcal or 85,000 cal. In order to make the distinction, the dietary calorie is written with a capital C.

$$1 \text{ kilocalorie} = 1 \text{ Calorie} = 1000 \text{ calories}$$

To say that the snack "contains" 85 Calories means that 85 kcal of energy are released when that snack is processed by your body.

Heat changes in chemical reactions are typically measured in joules rather than calories. The conversion between a joule and a calorie is shown below.

$$1 \text{ J} = 0.2390 \text{ cal or } 1 \text{ cal} = 4.184 \text{ J}$$

We can calculate the amount of heat released in kilojoules when a 400. Calorie hamburger is digested.

$$400 \cdot \text{Cal} = 400 \cdot \text{kcal} \times \frac{4.184 \text{ kJ}}{1 \text{ kcal}} = 1.67 \times 10^3 \text{ kJ}$$

Summary

- Processes of heat exchange between the system and surroundings are described.

Practice

Do the problems (as many as you have time for) at the link below:

http://www.chemteam.info/Thermochem/Thermochem-WS2.html

Review

1. What does the law of conservation of energy say?
2. What is a reaction called that gives off heat?
3. A cake is made by mixing ingredients and placing the material in an oven for baking. What type of reaction is involved?

- **calorie (cal):** The quantity of heat required to raise the temperature of 1 gram of water by 1°C.
- **endothermic:** Heat is absorbed by the system from the surroundings.
- **exothermic:** Heat is released by the system into the surroundings.
- **law of conservation of energy:** In any physical or chemical process, energy is neither created nor destroyed.
- **surroundings:** Everything in the universe that is not part of the system.
- **system:** The specific portion of matter in a given space that is being studied during an experiment or an observation.

17.4 Heat Capacity and Specific Heat

- Define heat capacity.
- Define specific heat.
- Perform calculations involving specific heat.

Which pool will warm up faster?

If a swimming pool and wading, both full of water at the same temperature were subjected to the same input of heat energy, the wading pool would certainly rise in temperature more quickly than the swimming pool. The heat capacity of an object depends both on its mass and its chemical composition. Because of its much larger mass, the swimming pool of water has a larger heat capacity than the bucket of water.

Heat Capacity and Specific Heat

Different substances respond to heat in different ways. If a metal chair sits in the bright sun on a hot day, it may become quite hot to the touch. An equal mass of water in the same sun will not become nearly as hot. We would say that water has a high **heat capacity** (the amount of heat required to raise the temperature of an object by 1°C.) Water is very resistant to changes in temperature, while metals in general are not. The **specific heat** of a substance is the amount of energy required to raise the temperature of 1 gram of the substance by 1°C. **Table** 17.1 lists the specific heats of some common substances. The symbol for specific heat is c_p, with the p subscript referring to the fact that specific heats are measured at constant pressure. The units for specific heat can either be joules per gram per degree (J/g°C) or calories per gram per degree (cal/g°C). This text will use J/g°C for specific heat.

TABLE 17.1: **Specific Heats of Some Common Substances**

Substance	**Specific Heat (J/g°C)**
Water (l)	4.18
Water (s)	2.06
Water (g)	1.87
Ammonia (g)	2.09
Ethanol (l)	2.44
Aluminum (s)	0.897
Carbon, graphite (s)	0.709
Copper (s)	0.385

TABLE 17.1: (continued)

Gold (s)	0.129
Iron (s)	0.449
Lead (s)	0.129
Mercury (l)	0.140
Silver (s)	0.233

Notice that water has a very high specific heat compared to most other substances. Water is commonly used as a coolant for machinery because it is able to absorb large quantities of heat (see **Table** 17.1). Coastal climates are much more moderate than inland climates because of the presence of the ocean. Water in lakes or oceans absorbs heat from the air on hot days and releases it back into the air on cool days.

FIGURE 17.5

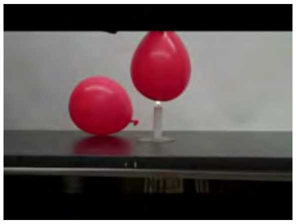
This power plant in West Virginia, like many others, is located next to a large lake so that the water from the lake can be used as a coolant. Cool water from the lake is pumped into the plant, while warmer water is pumped out of the plant and back into the lake.

Summary

- Heat capacity and specific heat are defined.

Practice

Watch the video and answer the questions below



MEDIA

Click image to the left for more content.

http://www.youtube.com/watch?v=QuWBtMy8L5A

1. What was in the first balloon?

2. What was in the send balloon?
3. Why did the first balloon not burst?
4. Why did the second balloon burst?

Review

1. What is heat capacity?
2. What is specific heat?
3. You have a 10 gram piece of aluminum and a 10 gram piece of gold sitting in the sun. Which metal will warm by ten degrees first?
4. You have a 20 gram piece of aluminum and a 40 gram piece of aluminum sitting in the sun. Which piece will arm by ten degrees first?

- **heat capacity:** The amount of heat required to raise the temperature of an object by 1°C.
- **specific heat:** The amount of energy required to raise the temperature of 1 gram of the substance by 1°C.

17.5 Specific Heat Calculations

- Perform specific heat calculations.

Does water have a high capacity for absorbing heat?

Yes. In a car radiator, it serves to keep the engine cooler than it would otherwise run. (In the picture above, the radiator is the black object on the left.) As the water circulates through the engine, it absorbs heat from the engine block. When it passes through the radiator, the cooling fan and the exposure to the outside environment allow the water to cool somewhat before it makes another passage through the engine.

Specific Heat Calculations

The specific heat of a substance can be used to calculate the temperature change that a given substance will undergo when it is either heated or cooled. The equation that relates heat (q) to specific heat (c_p), mass (m), and temperature change (ΔT) is shown below.

$$q = c_p \times m \times \Delta T$$

The heat that is either absorbed or released is measured in joules. The mass is measured in grams. The change in temperature is given by $\Delta T = T_f - T_i$, where T_f is the final temperature and T_i is the initial temperature.

Sample Problem: Calculating Specific Heat

A 15.0 g piece of cadmium metal absorbs 134 J of heat while rising from 24.0°C to 62.7°C. Calculate the specific heat of cadmium.

Step 1: List the known quantities and plan the problem.

Known

- heat = q = 134 J
- mass = m = 15.0 g
- $\Delta\text{T} = 62.7°\text{C} - 24.0°\text{C} = 38.7°\text{C}$

Unknown

- c_p of cadmium $=?\ \text{J/g°C}$

The specific heat equation can be rearranged to solve for the specific heat.

Step 2: Solve.

$$c_p = \frac{q}{m \times \Delta T} = \frac{134\ \text{J}}{15.0\ \text{g} \times 38.7°\text{C}} = 0.231\ \text{J/g°C}$$

Step 3: Think about your result.

The specific heat of cadmium, a metal, is fairly close to the specific heats of other metals. The result has three significant figures.

Since most specific heats are known, they can be used to determine the final temperature attained by a substance when it is either heated or cooled. Suppose that a 60.0 g sample of water at 23.52°C was cooled by the removal of 813 J of heat. The change in temperature can be calculated using the specific heat equation.

$$\Delta T = \frac{q}{c_p \times m} = \frac{813\ \text{J}}{4.18\ \text{J/g°C} \times 60.0\ \text{g}} = 3.24°\text{C}$$

Since the water was being cooled, the temperature decreases. The final temperature is:

$$T_f = 23.52°\text{C} - 3.24°\text{C} = 20.28°\text{C}$$

Summary

- Specific heat calculations are illustrated.

Practice

Work the problems at the link below:

http://www.sciencebugz.com/chemistry/chprbspheat.htm

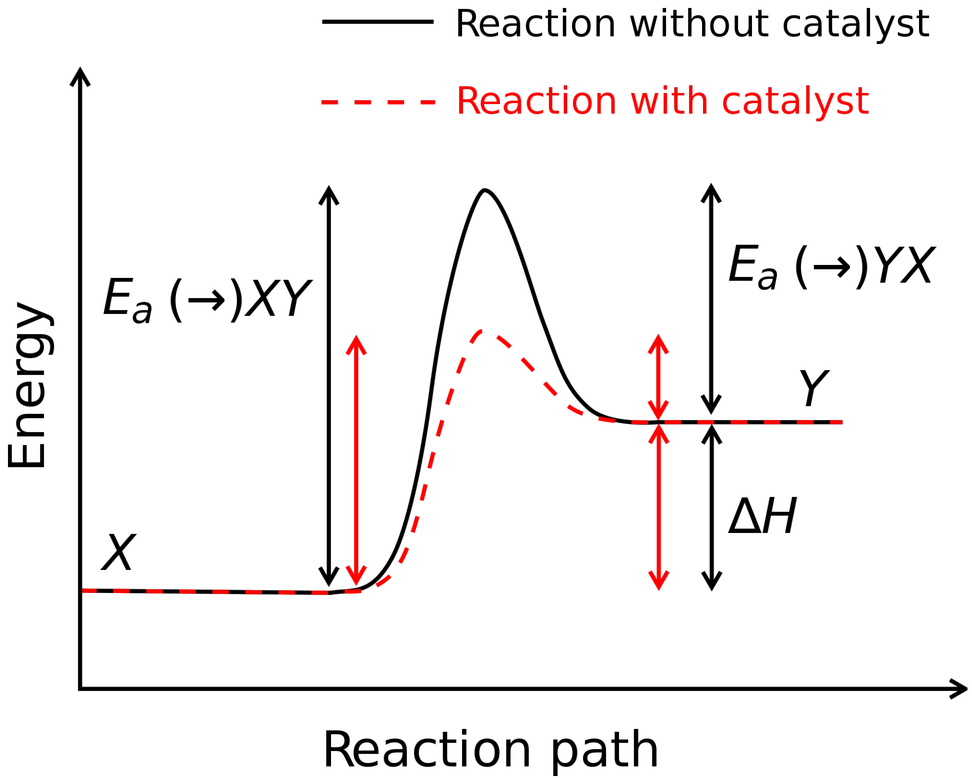
Review

1. Do different materials have different specific heats?
2. How does mass affect heat absorbed?
3. If we know the specific heat of a material, can we determine how much heat is released under a given set of circumstances?

- **specific heat:** The amount of energy required to raise the temperature of 1 gram of the substance by 1°C.

17.6 Enthalpy

- Define enthalpy.
- List factors that influence enthalpy.



Does the catalyst affect enthalpy?

The factors influencing a reaction are complicated and varied. Since a catalyst affects activation energy, we might assume it would have some sort of impact on enthalpy, but it does not. The change in enthalpy of a reaction depends solely on the chemical compositions of the reactants and products, not on the path taken to get from one to the other.

Enthalpy

Heat changes in chemical reactions are most often measured in the laboratory under conditions in which the reacting system is open to the atmosphere. In that case, the system is at a constant pressure. **Enthalpy** (H) is the heat content of a system at constant pressure. Chemists routinely measure changes in enthalpy of chemical systems as reactants are converted into products. The heat that is absorbed or released by a reaction at constant pressure is the same as the enthalpy change, and is given the symbol ΔH. Unless otherwise specified, all reactions in this material are assumed to take place at constant pressure.

The change in enthalpy of a reaction is a measure of the differences in enthalpy of the reactants and products. The enthalpy of a system is determined by the energies needed to break chemical bonds and the energies needed to form chemical bonds. Energy needs to be put into the system in order to break chemical bonds – they do not come apart spontaneously in most cases. Bond formation to produce products will involve release of energy. The change in enthalpy shows the trade-offs made in these two processes. Does it take more energy to break bonds that that needed to form bonds? If so, the reaction is endothermic and the enthalpy change is positive. If more energy is produced in bond formation than that needed for bond breaking, the reaction is exothermic and the enthalpy is negative.

Several factors influence the enthalpy of a system. Enthalpy is an extensive property, determined in part by the amount of material we work with. The state of reactants and products (solid, liquid, or gas) influences the enthalpy value for a system. The direction of the reaction affects the enthalpy value. A reaction that takes place in the opposite direction has the same numerical enthalpy value, but the opposite sign.

Summary

- Enthalpy is related to the heat of a reaction.
- Factors influencing entropy are described.

Practice

Read the material at the link below and answer the following questions:

http://www.ausetute.com.au/heatreact.html

1. What is the heat of reaction?
2. What units are used?
3. During the experimental measurement of heat of reaction, is heat lost to the surroundings or gained from the surroundings?

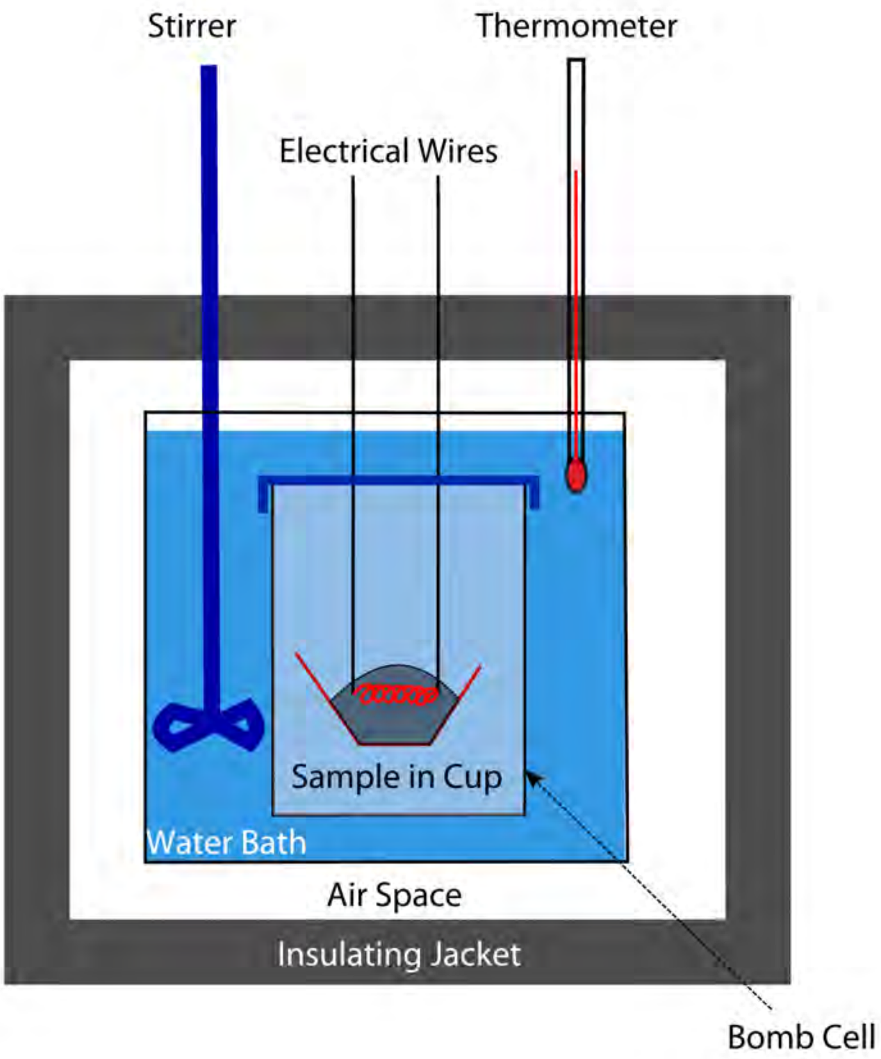
Review

1. What is enthalpy?
2. What is an extensive property?
3. Do the states of reactants and products influence enthalpy values?

- **enthalpy** (H)**:** The heat content of a system at constant pressure.

17.7 Calorimetry

- Define calorimetry.
- Perform calculations involving calorimetry relationships.



How many calories are in your food?

At one time, calories in foods were measured with a bomb calorimeter (see figure above). A weighed amount of the food would be placed in the calorimeter and the system was then sealed and filled with oxygen. An electric spark ignited the food-oxygen mixture. The amount of heat released when the food burned would give an idea of the food calories present. Today calories are calculated from the protein, carbohydrate, and fat content of the food (all determined by chemical analysis). No more bombs needed.

Calorimetry

Calorimetry is the measurement of the transfer of heat into or out of a system during a chemical reaction or physical process. A **calorimeter** is an insulated container that is used to measure heat changes. The majority of reactions that can be analyzed in a calorimetry experiment are either liquids or aqueous solutions. A frequently used and inexpensive calorimeter is a set of nested foam cups fitted with a lid to limit the heat exchange between the liquid in the cup and the air in the surroundings (see **Figure** 17.6). In a typical calorimetry experiment, specific volumes of the reactants are dispensed into separate containers and the temperature of each is measured. They are then mixed into the calorimeter, which starts the reaction. The reactant mixture is stirred until the reaction is complete, while the temperature of the reaction is continuously monitored.

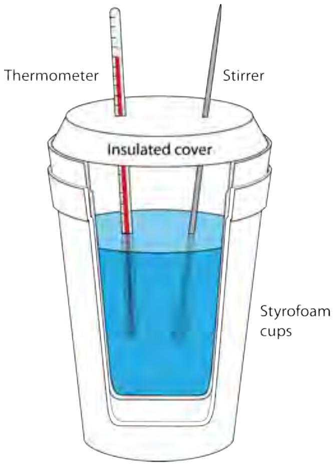


FIGURE 17.6

A simple constant-pressure calorimeter.

The key to all calorimetry experiments is the assumption that there is no heat exchange between the insulated calorimeter and the room. Consider the case of a reaction taking place between aqueous reactants. The water in which the solids have been dissolved is the surroundings, while the dissolved substances are the system. The temperature change that is measured is the temperature change that is occurring in the surroundings. If the temperature of the water increases as the reaction occurs, the reaction is exothermic. Heat was released by the system into the surrounding water. An endothermic reaction absorbs heat from the surroundings, so the temperature of the water decreases as heat leaves the surroundings to enter the system.

The temperature change of the water is measured in the experiment and the specific heat of water can be used to calculate the heat absorbed by the surroundings (q_{surr}).

$$q_{\text{surr}} = m \times c_p \times \Delta T$$

In the equation, m is the mass of the water, c_p is the specific heat of the water, and ΔT is $T_f - T_i$. The heat absorbed by the surroundings is equal, but opposite in sign, to the heat released by the system. Because the heat change is determined at constant pressure, the heat released by the system (q_{sys}) is equal to the enthalpy change (ΔH).

$$q_{\text{sys}} = \Delta H = -q_{\text{surr}} = -(m \times c_p \times \Delta T)$$

The sign of ΔH is positive for an endothermic reaction and negative for an exothermic reaction.

Sample Problem: Calorimetry and Enthalpy Changes

In an experiment, 25.0 mL of 1.00 M HCl at 25.0°C is added to 25.0 mL of 1.00 M NaOH at 25.0°C in a foam cup calorimeter. A reaction occurs and the temperature rises to 32.0°C. Calculate the enthalpy change (ΔH) in kJ for this reaction. Assume the densities of the solutions are 1.00 g/mL and that their specific heat is the same as that of water.

Step 1: List the known quantities and plan the problem.

Known

- $c_p = 4.18 \text{ J/g}^\circ\text{C}$
- $V_{\text{final}} = 25.0 \text{ mL} + 25.0 \text{ mL} = 50.0 \text{ mL}$
- $\Delta T = 32.0^\circ\text{C} - 25.0^\circ\text{C} = 7.0^\circ\text{C}$
- Density = 1.00 g/mL

Unknown

- $\Delta H = ? \text{ kJ}$

The volume and density can be used to find the mass of the solution after mixing. Then calculate the change in enthalpy by using $\Delta H = q_{\text{sys}} = -q_{\text{surr}} = -(m \times cp \times \Delta T)$.

Step 2: Solve.

$$m = 50.0 \text{ ml} \times \frac{1.00 \text{ g}}{\text{mL}} = 50.0 \text{ g}$$

$$\Delta H = -(m \times c_p \times \Delta T) = -(50.0 \text{ g} \times 4.18 \text{ J/g}^\circ\text{C} \times 7.0^\circ\text{C}) = -1463 \text{ J} = -1.5 \text{ kJ}$$

Step 3: Think about the result.

The enthalpy change is negative because the reaction releases heat to the surroundings, resulting in an increase in temperature of the water.

Summary

- The process of calorimetry is described.
- Calculations involving enthalpy changes are illustrated.

Practice

Work the problems at the link below:

http://misterguch.brinkster.net/PRA047.pdf

Review

1. What kinds of reactions are usually analyzed in a calorimeter?
2. What is a constant-pressure calorimeter?
3. Why are foam cups used in a calorimeter?

- **calorimeter:** An insulated container that is used to measure heat changes.
- **calorimetry:** The measurement of the transfer of heat into or out of a system during a chemical reaction or physical process.

17.8 Thermochemical Equation

- Define thermochemical equation.
- Define heat of reaction.

How best to heat?

Heating a home is becoming more and more expensive. Do we use gas, oil, electricity, wood? Part of the decision is based on which fuel will provide the highest amount of energy release when burned. Studies of thermochemistry can be very useful in getting reliable information for making these important choices.

Thermochemical Equation

When methane gas is combusted, heat is released, making the reaction exothermic. Specifically, the combustion of 1 mol of methane releases 890.4 kilojoules of heat energy. This information can be shown as part of the balanced equation.

$$CH_4(g)+2O_2(g)\rightarrow CO_2(g)+2H_2O(l)+890.4\text{ kJ}$$

The equation tells us that 1 mol of methane combines with 2 mol of oxygen to produce 1 mol of carbon dioxide and 2 mol of water. In the process, 890.4 kJ is released and so it is written as a product of the reaction. A **thermochemical equation** is a chemical equation that includes the enthalpy change of the reaction. The process in the above thermochemical equation can be shown visually in the **Figure** 17.7.

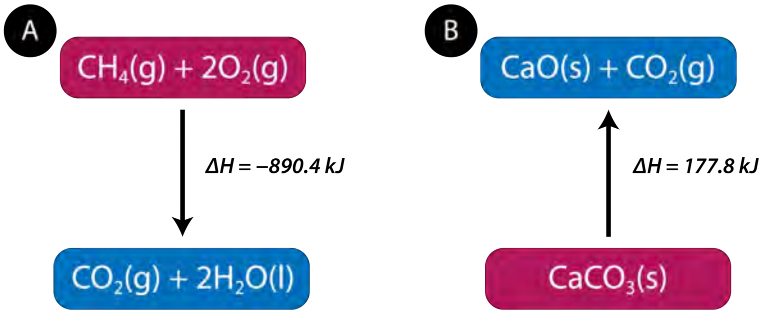


FIGURE 17.7

(A) As reactants are converted to products in an exothermic reaction, enthalpy is released into the surroundings. The enthalpy change of the reaction is negative. (B) As reactants are converted to products in an endothermic reaction, enthalpy is absorbed from the surroundings. The enthalpy change of the reaction is positive.

In the combustion of methane example, the enthalpy change is negative because heat is being released by the system. Therefore, the overall enthalpy of the system decreases. The **heat of reaction** is the enthalpy change for a chemical reaction. In the case above, the heat of reaction is −890.4 kJ. The thermochemical reaction can also be written in this way:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \quad \Delta H = -890.4 \text{ kJ}$$

Heats of reaction are typically measured in kilojoules. It is important to include the physical states of the reactants and products in a thermochemical equation as the value of the ΔH depends on those states.

Endothermic reactions absorb energy from the surroundings as the reaction occurs. When 1 mol of calcium carbonate decomposes into 1 mol of calcium oxide and 1 mol of carbon dioxide, 177.8 kJ of heat is absorbed. The process is shown visually in **Figure** 17.7 (B). The thermochemical reaction is shown below.

$$CaCO_3(s) + 177.8 \text{ kJ} \rightarrow CaO(s) + CO_2(g)$$

Because the heat is absorbed by the system, the 177.8 kJ is written as a reactant. The heat of reaction is positive for an endothermic reaction.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g) \quad \Delta H = 177.8 \text{ kJ}$$

The way in which a reaction is written influences the value of the enthalpy change for the reaction. Many reactions are reversible, meaning that the product(s) of the reaction are capable of combining and reforming the reactant(s). If a reaction is written in the reverse direction, the sign of the ΔH changes. For example, we can write an equation for the reaction of calcium oxide with carbon dioxide to form calcium carbonate.

$$CaO(s) + CO_2(g) \rightarrow CaCO_3(s) + 177.8 \text{ kJ}$$

The reaction is exothermic and thus the sign of the enthalpy change is negative.

$$\text{CaO}(s)+\text{CO}_2(g)\rightarrow\text{CaCO}_3(s)\quad\Delta H=-177.8\text{ kJ}$$

Summary

- The components of a thermochemical equation are described.

Practice

Read the material at the link below and work the problems on the screens

http://www.wisc-online.com/Objects/ViewObject.aspx?ID=GCH8805

Review

1. What does a thermochemical equation include?
2. Why would this information be important?
3. What happens to the sign of the enthalpy change when the reaction is reversed?

- **heat of reaction:** The enthalpy change for a chemical reaction.
- **thermochemical equation:** A chemical equation that includes the enthalpy change of the reaction.

17.9 Stoichiometric Calculations and Enthalpy Changes

- Perform calculations of enthalpy equations.

What will it cost?

There is a growing concern about the damage to the environment from emissions from manufacturing plants. Many companies are taking steps to reduce these harmful emissions by adding equipment that will trap the pollutants. In order to know what equipment (and how many) to order, studies need to be done to measure the amount of product currently produced. The since pollution is often both particulate and thermal, energy changes need to be determined in addition to the amounts of products released.

Stoichiometric Calculations and Enthalpy Changes

Chemistry problems that involve enthalpy changes can be solved by techniques similar to stoichiometry problems. Refer again to the combustion reaction of methane. Since the reaction of 1 mol of methane released 890.4 kJ, the reaction of 2 mol of methane would release $2 \times 890.4 \text{ kJ} = 1781 \text{ kJ}$. The reaction of 0.5 mol of methane would release $\frac{890.4 \text{ kJ}}{2} = 445.2 \text{ kJ}$. As with other stoichiometry problems, the moles of a reactant or product can be linked to mass or volume.

Sample Problem: Calculating Enthalpy Changes

Sulfur dioxide gas reacts with oxygen to form sulfur trioxide in an exothermic reaction according to the following thermochemical equation.

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g) + 198 \text{ kJ}$$

Calculate the enthalpy change that occurs when 58.0 g of sulfur dioxide is reacted with excess oxygen.

Step 1: List the known quantities and plan the problem.

Known

- mass SO_2 = 58.0 g
- molar mass SO_2 = 64.07 g/mol
- $\Delta H = -198$ kJ for the reaction of 2 mol SO_2

Unknown

- $\Delta H = ?$ kJ

The calculation requires two steps. The mass of SO_2 is converted to moles. Then the mol SO_2 is multiplied by the conversion factor of $\left(\frac{-198 \text{ kJ}}{2 \text{ mol SO}_2}\right)$.

Step 2: Solve.

$$\Delta H = 58.0 \text{ g SO}_2 \times \frac{1 \text{ mol SO}_2}{64.07 \text{ g SO}_2} \times \frac{-198 \text{ kJ}}{2 \text{ mol SO}_2} = -89.6 \text{ kJ}$$

Step 3: Think about your result.

The mass of sulfur dioxide is slightly less than 1 mol. Since 198 kJ is released for every 2 mol of SO_2 that reacts, the heat released when about 1 mol reacts is one half of 198. The 89.6 kJ is slightly less than half of 198. The sign of ΔH is negative because the reaction is exothermic.

Summary

- Calculations of energy changes in enthalpy equations are described.

Practice

Work the problems at the site below. No peaking at the answers.

http://msmcraesscience.weebly.com/uploads/5/1/4/4/5144948/enthalpy_stoichiometry_worksheet_1.pdf

Review

1. What do you need to determine to solve enthalpy stoichiometry problems?
2. If I react 1.75 moles of methane, how much energy will be involved?
3. I ran a reaction producing sulfur dioxide and releasing 267.3 kJ of energy. How many moles of sulfur dioxide were involved in the reaction?

17.10 Heats of Fusion and Solidification

- Define heat of fusion.
- Define heat of solidification.
- Perform calculations of energy changes during the transition from solid to liquid or liquid to solid.

What makes the ice melt?

Suppose you hold an ice cube in your hand. It feels cold because heat energy leaves your hand and enters the ice cube. What happens to the ice cube? It melts. However, the temperature during a phase change remains constant. So the heat that is being lost by your hand does not raise the temperature of the ice above its melting temperature of 0°C. Rather, all the heat goes into the change of state. Energy is absorbed during the process of changing ice into water. The water that is produced also remains at 0°C until all of the ice is melted.

Heats of Fusion and Solidification

All solids absorb heat as they melt to become liquids. The gain of heat in this endothermic process goes into changing the state rather than changing the temperature. The **molar heat of fusion** (ΔH_{fus}) of a substance is the heat absorbed by one mole of that substance as it is converted from a solid to a liquid. Since the melting of any substance absorbs heat, it follows that the freezing of any substance releases heat. The **molar heat of solidification** $(\Delta H_{\text{solid}})$ of a substance is the heat released by one mole of that substance as it is converted from a liquid to a solid. Since fusion and solidification of a given substance are the exact opposite processes, the numerical value of the molar heat of fusion is the same as the numerical value of the molar heat of solidification, but opposite in sign. In other words, $\Delta H_{\text{fus}} = -\Delta H_{\text{solid}}$. The **Figure** 17.8 shows all of the possible changes of state along with the direction of heat flow during each process.

Every substance has a unique value for its molar heat of fusion, depending on the amount of energy required to disrupt the intermolecular forces present in the solid. When 1 mol of ice at 0°C is converted to 1 mol of liquid water

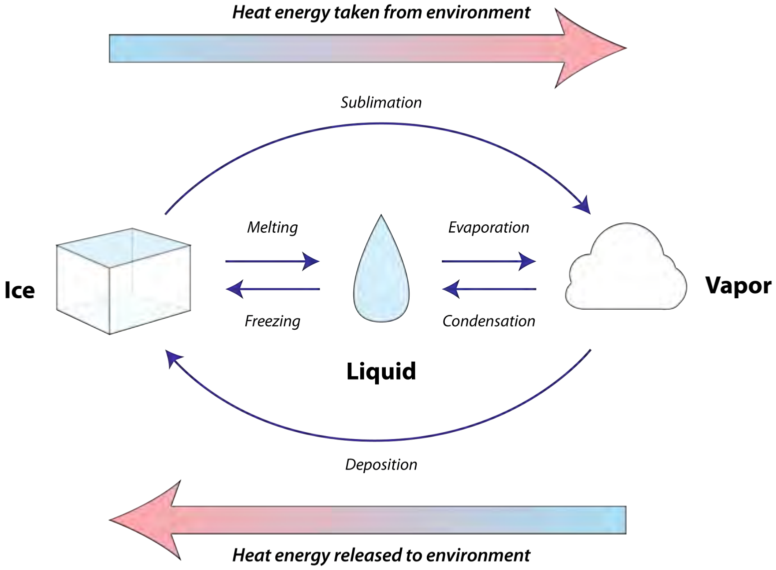


FIGURE 17.8

From left to right, heat is absorbed from the surroundings during melting, evaporation, and sublimation. Form right to left, heat is released to the surroundings during freezing, condensation, and deposition.

at 0°C, 6.01 kJ of heat are absorbed from the surroundings. When 1 mol of water at 0°C freezes to ice at 0°C, 6.01 kJ of heat are released into the surroundings.

$$\begin{array}{ll} H_2O(s) \rightarrow H_2O(l) & \Delta H_{\text{fus}} = 6.01 \text{ kJ/mol} \\ H_2O(l) \rightarrow H_2O(s) & \Delta H_{\text{fus}} = -6.01 \text{ kJ/mol} \end{array}$$

The molar heats of fusion and solidification of a given substance can be used to calculate the heat absorbed or released when various amounts are melted or frozen.

Enjoy the video about the heat of fusion at the link below:

MEDIA

Click image to the left for more content.

http://www.youtube.com/watch?v=jaaGqui9NVY

Sample Problem Heat of Fusion

Calculate the heat absorbed when 31.6 g of ice at 0°C is completely melted.

Step 1: List the known quantities and plan the problem.

Known

- mass = 31.6 g ice
- molar mass $H_2O(s)$ = 18.02 g/mol

- molar heat of fusion = 6.01 kJ/mol

Unknown

- $\Delta H = ?$ J

The mass of ice is first converted to moles. This is then multiplied by the conversion factor of $\left(\frac{6.01 \text{ kJ}}{1 \text{ mol}}\right)$ in order to find the kJ of heat absorbed.

Step 2: Solve.

$$31.6 \text{ g ice} \times \frac{1 \text{ mol ice}}{18.02 \text{ g ice}} \times \frac{6.01 \text{ kJ}}{1 \text{ mol ice}} = 10.5 \text{ kJ}$$

Step 3: Think about your result.

The given quantity is a bit less than 2 moles of ice, and so just less than 12 kJ of heat is absorbed by the melting process.

Summary

- Molar heats of fusion and solidification are defined.
- Calculations of heat changes during fusion and solidification are described.

Practice

Work problems 4-5 at the link below:

http://ths.sps.lane.edu/chemweb/unit4/problems/heatcalc/index.htm

Review

1. In the transition from liquid to solid, is energy absorbed or released?
2. In the transition from solid to liquid, is energy absorbed or released?
3. How much energy is released when one mole of water at 0°C changes from liquid to solid?

- **molar heat of fusion** (ΔH_{fus})**:** The heat absorbed by one mole of that substance as it is converted from a solid to a liquid.
- **molar heat of solidification** $(\Delta H_{\text{solid}})$**:** The heat released by one mole of that substance as it is converted from a liquid to a solid.

17.11 Heats of Vaporization and Condensation

- Define heat of vaporization.
- Define heat of condensation.
- Perform calculations involving heats of vaporization and condensation.

How much energy is available?

Natural resources for power generation have traditionally been waterfalls or use of oil, coal, or nuclear power to generate electricity. Research is being carried out to look for other renewable sources to run the generators. Geothermal sites (such as the geyser pictured above) are being considered because of the steam they produce. Capabilities can be estimated by knowing how much steam is released in a given time at a particular site.

Heat of Vaporization and Condensation

Energy is absorbed in the process of converting a liquid at its boiling point into a gas. As with the melting of a solid, the temperature of a boiling liquid remains constant and the input of energy goes into changing the state. The **molar heat of vaporization** (ΔH_{vap}) of a substance is the heat absorbed by one mole of that substance as it is converted from a liquid to a gas. As a gas condenses to a liquid, heat is released. The **molar heat of condensation** (ΔH_{cond}) of a substance is the heat released by one mole of that substance as it is converted from a gas to a liquid. Since vaporization and condensation of a given substance are the exact opposite processes, the numerical value of the molar heat of vaporization is the same as the numerical value of the molar heat of condensation, but opposite in sign. In other words, $\Delta H_{\text{vap}} = -\Delta H_{\text{cond}}$.

When 1 mol of water at 100°C and 1 atm pressure is converted to 1 mol of water vapor at 100°C, 40.7 kJ of heat are absorbed from the surroundings. When 1 mol of water vapor at 100°C condenses to liquid water at 100°C, 40.7 kJ of heat are released into the surroundings.

$$\begin{aligned} H_2O(l) &\rightarrow H_2O(g) \qquad \Delta H_{\text{fus}} = 40.7 \text{ kJ/mol} \\ H_2O(g) &\rightarrow H_2O(l) \qquad \Delta H_{\text{solid}} = -40.7 \text{ kJ/mol} \end{aligned}$$

Other substances have different values for their molar heats of fusion and vaporization and these are summarized in the **Table** 17.2.

TABLE 17.2: Molar Heats of Fusion and Vaporization

Substance	**ΔH_{fus} (kJ/mol)**	**ΔH_{vap} (kJ/mol)**
Ammonia (NH_3)	5.65	23.4
Ethanol (C_2H_5OH)	4.60	43.5
Methanol (CH_3OH)	3.16	35.3
Oxygen (O_2)	0.44	6.82
Water (H_2O)	6.01	40.7

Notice that for all substances, the heat of vaporization is substantially higher than the heat of fusion. Much more energy is required to change the state from a liquid to a gas than from a solid to a liquid. This is because of the large separation of the particles in the gas state. The values of the heats of fusion and vaporization are related to the strength of the intermolecular forces. All of the substances in the table above, with the exception of oxygen, are capable of hydrogen bonding. Consequently, the heats of fusion and vaporization of oxygen are far lower than the others.

Sample Problem: Heat of Vaporization

What mass of methanol vapor condenses to a liquid as 20.0 kJ of heat are released?

Step 1: List the known quantities and plan the problem.

Known

- $\Delta H = 20.0$ kJ
- $\Delta H_{\text{cond}} = -35.3$ kJ/mol
- molar mass $CH_3OH = 32.05$ kJ/mol

Unknown

- mass methanol = ? g

First the kJ of heat released in the condensation is multiplied by the conversion factor of $\left(\frac{1 \text{ mol}}{-35.3 \text{ kJ}}\right)$ to find the moles of methanol that condensed. Then, moles are converted to grams.

Step 2: Solve.

$$-20.0 \text{ kJ} \times \frac{1 \text{ mol } CH_3OH}{-35.3 \text{ kJ}} \times \frac{32.05 \text{ g } CH_3OH}{1 \text{ mol } CH_3OH} = 18.2 \text{ g } CH_3OH$$

Step 3: Think about your result.

Condensation is an exothermic process, so the enthalpy change is negative. Slightly more than one-half mole of methanol is condensed.

Summary

- Molar heats of condensation and vaporization are defined.
- Examples of calculations involving these parameters are illustrated.

Practice

Calculate problems 6-7 at the link below:

http://ths.sps.lane.edu/chemweb/unit4/problems/heatcalc/index.htm

Review

1. What is common to all the substance in the table except oxygen?
2. How much heat is needed to convert 2.7 moles of ethanol at its boiling point from liquid to vapor?
3. How many moles of water will condense from vapor to liquid if 45 Kj are removed?

- **molar heat of condensation** (ΔH_{cond})**:** The heat released by one mole of a substance as it is converted from a gas to a liquid.
- **molar heat of vaporization** (ΔH_{vap})**:** The heat absorbed by one mole of a substance as it is converted from a liquid to a gas.

17.12 Multi-Step Problems with Changes of State

- Perform energy calculations involving multiple changes of state.

Which takes more heat – melting or boiling?

You have a cube of ice. Which process will take more energy – the melting of that ice cube or the conversion of the water to steam? The short answer is that more energy is needed to convert the water to steam. The long answer is really a question: how do you get from one point to the other? What is the temperature of the ice? What is the mass of that ice cube? A lot goes into taking the material from the starting point to the end-point.

Multi-Step Problems with Changes of State

Heating curves show the phase changes that a substance undergoes as heat is continuously absorbed.

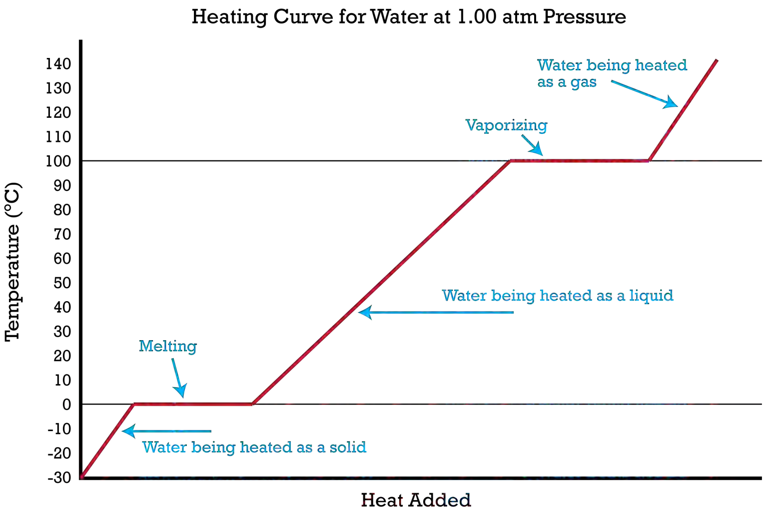


FIGURE 17.9

Heating curve of water.

The specific heat of a substance allows us to calculate the heat absorbed or released as the temperature of the substance changes. It is possible to combine that type of problem with a change of state to solve a problem involving multiple steps. The figure above shows ice at -30°C being converted in a five-step process to gaseous water (steam) at 140°C. It is now possible to calculate the heat absorbed during that entire process. The process and the required calculation is summarized below.

1. Ice is heated from -30°C to 0°C. The heat absorbed is calculated by using the specific heat of ice and the equation $\Delta H = c_p \times m \times \Delta T$.
2. Ice is melted at 0°C. The heat absorbed is calculated by multiplying the moles of ice by the molar heat of fusion.
3. Water at 0°C is heated to 100°C. The heat absorbed is calculated by using the specific heat of water and the equation $\Delta H = c_p \times m \times \Delta T$.
4. Water is vaporized to steam at 100°C. The heat absorbed is calculated by multiplying the moles of water by the molar heat of vaporization.
5. Steam is heated from 100°C to 140°C. The heat absorbed is calculated by using the specific heat of steam and the equation $\Delta H = c_p \times m \times \Delta T$.

Sample Problem: Multi-Step Problems using a Heating Curve

Calculate the total amount of heat absorbed (in kJ) when 2.00 mol of ice at -30.0°C is converted to steam at 140.0°C. The required specific heats can be found in the table in *Heat Capacity and Specific Heat*.

Step 1: List the known quantities and plan the problem.

Known

- 2.00 mol ice = 36.04 g ice
- $c_p(\text{ice}) = 2.06 \text{ J/g}^\circ\text{C}$
- $c_p(\text{water}) = 4.18 \text{ J/g}^\circ\text{C}$
- $c_p(\text{steam}) = 1.87 \text{ J/g}^\circ\text{C}$
- $\Delta H_{\text{fus}} = 6.01 \text{ kJ/mol}$
- $\Delta H_{\text{vap}} = 40.7 \text{ kJ/mol}$

Unknown

- $\Delta H_{\text{total}} = ? \text{ kJ}$

Follow the steps previously described. Note that the mass of the water is needed for the calculations that involve the specific heat, while the moles of water is needed for the calculations that involve changes of state. All heat quantities must be in kilojoules so that they can be added together to get a total for the five-step process.

Step 2: Solve.

1. $\Delta H_1 = 2.06 \text{ J/g}^\circ\text{C} \times 36.04 \text{ g} \times 30^\circ\text{C} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 2.23 \text{ kJ}$
2. $\Delta H_2 = 2.00 \text{ mol} \times \frac{6.01 \text{ kJ}}{1 \text{ mol}} = 12.0 \text{ kJ}$
3. $\Delta H_3 = 4.18 \text{ J/g}^\circ\text{C} \times 36.04 \text{ g} \times 100^\circ\text{C} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 15.1 \text{ kJ}$
4. $\Delta H_4 = 2.00 \text{ mol} \times \frac{40.7 \text{ kJ}}{1 \text{ mol}} = 81.4 \text{ kJ}$
5. $\Delta H_5 = 1.87 \text{ J/g}^\circ\text{C} \times 36.04 \text{ g} \times 40^\circ\text{C} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 2.70 \text{ kJ}$

$$\Delta H_{\text{total}} = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 = 113.4 \text{ kJ}$$

Step 3: Think about your result.

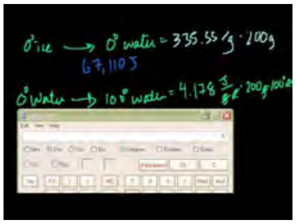
The total heat absorbed as the ice at -30°C is heated to steam at 140°C is 113.4 kJ. The largest absorption of heat comes during the vaporization of the liquid water.

Summary

- Multi-step calculations for changes of state are described.

Practice

Watch the video below and answer the following questions:



MEDIA

Click image to the left for more content.

http://www.youtube.com/watch?v=zz4KbvF_X-0

1. What is the specific heat of ice?
2. Why do you need the mass of ice?
3. What happens if you leave out the energy for a phase change?

Review

1. Why are two different sets of units used?
2. What other units problem do you need to be aware of?
3. What would you need to know to do calculations like this for acetone?

17.13 Heat of Solution

- Define heat of solution.
- Perform heat of solution calculations.

How do you make solutions safely?

When preparing dilutions of concentrated sulfuric acid, the directions usually call for adding the acid slowly to water with a lot of stirring. When this acid is mixed with water, a great deal of heat is released in the dissolving process. If water were added to acid, the water would quickly heat and splatter, causing harm to the person making the solution.

Heat of Solution

Enthalpy changes also occur when a solute undergoes the physical process of dissolving into a solvent. Hot packs and cold packs (see **Figure** 17.10) use this property. Many hot packs use calcium chloride, which releases heat when it dissolves according to the equation below.

$$\mathrm{CaCl_2}(s) \rightarrow \mathrm{Ca^{2+}}(aq) + 2\mathrm{Cl^-}(aq) + 82.8 \text{ kJ}$$

The **molar heat of solution** (ΔH_{soln}) of a substance is the heat absorbed or released when one mole of the substance is dissolved in water. For calcium chloride, $\Delta H_{\text{soln}} = -82.8$ kJ/mol.

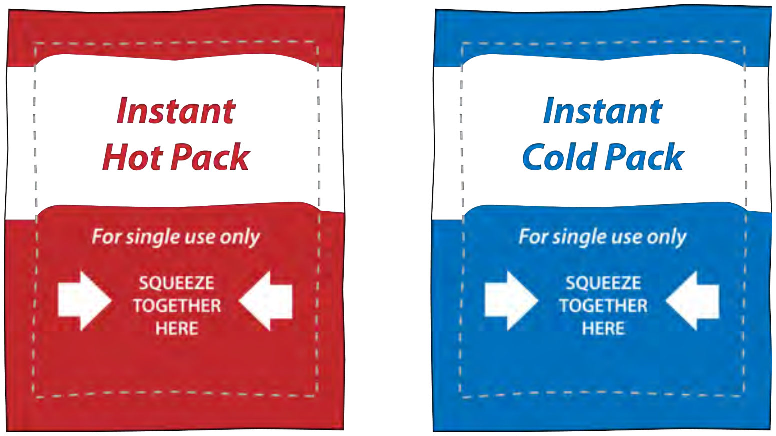


FIGURE 17.10

Chemical hot packs and cold packs work because of the heats of solution of the chemicals inside them. When the bag is squeezed, an inner pouch bursts, allowing the chemical to dissolve in water. Heat is released in the hot pack and absorbed in the cold pack.

Many cold packs use ammonium nitrate, which absorbs heat from the surroundings when it dissolves.

$$\text{NH}_4\text{NO}_3(s) + 25.7 \text{ kJ} \rightarrow \text{NH}_4^+(aq) + \text{NO}_3^-(aq)$$

Cold packs are typically used to treat muscle strains and sore joints. The cold pack is activated and applied to the affected area. As the ammonium nitrate dissolves, it absorbs heat from the body and helps to limit swelling. For ammonium nitrate, $\Delta H_{\text{soln}} = 25.7$ kJ/mol.

Sample Problem: Heat of Solution

The molar heat of solution, ΔH_{soln}, of NaOH is -445.1 kJ/mol. In a certain experiment, 5.00 g of NaOH is completely dissolved in 1.000 L of 20.0°C water in a foam cup calorimeter. Assuming no heat loss, calculate the final temperature of the water.

Step 1: List the known quantities and plan the problem.

Known

- mass NaOH = 5.00 g
- molar mass NaOH = 40.00 g/mol
- $\Delta H_{\text{soln}}(\text{NaOH}) = -445.1$ kJ/mol
- mass H_2O = 1.000 kg = 1000. g (assumes density = 1.00 g/mL)
- $T_{\text{initial}}(\text{H}_2\text{O}) = 20.0°\text{C}$
- $c_p(\text{H}_2\text{O}) = 4.18$ J/g°C

Unknown

- T_{final} of $\text{H}_2\text{O} = ?$ °C

This is a multiple-step problem: 1) the grams NaOH is converted to moles; 2) the moles is multiplied by the molar heat of solution; 3) the joules of heat released in the dissolving process is used with the specific heat equation and the total mass of the solution to calculate the ΔT; 4) the T_{final} is determined from ΔT.

Step 2: Solve.

$$5.00 \text{ g NaOH} \times \frac{1 \text{ mol NaOH}}{40.00 \text{ g NaOH}} \times \frac{-445.1 \text{ kJ}}{1 \text{ mol NaOH}} \times \frac{1000 \text{ J}}{1 \text{ kJ}} = -5.56 \times 10^4 \text{ J}$$

$$\Delta T = \frac{\Delta H}{c_p \times m} = \frac{-5.56 \times 10^4 \text{ J}}{4.18 \text{ J/g}^\circ\text{C} \times 1005 \text{ g}} = 13.2^\circ\text{C}$$

$$T_{\text{final}} = 20.0^\circ\text{C} + 13.2^\circ\text{C} = 33.2^\circ\text{C}$$

Step 3: Think about your result.

The dissolving process releases a large amount of heat, which causes the temperature of the solution to rise. Care must be taken when preparing concentrated solutions of sodium hydroxide because of the large amounts of heat released.

Summary

- Molar heat of solution is defined.
- Sample calculations using molar heat of solution are given.

Practice

Work the problems at the link below:

http://www.sciencegeek.net/Shockwave/HeatofSolution.htm

Review

1. Does NaOH in solution warm or cool the water?
2. How can you tell whether a material will produce an increase or decrease in heat when dissolved?
3. The sample problem was done at 20°C. Would the temperature increase be the same if the sample was run at 72°C?

- **molar heat of solution** (ΔH_{soln})**:** The heat absorbed or released when one mole of a substance is dissolved in water.

17.14 Heat of Combustion

- Define heat of combustion.
- Perform calculations involving heat of combustion.

What is gasohol?

In efforts to reduce gas consumption from oil, ethanol is often added to regular gasoline. It has a high octane rating and burns more slowly than regular gas. This "gasohol" is widely used in many countries. It produces somewhat lower carbon monoxide and carbon dioxide emissions, but does increase air pollution from other materials.

Molar Heat of Combustion

Many chemical reactions are combustion reactions. It is often important to know the energy produced in such a reaction so we can determine which fuel might be the most efficient for a given purpose. The **molar heat of combustion (He)** is the heat released when one mole of a substance is completely burned.

Typical combustion reactions involve the reaction of a carbon-containing material with oxygen to form carbon dioxide and water as products. If methanol is burned in air, we have:

$CH_3OH + O_2 \rightarrow CO_2 + 2H_2O \quad He = 890 \text{ kJ/mol}$

In this case, one mole of oxygen reacts with one mole of methanol to form one mole of carbon dioxide and two moles of water.

It should be noted that inorganic substances can also undergo a form of combustion reaction:

$2Mg + O_2 \rightarrow 2\ Mg$

In this case there is no water and no carbon dioxide formed. These reactions are generally not what we would be talking about when we discuss combustion reactions.

Sample Problem: Calculation of Heat of Combustion

Heats of combustion are usually determined by burning a known amount of the material in a bomb calorimeter with an excess of oxygen. By measuring the temperature change, the heat of combustion can be determined.

A 1.75 gram sample of ethanol is burned and produced a temperature increase of 55°C in 200 grams of water. Calculate the molar heat of combustion.

Step 1: List the known quantities and plan the problem.

Known

- mass of ethanol = 1.55 grams
- molar mass of ethanol = 46.1 g/mol
- mass of water = 200 grams
- c_p *water* : 4.18 *J/g°C*
- temperature increase = 55°C

Unknown

- He of ethanol

Step 2: Solve.

amount of ethanol used: $\frac{1.55 \text{ g}}{46.1 \text{ g/mol}} = 0.0336 \text{ moles}$

energy generated: $4.184 \text{ J/g}^\circ\text{C} \times 200 \text{ g} \times 55^\circ\text{C} = 46024 \text{ J} = 46.024 \text{ kJ}$

molar heat of combustion: $\frac{46.024 \text{ kJ}}{0.0336 \text{ moles}} = 1369 \text{ kJ/mol}$

Step 3: Think about your result:

The burning of ethanol produces a significant amount of heat.

Summary

- The molar heat of combustion is defined.
- Calculations using the molar heat of combustion are described.

Practice

Watch the video at the link below (heat of combustion of almond) and answer the following questions:

http://www.dlt.ncssm.edu/core/c11-2.htm

1. Why was the pellet pressed?
2. How did the scientist guarantee that excess oxygen was present?
3. Why as there a several minute wait before igniting the bomb?

Review

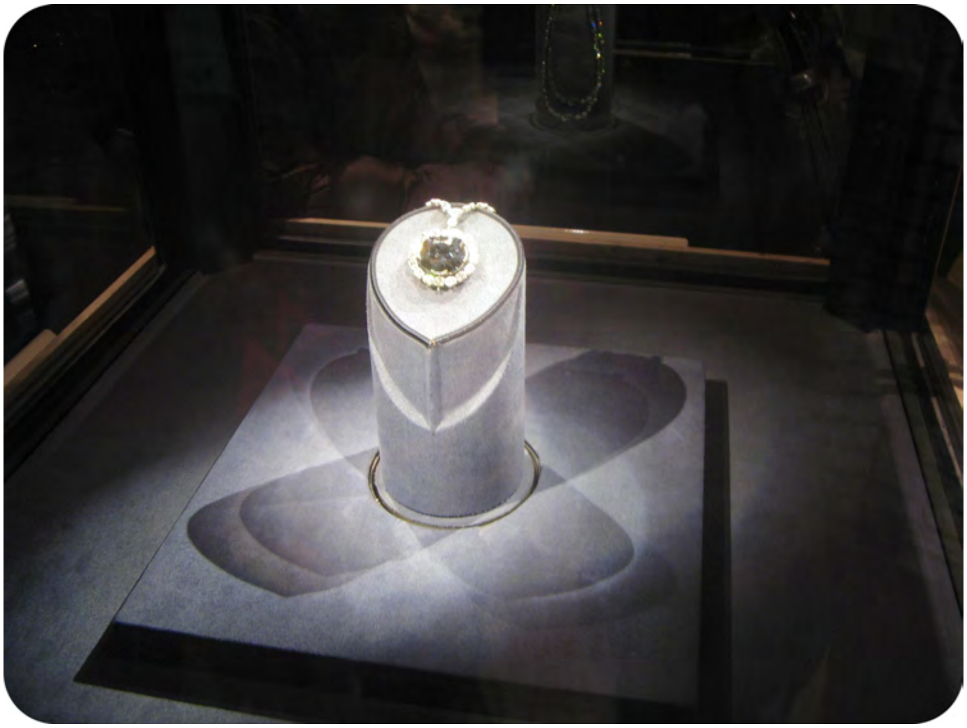
1. Write the reaction for the combustion of ethanol in oxygen?
2. What would be the limiting reagent in the reaction?

3. If you made an error in weighing the ethanol and added less than you planned on, would the heat of combustion result be higher or lower?

- **molar heat of combustion:** The heat released when one mole of a substance is completely burned.

17.15 Standard Heat of Formation

- Define standard heat of formation.
- List some factors affecting the standard heat of formation.



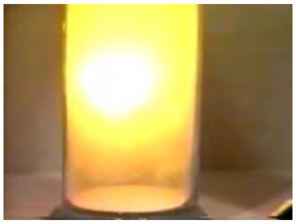
Is the Hope diamond just a very expensive pencil?

The Hope diamond is a very expensive piece of jewelry, currently worth about $350 million. A pencil can be purchased for less than a dollar. Both items contain carbon, but there is a big difference in how that carbon is organized. The diamond was formed under very different reaction conditions than the graphite, so it has a different heat of formation.

Standard Heat of Formation

A relatively straightforward chemical reaction is one in which elements are combined to form a compound. Sodium and chlorine react to form sodium chloride (see video below). Hydrogen and oxygen combine to form water. Like other reactions, these are accompanied by either the absorption or release of heat. The **standard heat of formation** $(\Delta H_f{}^\circ)$ is the enthalpy change associated with the formation of one mole of a compound from its elements in their standard states. The standard conditions for thermochemistry are 25°C and 101.3 kPa. Therefore, the standard state of an element is its state at 25°C and 101.3 kPa. For example, iron is a solid, bromine is a liquid, and oxygen is a gas under those conditions. The standard heat of formation of an element in its standard state is by definition equal to zero. The $\Delta H_f{}^\circ = 0$ for the diatomic elements, $H_2(g)$, $N_2(g)$, $O_2(g)$, $F_2(g)$, $Cl_2(g)$, $Br_2(l)$, and $I_2(g)$. The graphite form of solid carbon is its standard state with $\Delta H_f{}^\circ = 0$, while diamond is not its standard state. Some standard heats of formation are listed in the **Table** 17.3.

Watch a video of the reaction between sodium metal and chlorine gas



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http://www.youtube.com/watch?v=Ftw7a5ccubs.

TABLE 17.3: Standard Heats of Formation of Selected Substances

Substance	$\Delta H_f{}^\circ$(kJ/mol)	Substance	$\Delta H_f{}^\circ$ (kJ/mol)
Al_2O_3(s)	-1669.8	H_2O_2(l)	-187.6
$BaCl_2$(s)	-860.1	KCl(s)	-435.87
Br_2(g)	30.91	NH_3(g)	-46.3
C (s, graphite)	0	NO(g)	90.4
C (s, diamond)	1.90	NO_2(g)	33.85
CH_4(g)	-74.85	NaCl	-411.0
C_2H_5OH(l)	-276.98	O_3(g)	142.2
CO(g)	-110.5	P(s, white)	0
CO_2(g)	-393.5	P(s, red)	-18.4
CaO(s)	-635.6	PbO(s)	-217.86
$CaCO_3$(s)	-1206.9	S(rhombic)	0
HCl(g)	-92.3	S(monoclinic)	0.30
CuO(s)	-155.2	SO_2(g)	-296.1
$CuSO_4$(s)	-769.86	SO_3(g)	-395.2
Fe_2O_3(s)	-822.2	H_2S(g)	-20.15
H_2O(g)	-241.8	SiO_2	-859.3
H_2O(l)	-285.8	$ZnCl_2$	-415.89

Summary

- The standard heat of formation is defined.

Practice

Read the material at the link below and answer the questions:

http://www.chemteam.info/Thermochem/StandardEnthalpyFormation.html

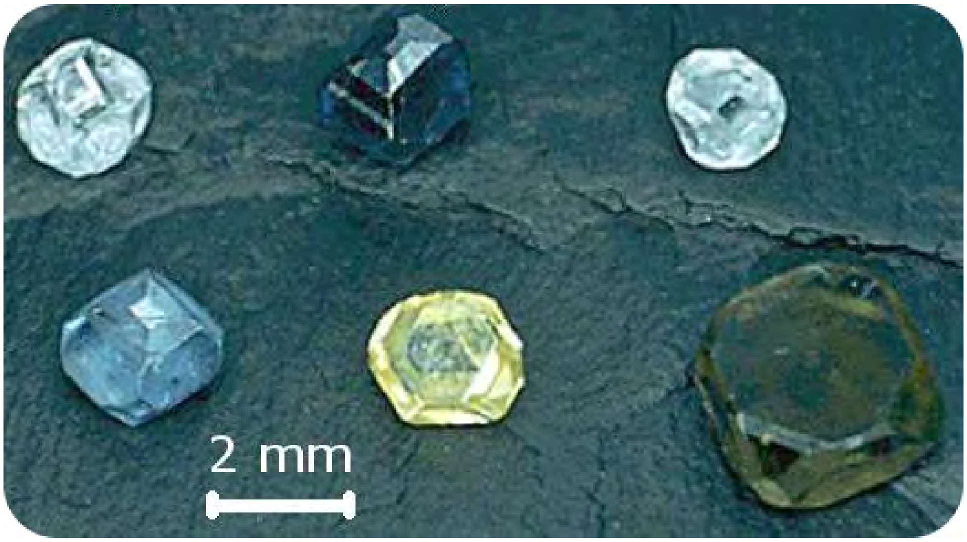
Review

1. What is the standard heat of formation for an element?
2. Does the standard heat of formation for water differ in the gaseous and liquid states?
3. What are temperature and pressure conditions for determining standard heat of formation?

standard heat of formation $(\Delta H_f{}^\circ)$**:** The enthalpy change associated with the formation of one mole of a compound from its elements in their standard states.

17.16 Calculating Heat of Reaction from Heat of Formation

- Calculate standard heat of reaction using standard heats of formation.



How are diamonds made?

Natural diamonds are mined from sites around the world. However, the price of natural diamonds is carefully controlled, so other sources for diamonds are being explored. Several different methods for producing synthetic diamonds are available, usually involving treating carbon at very high temperatures and pressures. The diamonds produced are now of high quality, but are primarily used in industrial applications. Diamonds are one of the hardest materials available and are widely used for cutting and grinding tools.

Calculating Heat of Reaction from Heat of Formation

An application of Hess's law allows us to use standard heats of formation to indirectly calculate the heat of reaction for any reaction that occurs at standard conditions. An enthalpy change that occurs specifically under standard conditions is called the **standard enthalpy (or heat) of reaction** and is given the symbol ΔH°. The standard heat of reaction can be calculated by using the following equation.

$$\Delta H^\circ = \sum n\Delta H_f^\circ(\text{products}) - \sum n\Delta H_f^\circ(\text{reactants})$$

The symbol Σ is the Greek letter sigma and means "the sum of". The standard heat of reaction is equal to the sum of all the standard heats of formation of the products minus the sum of all the standard heats of formation of the reactants. The symbol "n" signifies that each heat of formation must first be multiplied by its coefficient in the balanced equation.

TABLE 17.4: **Standard Heats of Formation of Selected Substances**

Substance	ΔH_f° (kJ/mol)	Substance	ΔH_f° (kJ/mol)

TABLE 17.4: (continued)

Al_2O_3(s)	-1669.8	H_2O_2(l)	-187.6
$BaCl_2$(s)	-860.1	KCl(s)	-435.87
Br_2(g)	30.91	NH_3(g)	-46.3
C (s, graphite)	0	NO(g)	90.4
C (s, diamond)	1.90	NO_2(g)	33.85
CH_4(g)	-74.85	NaCl	-411.0
C_2H_5OH(l)	-276.98	O_3(g)	142.2
CO(g)	-110.5	P(s, white)	0
CO_2(g)	-393.5	P(s, red)	-18.4
CaO(s)	-635.6	PbO(s)	-217.86
$CaCO_3$(s)	-1206.9	S(rhombic)	0
HCl(g)	-92.3	S(monoclinic)	0.30
CuO(s)	-155.2	SO_2(g)	-296.1
$CuSO_4$(s)	-769.86	SO_3(g)	-395.2
Fe_2O_3(s)	-822.2	H_2S(g)	-20.15
H_2O(g)	-241.8	SiO_2	-859.3
H_2O(l)	-285.8	$ZnCl_2$	-415.89

Sample Problem: Calculating Standard Heat of Reaction

Calculate the standard heat of reaction (ΔH°) for the reaction of nitrogen monoxide gas with oxygen to form nitrogen dioxide gas.

Step 1: List the known quantities and plan the problem.

Known

- $\Delta H_f{}^\circ$ for $\text{NO(g)} = 90.4$ kJ/mol
- $\Delta H_f{}^\circ$ for $\text{O}_2\text{(g)} = 0$ (element)
- $\Delta H_f{}^\circ$ for $\text{NO}_2\text{(g)} = 33.85$ kJ/mol

Unknown

- $\Delta H^\circ = ?$ kJ

First write the balanced equation for the reaction. Then apply the equation to calculate the standard heat of reaction for the standard heats of formation.

Step 2: Solve.

The balanced equation is: $2\text{NO(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{NO}_2\text{(g)}$

Applying the equation form the text:

$$\begin{aligned}\Delta H^\circ &= [2 \text{ mol NO}_2(33.85 \text{ kJ/mol})] - [2 \text{ mol NO}(90.4 \text{ kJ/mol}) + 1 \text{ mol O}_2(0 \text{ kJ/mol})] \\ &= -113 \text{ kJ}\end{aligned}$$

The standard heat of reaction is -113 kJ.

Step 3: Think about your result.

The reaction is exothermic, which makes sense because it is a combustion reaction and combustion reactions always release heat.

Summary

- Standard heats of reaction can be calculated from standard heats of formation.

Practice

Do the practice exercises at the link below:

http://wps.prenhall.com/wps/media/objects/3311/3390593/blb0507.html

Review

1. Is a Hess' Law calculation a direct determination of a standard heat of reaction?
2. What is the purpose of the n in the equation?
3. What does $\sum$ stand for?

- **standard heat of reaction:** An enthalpy change that occurs specifically under standard conditions.

17.17 References

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CHAPTER 18 Kinetics

Chapter Outline

18.1 Chemical Reaction Rate

- Define reaction rate.
- Calculate reaction rate when given time and change in concentration.

Two for the price of one

Drag racing is a sport where two cars start from a dead stop and drive as fast as they can down a quarter-miles trip. At the end of the strip are timers that determine both elapsed time (how long did it take for them to cover the quarter-mile) and top speed (how fast were they going as they went through the timer chute). Both pieces of data are important. One car may accelerate faster and get ahead that way, while the other care may be slower off the line, but can get up to a higher top speed at the end of the run.

Chemical Reaction Rate

Chemical reactions vary widely in the speeds with which they occur. Some reactions occur very quickly. If a lighted match is brought in contact with lighter fluid or another flammable liquid, it erupts into flame instantly and burns fast. Other reactions occur very slowly. A container of milk in the refrigerator will be good to drink for weeks before it begins to turn sour. Millions of years were required for dead plants under Earth's surface to accumulate and eventually turn into fossil fuels such as coal and oil.

Chemists need to be concerned with the rates at which chemical reactions occur. Rate is another word for speed. If a sprinter takes 11.0 s to run a 100 m dash, his rate or speed is given by the distance traveled divided by the time.

$$\text{speed} = \frac{\text{distance}}{\text{time}} = \frac{100 \text{ m}}{11.0 \text{ s}} = 9.09 \text{ m/s}$$

The sprinter's average running rate for the race is 9.09 m/s. We say that it is his average rate because he did not run at that speed for the entire race. At the very beginning of the race, while coming from a standstill, his rate must be slower until he is able to get up to his top speed. His top speed must then be greater than 9.09 m/s so that taken over the entire race, the average ends up at 9.09 m/s.

FIGURE 18.1

Runner.

Chemical reactions can't be measured in units of meters per second, as that would not make any sense. A **reaction rate** is the change in concentration of a reactant or product with time. Suppose that a simple reaction were to take place in which a 1.00 M aqueous solution of substance A was converted to substance B.

$$A(aq) \rightarrow B(aq)$$

Suppose that after 20.0 seconds, the concentration of A had dropped from 1.00 M to 0.72 M as A was slowly being converted to B. We can express the rate of this reaction as the change in concentration of A divided by the time.

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = -\frac{[A]_{\text{final}} - [A]_{\text{initial}}}{\Delta t}$$

A bracket around a symbol or formula means the concentration in molarity of that substance. The change in concentration of A is its final concentration minus its initial concentration. Because the concentration of A is decreasing over time, the negative sign is used. Thus, the rate for the reaction is positive and the units are molarity per second or M/s.

$$\text{rate} = -\frac{0.72 \text{ M} - 1.00 \text{ M}}{20.0 \text{ s}} = -\frac{-0.28 \text{ M}}{20.0 \text{ s}} = 0.014 \text{ M/s}$$

The molarity of A decreases by an average rate of 0.014 M every second. In summary, the rate of a chemical reaction is measured by the change in concentration over time for a reactant or product. The unit of measurement for a reaction rate is molarity per second (M/s).

Summary

- The reaction rate indicates how fast the reaction proceeds.

Practice

Read the material at the link below and answer the following questions:

http://chemwiki.ucdavis.edu/Physical_Chemistry/Kinetics/Reaction_Rates/The_Rate_of_a_Chemical_Reaction

1. Why is the rate of disappearance a negative value?
2. What is the average rate of reaction?
3. What is the instantaneous rate of reaction?

Review

1. What is another word for rate?
2. What does [ ] stand for?
3. What are the units of reaction rate?

- **reaction rate:** The change in concentration of a reactant or product with time.

18.2 Collision Theory

- Define collision theory.

Oops!

Car damage can be very expensive, especially if the person hitting your car does not have insurance. Many people have had the experience of backing up next another car when parallel parking and hearing that "bump". Fortunately, there is often no damage because the cars were not going fast enough. But every once in a while there is a rearrangement of the body parts of a car when it is hit with sufficient speed. Then things need to be fixed.

Collision Theory

The behavior of the atoms, molecules, or ions that comprise the reactants is responsible for the rates of a given chemical reaction. **Collision theory** is a set of principles that states that the reacting particles can form products when they collide with one another provided those collisions have enough kinetic energy and the correct orientation. Particles that lack the necessary kinetic energy may collide, but the particles will simply bounce off one another unchanged. The figure below illustrates the difference. In the first collision, the particles bounce off one another and no rearrangement of atoms has occurred. The second collision occurs with greater kinetic energy, and so the bond between the two red atoms breaks. One red atom bonds with the other molecule as one product, while the single red atom is the other product. The first collision is called an **ineffective collision**, while the second collision is called an **effective collision**.

Summary

- Collision theory explains how materials can collide and become new materials.

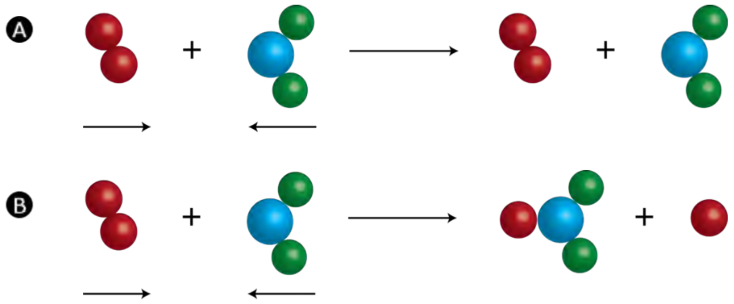


FIGURE 18.2

An ineffective collision (A) is one that does not result in product formation. An effective collision (B) is one in which chemical bonds are broken and a product is formed.

Practice

Watch the video at the link below and answer the following questions:

MEDIA

Click image to the left for more content.

http://www.youtube.com/watch?v=4n_hKAA87nM

1. What were the reactants?
2. What was the product?
3. What did the match do?

Review

1. How does a chemical reaction occur?
2. What are two requirements for collision to form a product?
3. Two molecules collide and then bounce off of one another. What kind of collision is that?

- **collision theory:** A set of principles that states that the reacting particles can form products when they collide with one another, provided those collisions have enough kinetic energy and the correct orientation.
- **effective collision:** Bonds break between atoms.
- **ineffective collision:** No rearrangement of atoms occurs.

18.3 Activation Energy

- Define activation energy.

How do fireworks light up the sky?

The sight of fireworks exploding across the night sky is always exciting. These materials, invented hundreds of years ago, can be dangerous if not handled properly. The chemicals do not react until the fuse burns down and heat is applied to the system. Then the rocket is launched and explodes high in the sky.

Activation Energy

Why do some chemical reactions occur readily while others require input of heat in order to take place? If we mix metallic sodium with water, a reaction occurs immediately, releasing a great deal of heat (enough to ignite the hydrogen gas that is formed). Group II metals, such as calcium, react at a much slower rate. Unlike the extremely vigorous reaction with sodium, the reaction with calcium is slow enough that we can trap the hydrogen gas released.

Supplying reactant particles with energy causes the bonds between the atoms to vibrate with a greater frequency. This increase in vibrational energy makes a chemical bond more likely to break and a chemical reaction more likely to occur when those particles collide with other particles. The **activation energy** for a reaction is the minimum energy that colliding particles must have in order to undergo a reaction. Some reactions occur readily at room temperature because the reacting particles already have the requisite activation energy at that temperature. Other reactions only occur when heated because the particles do not have enough energy unless an external source of heat provides the particles with more kinetic energy.

FIGURE 18.3

Calcium metal stored in an argon atmosphere.

Summary

- Activation energy is defined for a chemical reaction.

Practice

Watch the video at the link below and answer the questions:

MEDIA

Click image to the left for more content.

http://www.youtube.com/watch?v=u_1uLP30uxY

1. Does magnesium react with water at room temperature?
2. How did the speaker get magnesium to react with water?
3. What is one product of this reaction?

Review

1. Does sodium react faster or slower with water than calcium does?
2. How does vibrational energy contribute to a reaction?
3. Before some molecules react, what has to happen?

- **activation energy:** The minimum energy that colliding particles must have in order to undergo a reaction.

18.4 Potential Energy Diagrams

- Describe the potential energy diagram for an endothermic reaction.
- Describe the potential energy diagram for an exothermic reaction.
- Define activation energy.

What was Sisyphus's punishment?

Sisyphus was a mythological being who had been a very evil king. As a punishment, he was supposed to roll a large stone up to the top of a long hill. A spell had been placed on the stone so that it would roll back down before reaching the top, never to complete the task. Sisyphus was condemned to an eternity of trying to get to the top of the hill, but never succeeding.

Potential Energy Diagrams

The energy changes that occur during a chemical reaction can be shown in a diagram called a potential energy diagram, or sometimes called a reaction progress curve. A **potential energy diagram** shows the change in potential energy of a system as reactants are converted into products. The **Figure** 18.4 shows basic potential energy diagrams for an endothermic (A) and an exothermic (B) reaction. Recall that the enthalpy change (ΔH) is positive for an endothermic reaction and negative for an exothermic reaction. This can be seen in the potential energy diagrams. The total potential energy of the system increases for the endothermic reaction as the system absorbs energy from the surroundings. The total potential energy of the system decreases for the exothermic reaction as the system releases energy to the surroundings.

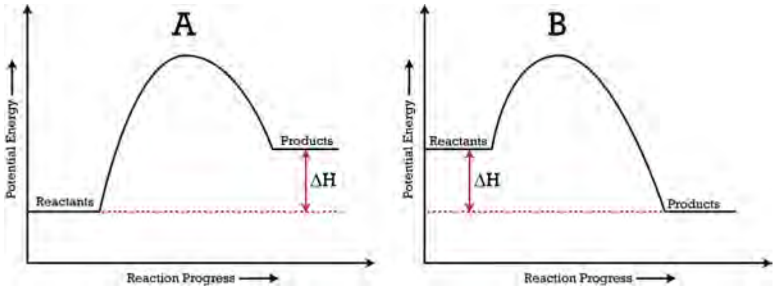


FIGURE 18.4

A potential energy diagram shows the total potential energy of a reacting system as the reaction proceeds. (A) In an endothermic reaction, the energy of the products is greater than the energy of the reactants and ΔH is positive. (B) In an exothermic reaction, the energy of the products is lower than the energy of the reactants and ΔH is negative.

The activation energy for a reaction is illustrated in the potential energy diagram by the height of the hill between the reactants and the products. For this reason, the activation energy of a reaction is sometimes referred to as the activation energy barrier. Reacting particles must have enough energy so that when they collide they can overcome that barrier (see **Figure** 18.5).

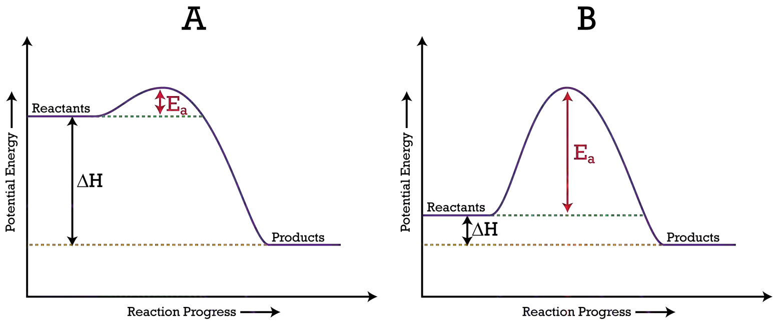


FIGURE 18.5

The activation energy (E_a) of a reaction is the barrier that must be overcome for the reactants to be able to become products. (A) The activation energy is low, meaning that the reaction is likely to be fast. (B) The activation energy is high, meaning that the reaction is likely to be slow.

Summary

- Potential energy diagrams for endothermic and exothermic reactions are described.
- Diagrams of activation energy and reaction progress are given.

Practice

Do problems 1-9 at the following link:

http://www-pvhs.stjohns.k12.fl.us/teachers/veatchd/12F0088C-0118C716.63/potential%20energy%20diagram%20worksheet.pdf

Review

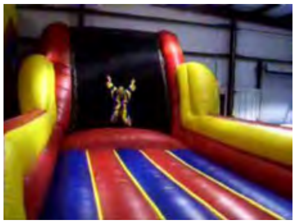
1. In an endothermic reaction, is the potential energy of the products higher or lower that the potential energy of the reactants?
2. In an exothermic reaction, is the potential energy of the products higher or lower that the potential energy of the reactants?
3. What does activation energy tell us?

- **potential energy diagram:** Shows the change in potential energy of a system as reactants are converted into products.

18.5 Activated Complex

- Define the activated complex.

Watch a short video about the strange sport of Velcro-jumping



MEDIA

Click image to the left for more content.

http://www.youtube.com/watch?v=BjJObIpqRK0

Will it stick?

Velcro is a synthetic material that allows fabrics (among other things) to stick together. Another more unusual use for Velcro is the sport (?) of "Velcro-jumping". The participant wears clothing made of Velcro and jumps at a Velcro-covered wall. Sometimes the collision with the wall will result in the person sticking to the wall. Other times the person simply bounces off the wall and does not connect.

Activated Complex

Reactant particles sometimes collide with one other and yet remain unchanged by the collision. Other times, the collision leads to the formation of products. The state of the particles that is in between the reactants and products is called the activated complex. An **activated complex** is an unstable arrangement of atoms that exists momentarily at the peak of the activation energy barrier. Because of its high energy, the activated complex exists for an extremely short period of time (about 10^{-13}s). There is equal likelihood that the activated complex either reforms the original reactants or goes on to form products. The **Figure** 18.6 shows the formation of a possible activated complex between colliding hydrogen and oxygen molecules. Because of their unstable nature and brief existence, very little is known about the exact structures of many activated complexes.

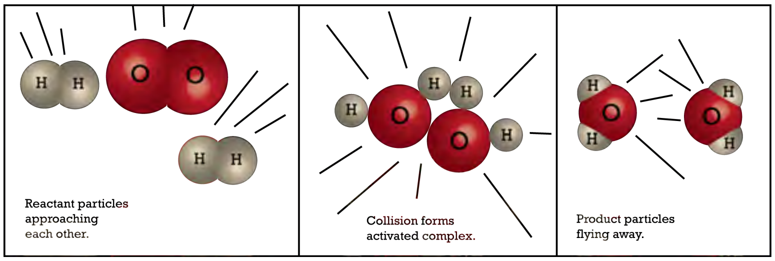


FIGURE 18.6

An activated complex is a short-lived state in which the colliding particles are at the peak of the potential energy curve.

Summary

- The role of the activated complex in reactions is described.

Practice

Watch the video at the link below and answer the following questions:

MEDIA

Click image to the left for more content.

http://www.youtube.com/watch?v=rl50M-wNVcs

1. What were the reactants?
2. What colors were the reactants?
3. What color was the activated complex?
4. What were the structures of the products?
5. What color was the final solution?

Review

1. Do all collisions of reactant particles lead to products?
2. How long does the activated complex usually last?
3. How does this compare with the activated complex in the video you watched?

- **activated complex:** An unstable arrangement of atoms that exists momentarily at the peak of the activation energy barrier.

18.6 Factors Affecting Reaction Rate

- List and describe factors that affect reaction rate.

What are the chances of a fender-bender on the highway?

Driving on a crowded freeway can get exciting. Lots of cars, drivers who aren't paying attention, people who speed, people who drive too slow – the chances of a collision are rather high. A lot of cars in a particular amount of space equals a high car concentration and many opportunities for unwanted connections with other cars.

Factors Affecting Reaction Rates

By their nature, some reactions occur very quickly, while others are very slow. However, certain changes in the reacting conditions can have an effect on the rate of a given chemical reaction. Collision theory can be utilized to explain these rate effects.

Concentration

An increase in the concentration of one or more reacting substances results in an increase in the rate of reaction. When more particles are present in a given amount of space, a greater number of collisions will naturally occur between those particles. Since the rate of a reaction is dependent on the number of collisions occurring between reactants, the rate increases as the concentration increases.

Pressure

When the pressure of a gas is increased its particles are forced closer together, decreasing in the process the amount of empty space between the particles. Therefore, an increase in the pressure of a gas is also an increase in the concentration of the gas. For gaseous reactions, an increase in pressure increases the rate of reaction for the same reasons as described for an increase in concentration. Higher gas pressure leads to a greater number of collisions between reacting particles.

Surface Area

A large log placed in a fire will burn relatively slowly. If the same mass of wood were added to the fire in the form of small twigs, they would burn much more quickly. This is because the twigs provide a greater surface area than the log does. An increase in the surface area of a reactant increases the rate of a reaction. Surface area is larger when a given amount of a solid is present as smaller particles. A powdered reactant has a greater surface area than the same reactant as a solid chunk. In order to increase the surface area of a substance, it may be ground into smaller particles or dissolved into a liquid. In solution, the dissolved particles are separated from each other and will react more quickly with other reactants.

Temperature

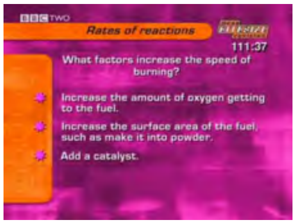
Raising the temperature of a chemical reaction usually results in a higher rate of reaction. When the reactant particles are heated, they move faster and faster. This results in a greater frequency of collisions. A more important effect of the temperature increase is that the collisions occur with a greater force and are thus more likely to surmount the activation energy barrier and go on to form products. Increasing the temperature of a reaction increases the number of effective collisions between reacting particles, so the reaction rate increases.

Summary

- Factors affecting reaction rate are:
    - concentration of reactants
    - pressure (if gas)
    - surface area
    - temperature

Practice

Watch the video at the link below and answer the following questions:



Rates of reactions

What factors increase the speed of burning?

- Increase the amount of oxygen getting to the fuel.
- Increase the surface area of the fuel, such as make it into powder.
- Add a catalyst.

MEDIA

Click image to the left for more content.

http://www.youtube.com/watch?v=UWkzS-HaxZE

1. What factor was demonstrated by adding oxygen to the fire?

2. What was shown with the aluminum powder?
3. What factor was mentioned, but not demonstrated?

Review

1. How does an increase in concentration of reactant increase rate?
2. Why would rates increase with a larger surface area of reactants?
3. What effect does temperature have on reaction rate?

18.7 Catalysts

- Define catalyst.
- Explain how catalysts influence the rate of a chemical reaction.

Where did the sun go?

Gasoline-powered vehicles emit a lot of harmful materials. Nitrogen oxides are formed when atmospheric nitrogen reacts with oxygen at the high temperatures found in a car engine. Carbon monoxide is a by-product of incomplete combustion of hydrocarbons. Evaporated and unused fuel releases volatile hydrocarbons into the atmosphere to help form smog. The presence of a catalytic converter in the exhaust system of the car causes these materials to react and be changed into less harmful products.

Catalysts

Sometimes a substance can be added to a chemical reaction and it will cause that reaction to undergo a dramatic increase in rate. Hydrogen peroxide is used as a disinfectant for scrapes and cuts and is found in many medicine cabinets as a 3% aqueous solution. Hydrogen peroxide naturally decomposes to produce water and oxygen gas, but the reaction is very slow. A bottle of hydrogen peroxide will last for several years before it needs to be replaced. However, the addition of just a small amount of manganese(IV) oxide to hydrogen peroxide will cause it to decompose completely in just a matter of minutes. A **catalyst** is a substance that increases the rate of a chemical reaction by lowering the activation energy without being used up in the reaction. After the reaction occurs, a catalyst returns to its original state and so catalysts can be used over and over again. Because it is neither a reactant nor a product, a catalyst is shown in a chemical equation by being written above the yield arrow.

$$2\text{H}_2\text{O}_2(aq) \xrightarrow{\text{MnO}_2} 2\text{H}_2\text{O}(l) + \text{O}_2(g)$$

A catalyst works by changing the specific way in which the reaction occurs, called its mechanism. The important outcome from the use of a catalyst is that the overall activation energy of the reaction is lowered (see **Figure** 18.7). With a lower activation energy barrier, a greater percentage of reactant molecules are able to have effective collisions and the reaction rate increases.

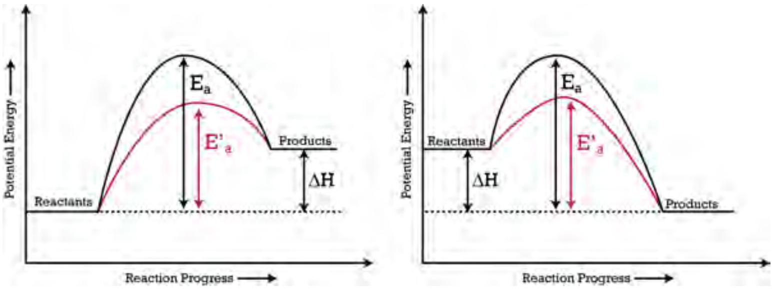


FIGURE 18.7

The addition of a catalyst to a reaction lowers the activation energy, increasing the rate of the reaction. The activation energy of the uncatalyzed reaction is shown by Ea, while the catalyzed reaction is shown by Ea'. The heat of reaction (ΔH) is unchanged by the presence of the catalyst.

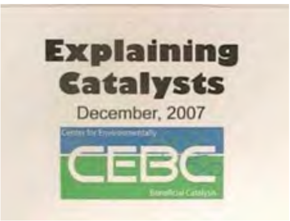
Catalysts are extremely important parts of many chemical reactions. Enzymes in your body act as nature's catalysts, allowing important biochemical reactions to occur at reasonable rates. Chemical companies constantly search for new and better catalysts to make reactions go faster and thus make the company more profitable.

Summary

- The function of a catalyst is described.

Practice

Watch the video at the link below and answer the following questions:



MEDIA

Click image to the left for more content.

http://www.youtube.com/watch?v=9KQdF1bnXHE

1. What dye is used on blue jeans?
2. What do enzymes do for the blue jeans?
3. List three issues that exist for uncatalyzed reactions.

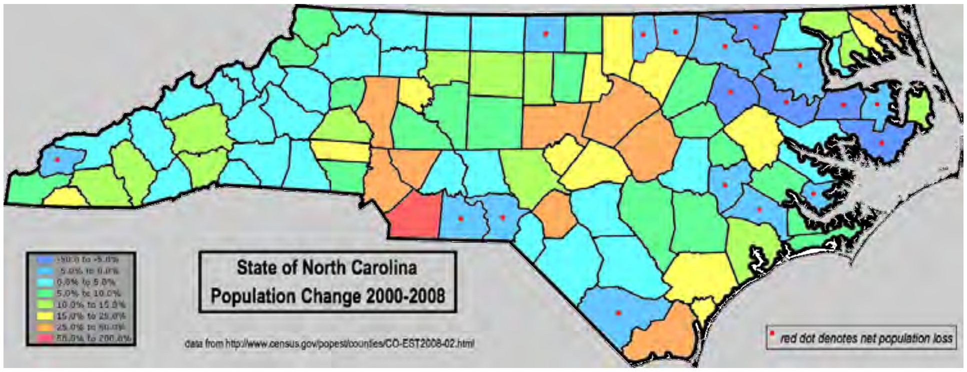
Review

1. What does a catalyst affect in a chemical reaction?
2. Is the ΔH for the process affected?
3. When writing a chemical equation, where do we indicate the catalyst?

- **catalyst:** A substance that increases the rate of a chemical reaction by lowering the activation energy without being used up in the reaction.

18.8 Rate Law and Specific Rate Constant

- Define rate law.
- Define specific rate constant.



What are the migration patterns of the current population?

Where are people moving from and where are they moving to? How fast is the population changing in different areas? These are important questions for people involved in deciding about where to build schools or hospitals or where to open new businesses. If an area is growing rapidly, action needs to be taken soon to accommodate the growth. How fast the growth is will determine how many schools to build. Rates of change affect a lot of decisions.

Rate Law and Specific Rate Constant

Consider a simple chemical reaction in which reactant A is converted into product B according to the equation below.

$$A \rightarrow B$$

The rate of reaction is given by the change in concentration of A as a function of time. The rate of disappearance of A is also proportional to the concentration of A.

$$-\frac{\Delta[A]}{\Delta t} \; \alpha \; [A]$$

Since the rate of a reaction generally depends upon collision frequency, it stands to reason that as the concentration of A increases, the rate of reaction increases. Likewise, as the concentration of A decreases, the rate of reaction decreases. The expression for the rate of the reaction can be shown as follows:

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} \quad \text{or} \quad \text{rate} = k[A]$$

The proportionality between the rate and $[A]$ becomes an equal sign by the insertion of a constant (k). A **rate law** is an expression showing the relationship of the reaction rate to the concentrations of each reactant. The **specific rate**

constant (k) is the proportionality constant relating the rate of the reaction to the concentrations of reactants. The rate law and the specific rate constant for any chemical reaction must be determined experimentally. The value of the rate constant is temperature dependent. A large value of the rate constant means that the reaction is relatively fast, while a small value of the rate constant means that the reaction is relatively slow.

Summary

- The rate law and specific rate constant are defined.

Practice

Read the material at the link below and answer the following questions:

http://www.differencebetween.com/difference-between-reaction-rate-and-vs-specific-rate-constant/

1. Why is the sign for reactant concentration negative?
2. Why is the sign for product concentration positive?
3. What do the lower-case letters in the rate equation represent?

Review

1. What is a rate law?
2. What is a specific rate constant?
3. How are these parameters determined?

- **rate law:** An expression showing the relationship of the reaction rate to the concentrations of each reactant.
- **specific rate constant** (k)**:** The proportionality constant relating the rate of the reaction to the concentrations of reactants.

18.9 Order of Reaction

- Describe the kinetic characteristics of a first-order reaction.

How harmful are forest fires?

Forest fires cause extensive damage when they occur. Both plant and animal life are harmed during these events. The severity of a forest fire depends on how much plant life is available to burn – the more available dry plant material, the more serious the fire and the more rapidly it will spread.

Order of Reaction

In the reaction $A \rightarrow B$, the rate of the reaction is directly proportional to the concentration of A raised to the first power. That is to say, $[A] = [A]^1$. A **first-order reaction** is a reaction in which the rate is proportional to the concentration of only one reactant. As a first-order reaction proceeds, the rate of reaction decreases because the concentration of the reactant decreases (**Figure** 18.8). The graph of concentration versus time is curved. The reaction rate $\left(\frac{\Delta[A]}{\Delta t}\right)$ can be determined graphically by the slope of a tangent to the curve at any point. The rate of the reaction at the time shown with the red triangle is given by:

$$\text{rate} = -\frac{[A]_{\text{final}} - [A]_{\text{initial}}}{\Delta t} = -\frac{0.35 \text{ M} - 0.63 \text{ M}}{3.0 \text{ s} - 1.0 \text{ s}} = 0.14 \text{ M/s}$$

The rates of some reactions depend on the concentrations of more than one reactant. Consider a reaction in which a molecule of A collides with a molecule of B to form product C.

$$A + B \rightarrow C$$

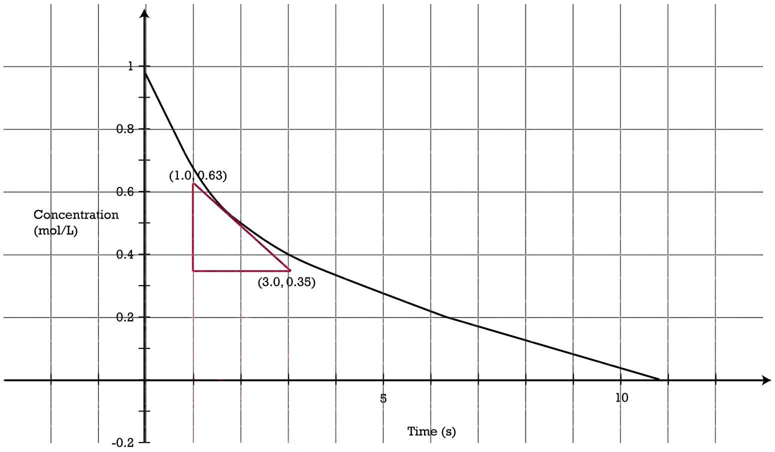


FIGURE 18.8

This graph shows how the concentration of a reactant changes as a reaction proceeds. The rate of the reaction is determined at any point by measuring the slope of a tangent to the curve.

Doubling the concentration of A alone would double the reaction rate. Likewise, doubling the concentration of B alone would also double the rate. The rate law must reflect the rate dependence on both reactants.

$$\text{rate} = k[A][B]$$

This reaction is said to be first order with respect to A and first order with respect to B. Overall, it is a second-order reaction. The rate law and the order of a reaction must be determined experimentally.

Summary

- A first-order reaction is described.

Practice

Read the material at the link below and answer the following questions:

1. What is a zero-order reaction?
2. What is a second-order reaction?
3. How is the order of a two-reactant reaction determined?

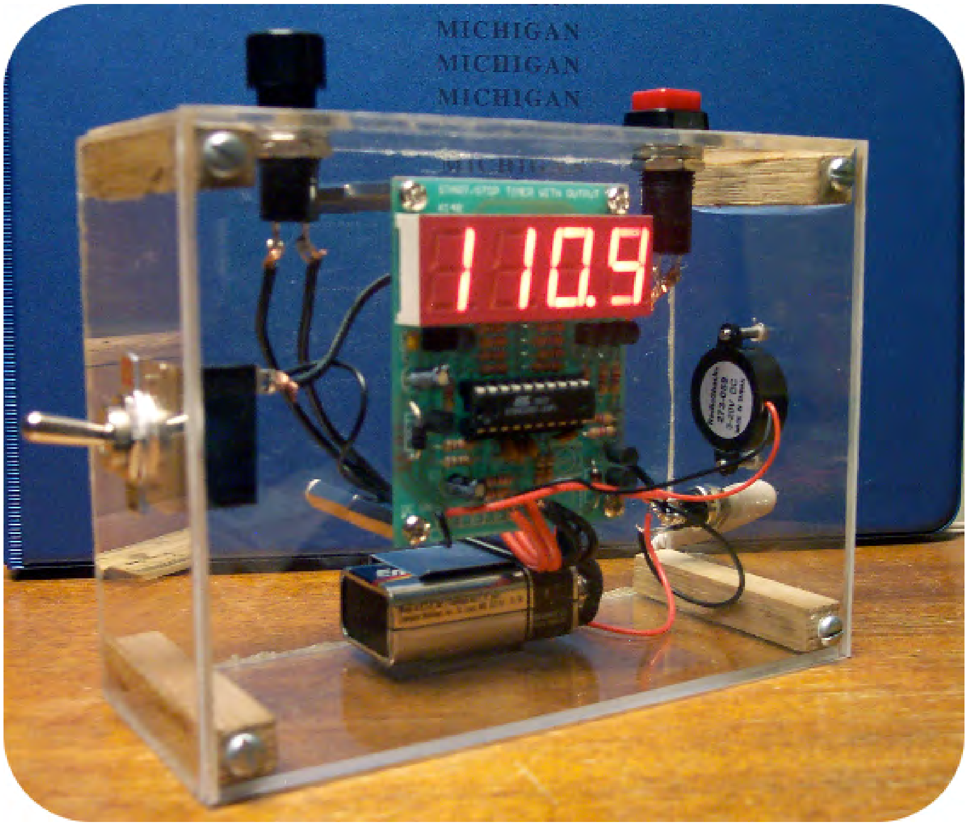
Review

1. What is a first-order reaction?
2. How is the instantaneous rate determined?
3. How do we determine rate law and reaction order?

- **first-order reaction:** A reaction in which the rate is proportional to the concentration of only one reactant.

18.10 Determining the Rate Law from Experimental Data

- Use experimental data to determine the rate law for a reaction.



How fast?

Determining the amount of time something required calls for a timer. These devices can be simple kitchen timers (not very precise) or complex systems that can measure to a fraction of a second. Accurate time measurement is essential in kinetics studies for assessing rates of chemical reactions.

Determining the Rate Law from Experimental Data

In order to experimentally determine a rate law, a series of experiments must be performed with various starting concentrations of reactants. The initial rate law is then measured for each of the reactions. Consider the reaction between nitrogen monoxide gas and hydrogen gas to form nitrogen gas and water vapor.

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$$

The following data were collected for this reaction at 1280°C.

TABLE 18.1:

Experiment	**[NO]**	**[H_2]**	**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 order with respect to 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. The initial rate of the reaction quadrupled, since $\frac{5.00\times10^{-5}}{1.25\times10^{-5}} = 4$. Therefore, the order of the reaction with respect to NO is 2. In other words, rate α $[\text{NO}]^2$. Because $2^2 = 4$, the doubling of [NO] results in a rate that is four times greater.

Comparing experiments 2 and 3: the concentration of H_2 was doubled while the concentration of NO was held constant. The initial rate of the reaction doubled, since $\frac{1.00\times10^{-4}}{5.00\times10^{-5}} = 2$. Therefore, the order of the reaction with respect to H_2 is 1, or rate α $[H_2]^1$. Because $2^1 = 2$, the doubling of H_2 results in a rate that is twice as great.

The overall rate law then includes both of these results.

$$\text{rate} = k[\text{NO}]^2[\text{H}_2]$$

The sum of the exponents is $2+1=3$, making the reaction third-order overall. Once the rate law for a reaction is determined, the specific rate constant can be found by substituting the data for any of the experiments into the rate law and solving for k.

$$k = \frac{\text{rate}}{[\text{NO}]^2[\text{H}_2]} = \frac{1.25 \times 10^{-5}\ \text{M/s}}{(0.0050\ \text{M})^2(0.0020\ \text{M})} = 250\ \text{M}^{-2}\text{s}^{-1}$$

Notice that the rate law for the reaction does not relate to the balanced equation for the overall reaction. The coefficients of NO and H_2 are both 2, while the order of the reaction with respect to the H_2 is only one. The units for the specific rate constant vary with the order of the reaction. So far, we have seen reactions that are first or second order with respect to a given reactant. Occasionally, the rate of a reaction may not depend on the concentration of one of the reactants at all. In this case, the reaction is said to be zero-order with respect to that reactant.

Summary

- The process of using experimental data to determine a rate law is described.

Practice

Use the site below to practice determination of rate constant with experimental data.

http://ibchem.com/IB/ibnotes/full/kin_htm/order_calculation.htm

Review

1. How do you carry out experiments for determining rate constants?

2. Why is the reaction order with regard to NO a value of 2?
3. Why is the reaction order with regard to hydrogen value of 1?

18.11 Reaction Mechanisms and the Elementary Step

- Define reaction mechanism.
- Define elementary step.

Up in the air

What most people see of an airplane is the final product. They do not see the long, complex assembly line that begins with a few parts and gradually becomes the finished product. Assembly lines are intricate organizations that go through a series of complicated steps to bring hundreds (maybe thousands) of parts together into the completed aircraft.

Reaction Mechanisms and the Elementary Step

Chemical reactions rarely occur in one simple step. 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. 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.

Summary

- The idea of a reaction mechanism is described.

Practice

Read the material at the web site below and answer the following questions:

http://chemwiki.ucdavis.edu/Physical_Chemistry/Kinetics/Rate_Laws/Reaction_Mechanisms/Reaction_Mechanisms

1. Will kinetics allow us always to determine the mechanism of a particular reaction?
2. What must a reaction mechanism tell us?
3. What is a unimolecular elementary process?
4. What is a bimolecular elementary process?

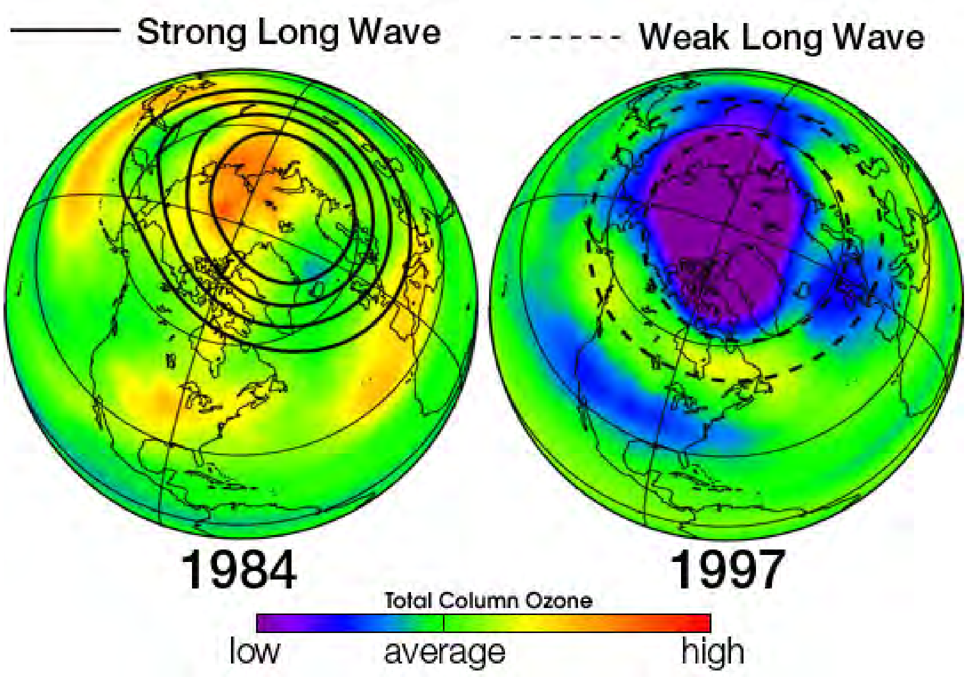
Review

1. Do chemical reactions usually occur in a single step?
2. What does the overall balanced equation not tell us?
3. How do overall reactions usually proceed?

- **elementary step (or elementary reaction):** 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.

18.12 Intermediate

- Define intermediate.
- Describe the role of intermediates in reaction mechanisms.



Ozone depletetion

Ozone (O_3) depletion in the atmosphere is of significant concern. This gas serves as a protection against the ultraviolet rays of the sun. Ozone is naturally depleted in addition to the depletion caused by human-made chemicals. The depletion reaction is a two-step process:

$$O_3 + \text{ultraviolet light} \rightarrow O_2 + O\cdot(\text{free radical}) \text{ slow reaction}$$
$$O\cdot + O_3 \rightarrow 2O_2 \text{ fast reaction}$$

The free radical is not a part of the overall equation, but can be detected in the lab.

Intermediate

Reaction mechanisms describe how the material in a chemical reaction gets from the initial reactants to the final products. One reaction that illustrates a reaction mechanism is 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 with one O_2 molecule. However, careful analysis of the reaction has detected the presence of N_2O_2 during the reaction. A proposed mechanism for the reaction consists of two elementary steps:

Step 1: $2NO(g) \rightarrow N_2O_2(g)$

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:

$$\begin{array}{r} 2NO(g) \rightarrow \cancel{N_2O_2(g)} \\ \underline{\cancel{N_2O_2(g)} + O_2(g) \rightarrow 2NO_2(g)} \\ 2NO(g) + O_2(g) \rightarrow 2NO_2(g) \end{array}$$

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 which appears in the mechanism of a reaction, but not in the overall balanced equation. An intermediate is always formed in an early step in the mechanism and consumed in a later step.

FIGURE 18.9

Nitrogen dioxide (left) and dinitrogen tetroxide (right).

Summary

- The role of intermediates in reaction mechanisms is described.

Practice

Read the material at the link below and answer the questions at the end:

http://chemwiki.ucdavis.edu/Physical_Chemistry/Kinetics/Rate_Laws/Reaction_Mechanisms/Reaction_Mechanisms

Review

1. What is the intermediate in the reaction described above?
2. Do we see this intermediate in the actual reaction mix?

3. Where do we first see an intermediate in a reaction mechanism?
4. What happens to the intermediate?

- **intermediate:** A species which appears in the mechanism of a reaction, but not in the overall balanced equation.

18.13 Molecularity

- Define molecularity.
- Give reaction examples to illustrate the definition.

One piece at a time

Many people enjoy putting jigsaw puzzles together. Often these puzzles come in a box, so you have to spread all the pieces out before you start. Nowadays you can also find internet sites that have jigsaw puzzles. You can choose the level of difficulty, the shape of the pieces – and you can time yourself to see how well you did compare to others that tried the puzzle. The puzzle looks complicated with the final product often numbering hundreds of pieces. However, in assembling the puzzle, you have a series of elementary steps and the puzzle goes together one piece at a time.

Molecularity of a Reaction

The **molecularity** of a reaction is the number of molecules reacting in an elementary step. A unimolecular reaction is one in which only one reacting molecule participates in the reaction. Two reactant molecules collide with one another in a bimolecular reaction. A termolecular reaction involves three reacting molecules in one elementary step. Termolecular reactions are relatively rare because they involve the simultaneous collision of three molecules in the correct orientation, a rare event. When termolecular reactions do occur, they tend to be very slow.

If we have the reaction:

$$2NO(g)+O_2(g) \rightarrow 2NO_2(g)$$

We might guess that the reaction was termolecular since it appears that three molecules of reactants are involved. However, our definition of molecularity states that we need to look at an elementary step and not the overall reaction. Data on the reaction mechanism shows us that the reaction occurs in two steps:

Step 1: $2\text{NO}(g) \rightarrow \text{N}_2\text{O}_2(g)$

Step 2: $\text{N}_2\text{O}_2(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g)$

So we see that each elementary step is bimolecular and not termolecular. Notice that the colliding molecules may be the same (as in step 1 above) or different (as in step 2 above).

Another reaction involves the conversion of ozone (O_3) to oxygen (O_2) with ultraviolet light. The two elementary steps are as follows:

$$\begin{aligned}&\text{O}_3 + \text{ultraviolet light} \rightarrow \text{O}_2 + \text{O}\cdot(\text{free radical}) \text{ slow reaction}\\&\text{O}\cdot + \text{O}_3 \rightarrow 2\text{O}_2 \text{ fast reaction}\end{aligned}$$

The first step is unimolecular (one molecule of ozone reacts) and the second step is bimolecular (one ozone free radical and one ozone molecule react together).

Summary

- Molecularity is defined and examples are given.

Practice

Do the molecularity parts of problems 4 and 5 at the link below:

http://faculty.scottsdalecc.edu/borick/files/2011/05/8-30HW.pdf

Review

1. What is a unimolecular reaction?
2. What is a bimolecular reaction?
3. Why are termolecular reactions rare?

- **molecularity:** The number of molecules reacting in an elementary step.

18.14 Rate-Determining Step

- Define rate-determining step.

Waiting in line

Airline travel can be very frustrating. You usually have to get to the airport two hours before your flight leaves. You stand in line to check your baggage and get your boarding pass. Then you stand in line for your security screen. Finally, you wait in line to board the plane. Since there are only so many ticket agents, not everybody can be waited on immediately. The same with the security screen – only so many body scanners are available. And getting on the plane involves going one-by-one down a very narrow aisle to get to your seat. All these limits to slow you down.

Rate-Determining Step

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 sequence of steps in a 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. The decomposition of hydrogen peroxide is discussed below and illustrates how reaction mechanisms can be determined through experimental studies.

Decomposition of Hydrogen Peroxide

Recall that a catalyst is a substance, which increases the rate of a chemical reaction without being consumed. Catalysts lower the overall activation energy for a reaction by providing an alternative mechanism for the reaction to follow. One such catalyst for the decomposition of hydrogen peroxide is iodide ions (I^-).

$$2H_2O_2(aq) \xrightarrow{I^-} 2H_2O(l) + O_2(g)$$

By experiment, the rate of reaction is found to be first-order with respect to both H_2O_2 and I^- and second-order overall.

$$\text{rate} = k[H_2O_2][I^-]$$

The reaction cannot occur in one step corresponding to the overall balanced equation. If it did, the reaction would be second-order with respect to H_2O_2 since the coefficient of the H_2O_2 in the balanced equation is a 2. A reaction mechanism can be constructed which accounts for the rate law and for the detection of the IO^- ion as an intermediate. It consists of two bimolecular elementary steps.

Step 1: $H_2O_2(aq) + I^-(aq) \rightarrow H_2O(l) + IO^-(aq)$

Step 2: $H_2O_2(aq) + IO^-(aq) \rightarrow H_2O(l) + O_2 + I^-(aq)$

If step 1 is the rate-determining step, then the rate law for that step will be the rate law for the overall reaction.

$$\text{rate} = k[H_2O_2][I^-]$$

The rate law for the slow step of the proposed mechanism agrees with the overall experimentally determined rate law. The IO^- is present as an intermediate in the reaction. The iodide ion catalyst also appears in the mechanism. It is consumed in the first elementary step and then is regenerated in the second step. That is the requirement for a catalyst – that is that it is not used up in the reaction.

Summary

- The rate-determining step in a reaction is defined.
- The process for determining the rate-determining step is described.

Practice

Read the material at the link below and work the practice problem:

http://chemwiki.ucdavis.edu/Physical_Chemistry/Kinetics/Rate_Laws/Reactions/Rate-Determining_Step

Review

1. What is the rate-limiting step in a reaction?
2. Can we determine the rate-limiting step simply by looking at the reaction mechanism?
3. In the hydrogen peroxide example above, why was step 1 determined to be the rate-limiting step?

- **rate-determining step:** The slowest step in the sequence of steps in a reaction mechanism.

18.15 Mechanisms and Potential Energy Diagrams

- Draw and label a potential energy diagram for a two-step reaction.
- Describe the use of a potential energy diagram for identifying the rate-limiting step in a multi-step reaction.

Roller coasters-fun or frightful?

For many people, a roller coaster is the epitome of excitement, while for others it is a torture device to be avoided at all costs (and some folks are in-between). For a roller coaster, the rate-limiting step is the climb up to the top at the beginning of the ride, where the cars are hauled slowly to the peak of the ride. This peak must be the highest because the potential energy at this point must be enough to cause the roller coaster to move through the smaller peaks without stopping.

Potential Energy Diagrams

The potential energy diagram can illustrate the mechanism for a reaction by showing each elementary step of the reaction with distinct activation energy (see **Figure** 18.10).

The reaction whose potential energy diagram is shown in the figure is a two-step reaction. The activation energy for each step is labeled E_{a1} and E_{a2}. Each elementary step has its own activated complex, labeled AC_1 and AC_2. Note that the overall enthalpy change of the reaction (ΔH) is unaffected by the individual steps, since it depends only on the initial and final states.

In this example, the rate-limiting step in the reaction is the first step, leading to the formation of the activated complex AC_1. The activation energy is higher for this step than for step two, which has a considerably lower activation energy. If the rate-limiting step were the second step, the peak labeled AC_2 would be higher than the peak for AC_1 and E_{a2} would be greater than E_{a1}. The same approach can be taken for a potential energy diagram with more than two peaks.

Summary

- A potential energy diagram for a two-step reaction is shown and labeled.

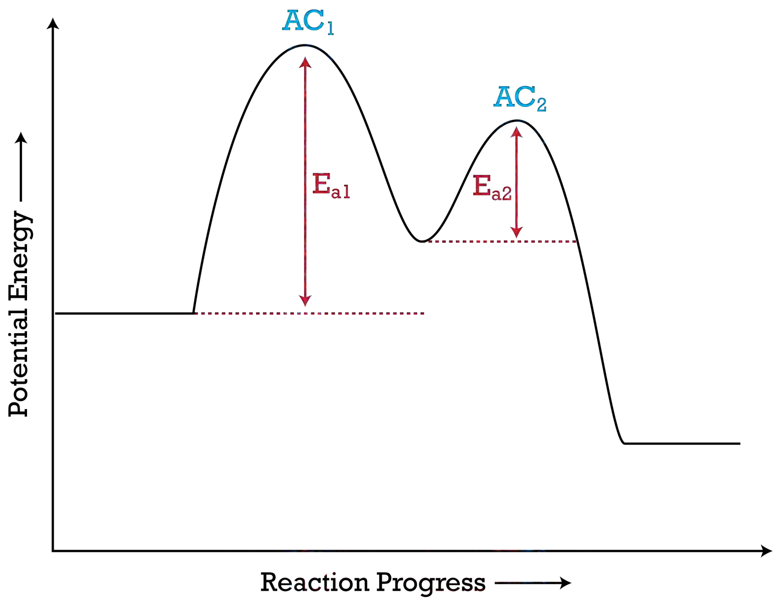


FIGURE 18.10

The potential energy diagram shows an activation energy peak for each of the elementary steps of the reaction. The valley between represents the intermediate for the reaction.

Practice

View the section on two-step reactions at the site below and then do the self-test (both buttons are at the top of the slide). Don't worry about ΔG – just consider it an indication of activation energy as is ΔE in the diagram above.

http://www.wfu.edu/chem/courses/energydiagram/index.html

Review

1. What does a potential energy diagram tell us?
2. In the diagram above, which step has the highest activation energy?
3. If a catalyst lowered the step one activation energy to a value lower than the step two activation energy, which step would be rate-limiting?

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CHAPTER 19 Equilibrium

Chapter Outline

19.1 Reversible Reaction

- Define reversible reaction.
- Give examples of reversible reactions.

How do you change the colors of a solution?

A solution of cobalt chloride in water is pink due to the presence of the solvated Co^{2+} ion. If sufficient HCl is added, the solution turns blue as the ${CoCl_4}^{2-}$ ion forms. The reaction can be shifted back to the pink form if more water is added to the solution.

Reversible Reactions

Up until this point, we have written the equations for chemical reactions in a way that would seem to indicate that all reactions proceed completely until all the reactants have been converted into products. In reality, a great many chemical reactions do not proceed entirely to completion. A **reversible reaction** is a reaction in which the conversion of reactants to products and the conversion of products to reactants occur simultaneously. One example of a reversible reaction is the reaction of hydrogen gas and iodine vapor to from hydrogen iodide. The forward and reverse reactions can be written as follows.

$$\begin{aligned} \text{Forward reaction :} \quad & H_2(g)+I_2(g) \rightarrow 2HI(g) \\ \text{Reverse reaction :} \quad & 2HI(g) \rightarrow H_2(g)+I_2(g) \end{aligned}$$

In the forward reaction, hydrogen and iodine combine to form hydrogen iodide. In the reverse reaction, hydrogen iodide decomposes back into hydrogen and iodine. The two reactions can be combined into one equation by the use of a double arrow.

$$H_2(g) + I_2(g) \rightleftarrows 2HI(g)$$

The double arrow is the indication that the reaction is reversible.

When hydrogen and iodine gases are mixed in a sealed container, they begin to react and form hydrogen iodide. At first, only the forward reaction occurs because no HI is present. As the forward reaction proceeds, it begins to slow down as the concentrations of the H_2 and the I_2 decrease. As soon as some HI has formed, it begins to decompose back into H_2 and I_2. The rate of the reverse reaction starts out slow because the concentration of HI is low. Gradually, the rate of the forward reaction decreases while the rate of the reverse reaction increases. Eventually the rate of combination of H_2 and I_2 to produce HI becomes equal to the rate of decomposition of HI into H_2 and I_2. When the rates of the forward and reverse reactions have become equal to one another, the reaction has achieved a state of balance.

Summary

- A reversible reaction is defined.

Practice

Read the material at the link below and answer the following questions:

http://www.xtremepapers.com/revision/gcse/chemistry/reversible_reactions.php

1. What color is hydrated copper sulfate?
2. If the forward reaction is exothermic, how would you increase the yield of product?
3. How can we increase the formation of ammonia in the Haber process?

Review

1. Do all chemical reactions proceed to completion?
2. Why is the reaction given above considered a reversible reaction?
3. How do we designate a reversible reaction?

- **reversible reaction:** A reaction in which the conversion of reactants to products and the conversion of products to reactants occur simultaneously.

19.2 Chemical Equilibrium

- Define chemical equilibrium.
- List conditions for equilibrium.

Pull hard

A tug of war involves two teams at the ends of a rope. The goal is to pull the other team over a line in the middle. At first, there is a great deal of tension on the rope, but no apparent movement. A bystander might think that there is nothing happening. In reality, there is a great deal of tension on the rope as the two teams pull in opposite directions at the same time.

Chemical Equilibrium

Hydrogen and iodine gases react to form hydrogen iodide according to the following reaction:

$$\begin{aligned} &H_2(g) + I_2(g) \rightleftarrows 2HI(g) \\ \text{Forward reaction:}\quad & H_2(g) + I_2(g) \rightarrow 2HI(g) \\ \text{Reverse reaction:}\quad & 2HI(g) \rightarrow H_2(g) + I_2(g) \end{aligned}$$

Initially, only the forward reaction occurs because no HI is present. As soon as some HI has formed, it begins to decompose back into H_2 and I_2. Gradually, the rate of the forward reaction decreases while the rate of the reverse reaction increases. Eventually the rate of combination of H_2 and I_2 to produce HI becomes equal to the rate of decomposition of HI into H_2 and I_2. When the rates of the forward and reverse reactions have become equal to one another, the reaction has achieved a state of balance. **Chemical equilibrium** is the state of a system in which the rate of the forward reaction is equal to the rate of the reverse reaction.

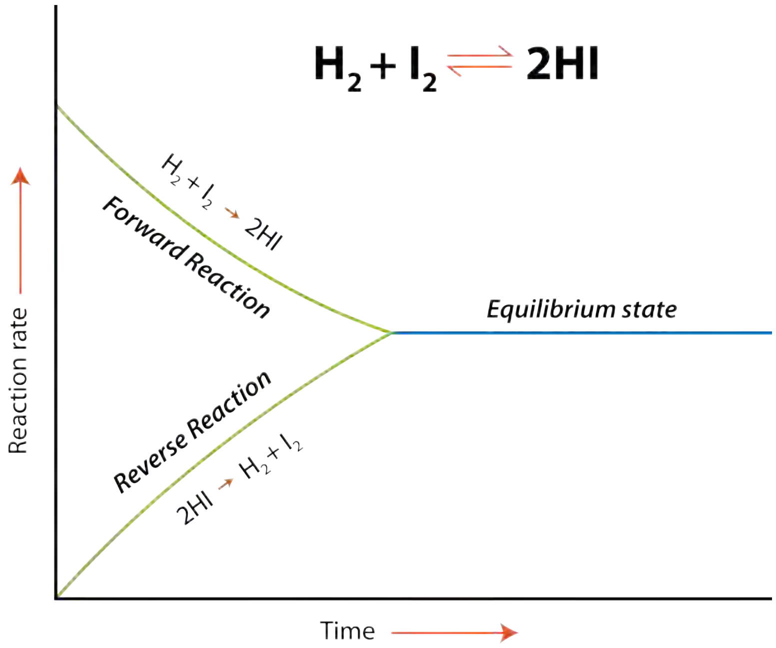


FIGURE 19.1

Equilibrium in reaction: $H_2(g) + I_2(g) \rightarrow 2HI(g)$.

Chemical equilibrium can be attained whether the reaction begins with all reactants and no products, all products and no reactants, or some of both. The **Figure** 19.2 shows changes in concentration of H_2, I_2, and HI for two different reactions. In the reaction depicted by the graph on the left (A), the reaction begins with only H_2 and I_2 present. There is no HI initially. As the reaction proceeds towards equilibrium, the concentrations of the H_2 and I_2 gradually decrease, while the concentration of the HI gradually increases. When the curve levels out and the concentrations all become constant, equilibrium has been reached. At equilibrium, concentrations of all substances are constant. In reaction B, the process begins with only HI and no H_2 or I_2. In this case, the concentration of HI gradually decreases while the concentrations of H_2 and I_2 gradually increase until equilibrium is again reached. Notice that in both cases, the relative position of equilibrium is the same, as shown by the relative concentrations of reactants and products. The concentration of HI at equilibrium is significantly higher than the concentrations of H_2 and I_2. This is true whether the reaction began with all reactants or all products. The position of equilibrium is a property of the particular reversible reaction and does not depend upon how equilibrium was achieved.

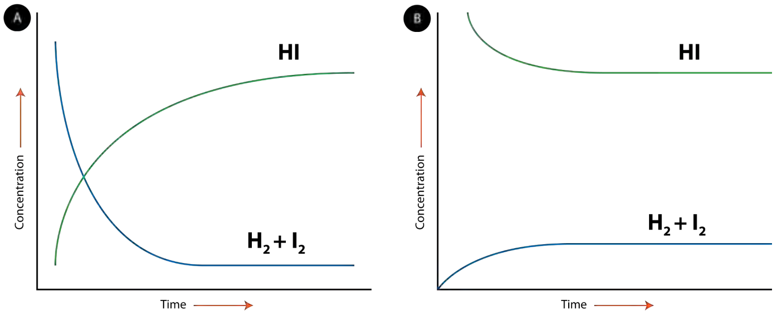


FIGURE 19.2

Equilibrium between reactants and products.

Conditions for Equilibrium and Types of Equilibrium

It may be tempting to think that once equilibrium has been reached, the reaction stops. Chemical equilibrium is a dynamic process. The forward and reverse reactions continue to occur even after equilibrium has been reached. However, because the rates of the reactions are the same, there is no change in the relative concentrations of reactants and products for a reaction that is at equilibrium. The conditions and properties of a system at equilibrium are summarized below.

1. The system must be closed, meaning no substances can enter or leave the system.
2. Equilibrium is a dynamic process. Even though we don't necessarily see the reactions, both forward and reverse are taking place.
3. The rates of the forward and reverse reactions must be equal.
4. The amount of reactants and products do not have to be equal. However, after equilibrium is attained, the amounts of reactants and products will be constant.

Summary

- The concept of chemical equilibrium is described.
- Conditions for chemical equilibrium are listed.

Practice

Read the material at the link below and answer the following questions:

http://www.chemguide.co.uk/physical/equilibria/introduction.html#top

1. What is a closed system?
2. What is a dynamic system?
3. What happens if you change the relative rates of the forward and back reactions?

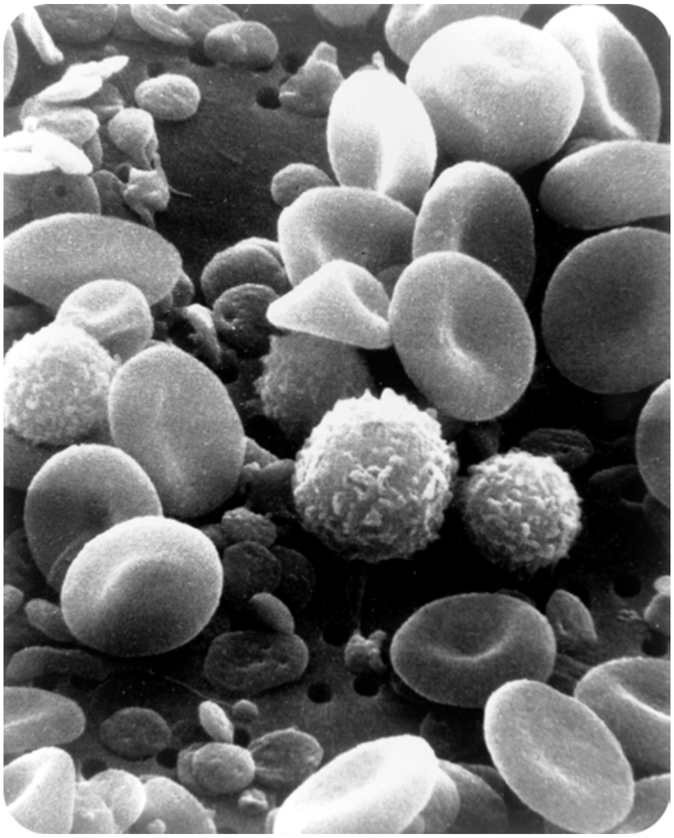
Review

1. What is chemical equilibrium?
2. In the reaction illustrated in the text, does the equilibrium concentration of HI equal the equilibrium concentrations of H_2 and I_2?
3. Does the position at equilibrium depend upon how the equilibrium was reached?

- **chemical equilibrium:** The state of a system in which the rate of the forward reaction is equal to the rate of the reverse reaction.

19.3 Equilibrium Constant

- Define equilibrium constant.
- Write the equation for the general equilibrium constant.



Carbon monoxide poisoning

Red blood cells transport oxygen to the tissues so they can function. In the absence of oxygen, cells cannot carry out their biochemical responsibilities. Oxygen moves to the cells attached to hemoglobin, a protein found in the red cells. In cases of carbon monoxide poisoning, CO binds much more strongly to the hemoglobin, blocking oxygen attachment and lowering the amount of oxygen reaching the cells. Treatment involves the patient breathing pure oxygen to displace the carbon monoxide. The equilibrium reaction shown below illustrates the shift toward the right when excess oxygen is added to the system:

$$\text{Hb(CO)}_4(aq) + 4\text{O}_2(g) \leftrightarrows \text{Hb(O}_2)_4(aq) + 4\text{CO}(g)$$

Equilibrium Constant

The general value of the equilibrium constant gives us information about whether the reactants or the products are favored at equilibrium. Since the product concentrations are in the numerator of the equilibrium expression, a $K_{eq} > 1$ means that the products are favored over the reactants. A $K_{eq} < 1$ means that the reactants are favored over the products.

Consider the hypothetical reversible reaction in which reactants A and B react to form products C and D. This equilibrium can be shown below, where the lower case letters represent the coefficients of each substance.

$$aA + bB \rightleftarrows cC + dD$$

As we have established, the rates of the forward and reverse reactions are the same at equilibrium, and so the concentrations of all of the substances are constant. Since that is the case, it stands to reason that a ratio of the concentrations for any given reaction at equilibrium maintains a constant value. The **equilibrium constant** (K_{eq}) is the ratio of the mathematical product of the concentrations of the products of a reaction to the mathematical product of the concentrations of the reactants of the reaction. Each concentration is raised to the power of its coefficient in the balanced chemical equation. For the general reaction above, the equilibrium constant expression is written as follows:

$$K_{eq} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

The concentrations of each substance, indicated by the square brackets around the formula, are measured in molarity units (mol/L).

The value of the equilibrium constant for any reaction is only determined by experiment. As detailed in the above section, the position of equilibrium for a given reaction does not depend on the starting concentrations and so the value of the equilibrium constant is truly constant. It does, however, depend on the temperature of the reaction. This is because equilibrium is defined as a condition resulting from the rates of forward and reverse reactions being equal. If the temperature changes, the corresponding change in those reaction rates will alter the equilibrium constant. For any reaction in which a K_{eq} is given, the temperature should be specified.

Summary

- The equilibrium constant for a reversible reaction is described.

Practice

Read the material at the link below and answer the following questions:

1. What is a homogeneous equilibrium?
2. What is a heterogeneous equilibrium?
3. What goes in the numerator in an equilibrium expression?
4. Why is it important to write your equilibrium equation out before setting up the equilibrium constant?

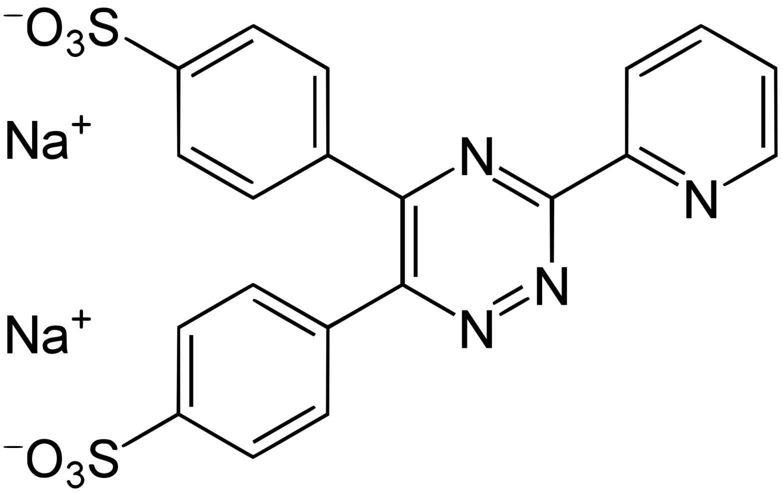
Review

1. What does the equilibrium constant tell us?
2. What does it mean if the K_{eq} is >1?
3. What does it mean if the K_{eq} is <1?
4. Does the position of equilibrium depend on the starting concentrations?

- **equilibrium constant** (K_{eq})**:** The ratio of the mathematical product of the concentrations of the products of a reaction to the mathematical product of the concentrations of the reactants of the reaction. Each concentration is raised to the power of its coefficient in the balanced chemical equation.

19.4 Calculations with Equilibrium Constants

- Perform equilibrium constant calculations.



Iron-poor blood?

Iron is an important component of red cells. Patients who have low iron will usually be anemic and have a lower than normal number of red blood cells. One way to assess serum iron concentration is with the use of Ferrozine, a complex organic molecule. Ferrozine forms a product with Fe^{3+}, producing a pink color. In order to determine factors affecting the reaction, we need to measure the equilibrium constant. If the equilibrium does not lie far in the direction of products, precautions need to be taken when using this material to measure iron in serum.

Calculations with Equilibrium Constants

The general value of the equilibrium constant gives us information about whether the reactants or the products are favored at equilibrium. Since the product concentrations are in the numerator of the equilibrium expression, a $K_{eq} > 1$ means that the products are favored over the reactants. A $K_{eq} < 1$ means that the reactants are favored over the products.

Though it would often seem that the K_{eq} value would have various units depending on the values of the exponents in the expression, the general rule is that any units are dropped. All K_{eq} values will be reported as having no units.

Sample Problem: Calculating an Equilibrium Constant

Equilibrium occurs when nitrogen monoxide gas reacts with oxygen gas to form nitrogen dioxide gas.

$$2NO(g) + O_2(g) \rightleftarrows 2NO_2(g)$$

At equilibrium at 230°C, the concentrations are measured to be [NO] = 0.0542 M, $[O_2]$ = 0.127 M, and $[NO_2]$ = 15.5 M. Calculate the equilibrium constant at this temperature.

Step 1: List the known values and plan the problem.

Known

- $[NO] = 0.0542$ M
- $[O_2] = 0.127$ M
- $[NO_2] = 15.5$ M

Unknown

- K_{eq} value

The equilibrium expression is first written according to the general form in the text. The equilibrium values are substituted into the expression and the value calculated.

Step 2: Solve.

$$K_{eq} = \frac{[NO_2]^2}{[NO]^2\,[O_2]}$$

Substituting in the concentrations at equilibrium:

$$K_{eq} = \frac{(15.5)^2}{(0.0542)^2\,(0.127)} = 6.44 \times 10^5$$

Step 3: Think about your result.

The equilibrium concentration of the product NO_2 is significantly higher than the concentrations of the reactants NO and O_2. As a result, the K_{eq} value is much larger than 1, an indication that the product is favored at equilibrium.

The equilibrium expression only shows those substances whose concentrations are variable during the reaction. A pure solid or a pure liquid does not have a concentration that will vary during a reaction. Therefore, an equilibrium expression omits pure solids and liquids and only shows the concentrations of gases and aqueous solutions. The decomposition of mercury(II) oxide can be shown by the following equation, followed by its equilibrium expression.

$$2HgO(s) \rightleftarrows 2Hg(l) + O_2(g) \qquad K_{eq} = [O_2]$$

The stoichiometry of an equation can also be used in a calculation of an equilibrium constant. At 40°C, solid ammonium carbamate decomposes to ammonia and carbon dioxide gases.

$$NH_4CO_2NH_2(s) \rightleftarrows 2NH_3(g) + CO_2(g)$$

At equilibrium, the $[CO_2]$ is found to be 4.71×10^{-3} M. Can the K_{eq} value be calculated from just that information? Because the ammonium carbamate is a solid, it is not present in the equilibrium expression.

$$K_{eq} = [NH_3]^2[CO_2]$$

The stoichiometry of the chemical equation indicates that as the ammonium carbamate decomposes, 2 mol of ammonia gas is produced for every 1 mol of carbon dioxide. Therefore, at equilibrium, the concentration of the ammonia will be twice the concentration of carbon dioxide. So $[NH_3] = 2 \times (4.71 \times 10^{-3}) = 9.42 \times 10^{-3}$ M. Substituting these values into the K_{eq} expression:

$$K_{eq} = (9.42 \times 10^{-3})^2(4.71 \times 10^{-3}) = 4.18 \times 10^{-7}$$

Using Equilibrium Constants

The equilibrium constants are known for a great many reactions. Hydrogen and bromine gases combine to form hydrogen bromide gas. At 730°C, the equation and K_{eq} are given below.

$$\mathrm{H_2}(g) + \mathrm{Br_2}(g) \rightleftarrows 2\mathrm{HBr}(g) \qquad K_{eq} = 2.18 \times 10^6$$

A certain reaction is begun with only HBr. When the reaction mixture reaches equilibrium at 730°C, the concentration of bromine gas is measured to be 0.00243 M. What is the concentration of the H_2 and the HBr at equilibrium?

Since the reaction begins with only HBr and the mole ratio of H_2 to Br_2 is 1:1, the concentration of H_2 at equilibrium is also 0.00243 M. The equilibrium expression can be rearranged to solve for the concentration of HBr at equilibrium.

$$\begin{aligned} K_{eq} &= \frac{[\mathrm{HBr}]^2}{[\mathrm{H_2}][\mathrm{Br_2}]} \\ [\mathrm{HBr}] &= \sqrt{K_{eq}[\mathrm{H_2}][\mathrm{Br_2}]} \\ &= \sqrt{2.18 \times 10^6 (0.00243)(0.00243)} = 3.59\ \mathrm{M} \end{aligned}$$

Since the value of the equilibrium constant is very high, the concentration of HBr is much greater than that of H_2 and Br_2 at equilibrium.

Summary

- Calculation of an equilibrium constant is described.

Practice

Work problems 1-4 at the link below:

http://www.chemtopics.com/unit10/ppu10.pdf

Review

1. What are the units for K_{eq}?
2. Why is the temperature specified in equilibrium problems?
3. Why don't we include solids or liquids in equilibrium calculations?

19.5 LeChâtelier's Principle

- State Le Châtelier's principle.

How far down?

There are people who enjoy going up in an airplane, strapping on a parachute, and diving out the door to free-fall and then open the chute and drop to the ground. This stressful activity (so they say) relieves the stress of everyday life. The release of adrenaline caused by this stressful behavior is said to promote a mood enhancement that helps you deal better with other stresses in your daily life.

Le Châtelier's Principle

Chemical equilibrium was studied by French chemist Henri Le Châtelier (1850-1936) and his description of how a system responds to a stress to equilibrium has become known as **Le Châtelier's principle**: When a chemical system that is at equilibrium is disturbed by a stress, the system will respond in order to relieve the stress. Stresses to a chemical system involve changes in the concentration 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. The change to the equilibrium position in every case is either a favoring of the forward reaction or a favoring of the reverse reaction. When the forward reaction is favored, the concentrations of products increases, while the concentrations of reactants decreases. When the reverse reaction is favored, the concentrations of products decreases, while the concentrations of reactants increases.

TABLE 19.1:

Original Equilibrium	Favored Reaction	Result

TABLE 19.1: (continued)

$A \rightleftarrows B$	forward: $A \rightarrow B$	[A] decreases; [B] increases
$A \rightleftarrows B$	reverse: $A \leftarrow B$	[A] increases; [B] decreases

FIGURE 19.3

Henri Le Châtelier

Summary

- Le Châtelier's principle describes how a reaction system at equilibrium is influenced by stress.

Practice

Read Le Châtelier's biography at the link below and answer the following questions:

http://www.chemteam.info/Equilibrium/LeChatelier-Bio.html

1. Who gave him his early training in math and chemistry?
2. What was his first area of investigation?
3. What was another area of interest?
4. When did he first propose his principle?

Review

1. What does Le Châtelier's principle state?
2. If the forward reaction is favored in the equilibrium, what will increase?
3. If the reverse reaction is favored in the equilibrium, what will increase?

- **Le Châtelier's principle:** When a chemical system that is at equilibrium is disturbed by a stress, the system will respond in order to relieve the stress.

19.6 Effect of Concentration

- Describe the effects of concentration changes on the equilibrium of a reaction.

Phenolphthalein is one of those chemicals that has one structure in a high acid environment and another structure in a low acid environment. If the hydrogen ion concentration is high, the compound is colorless, but turns red if the hydrogen ion concentration is low. By adding hydrogen ions to the solution or removing them through a chemical reaction, we can vary the color of the dye.

Effect of Concentration

A change in 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.

$$N_2(g) + 3H_2(g) \rightleftarrows 2NH_3(g)$$

If the concentration of one substance in a system is increased, the system will respond by favoring the reaction that removes 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. The forward reaction speeds up temporarily as a result of the addition of a reactant. The position of equilibrium shifts as more NH_3 is produced. 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 the **Figure** 19.4, if more N_2 is added, a new equilibrium is achieved by the system. The new concentration of NH_3 is higher because of the favoring of the forward reaction. The new concentration of the H_2 is lower. The concentration of N_2 is higher than in the original equilibrium, but went down slightly following the addition of the 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.

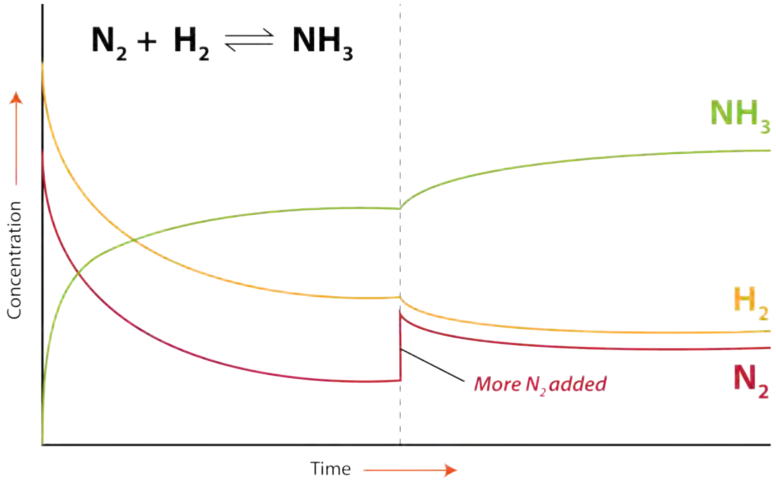


FIGURE 19.4

The Haber-Bosch process is an equilibrium between reactant N_2 and H_2 and product NH_3.

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 increased formation of the reactants, N_2 and H_2.

An equilibrium can also be disrupted by the removal of one of the substances. 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 effect of changes in concentration on an equilibrium system according to Le Châtelier's Principle is summarized below.

TABLE 19.2:

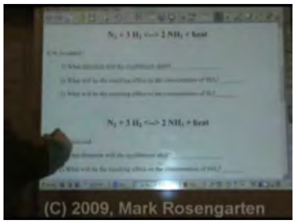
Stress	Response
addition of reactant	forward reaction favored
addition of product	reverse reaction favored
removal of reactant	reverse reaction favored
removal of product	forward reaction favored

Summary

- The effects of concentration changes on an equilibrium are described.

Practice

Watch the video at the link below and answer the following questions:



MEDIA

Click image to the left for more content.

http://www.youtube.com/watch?v=hfaC_ksuJ1k

1. What is stress in an equilibrium reactant?
2. What happens if more reactants are added?
3. What happens if you remove product?

Review

1. In the Haber process, what happens if you add more hydrogen gas?
2. You miscalculate and add too little nitrogen gas. Which way will the equilibrium shift?
3. A mislabeled tank pumps in extra ammonia. What happens to the equilibrium?

19.7 Effect of Temperature

- Describe how temperature affects the direction of an equilibrium reaction.

Don't inhale

We tend to think of carbon monoxide only as a hazardous gas produced from incomplete combustion of carbon products. However, there is a large market for industrially-manufactured carbon monoxide that is used to synthesize most of the acetic acid produced in the world. One reaction that leads to CO formation involves its formation by passing air over excess carbon at high temperatures. The initial product (carbon dioxide) equilibrates with the remaining hot carbon, forming carbon monoxide. At lower temperatures, CO_2 formation is favored while CO is the predominant product above 800°C.

Effect of 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, as a thermochemical equation.

$$N_2(g)+3H_2(g) \rightleftarrows 2NH_3(g)+91\text{ kJ}$$

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, 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.

A decrease in the temperature of a system favors the direction of the reaction that releases heat, the exothermic direction. For the Haber-Bosch process, a decrease in temperature favors the forward reaction. The concentration of NH_3 in the system increases, while the concentrations of N_2 and H_2 decrease.

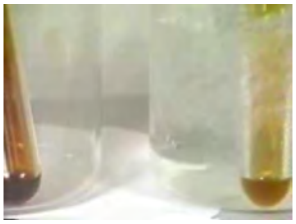
For changes in concentration, the system responds in such a way that the value of the equilibrium constant, K_{eq}, is unchanged. However, a change in temperature shifts the equilibrium and the K_{eq} value either increases or decreases. As discussed in the previous section, values of K_{eq} are dependent 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 reaction in which nitrogen tetroxide is in equilibrium with nitrogen dioxide.

$$\mathrm{N_2O_4}(g) + \mathrm{heat} \rightleftarrows 2\mathrm{NO_2}(g)$$

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 temperature of the system will favor the forward reaction. Conversely, a decrease in temperature will favor the reverse reaction.

Watch a video demonstrating the effect of temperature on the equilibrium between NO_2 and N_2O_4.



MEDIA

Click image to the left for more content.

http://www.youtube.com/watch?v=tlGrBcgANSY

Summary

- The effect of temperature on the direction of an equilibrium reaction is described.

Practice

Read the material at the link below and do the problems:

http://chemwiki.ucdavis.edu/Physical_Chemistry/Chemical_Equilibrium/Effect_Of_Temperature_On_Equilibrium_-Composition

Review

1. Which is the exothermic direction in the Haber process?
2. If we put more heat energy into the system, which way will the equilibrium shift?
3. How can we pull the reaction more strongly to the right?

19.8 Effect of Pressure

- Describe the effect of pressure on an equilibrium reaction.

A dual purpose

The ammonia storage tank in the picture above does two things, One it stores ammonia at high pressure to minimize the reverse reaction that would lead to less ammonia and more nitrogen and hydrogen. Secondly, it sends an important message. Ammonia is used to make methamphetamine, a dangerous drug of abuse. Locks and other safety mechanisms built into the tanks help stop the theft of ammonia to be used in this illicit activity.

Effect of 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 the **Figure ??**.

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 is now confined in a smaller space and so the pressure has increased. According to LeChâtelier'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 one molecule of N_2 combines with three molecules of H_2 to form two molecules of NH_3. The overall result is a decrease in the number of gas molecules in the entire system. This in turn decreases the pressure and provides a relief to the original stress of a pressure increase. An increase in pressure on an equilibrium system favors the reaction which produces fewer total moles of gas. In this case, it is the forward reaction that is favored.

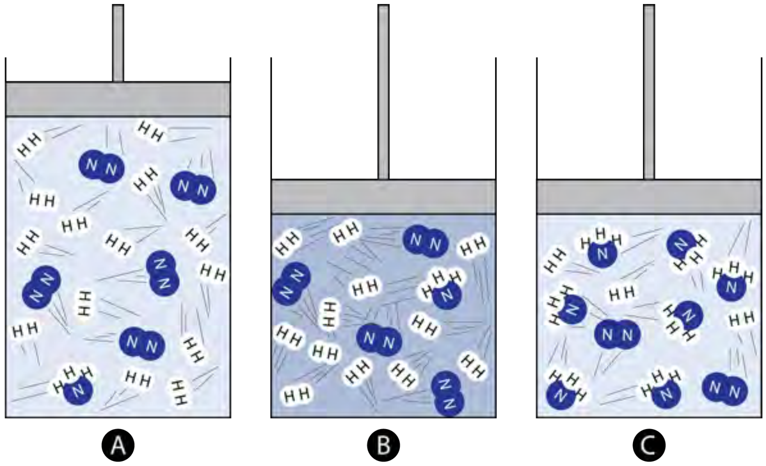


FIGURE 19.5

Effect of pressure on ammonia formation.

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 increases and so would the pressure. A decrease in pressure on an equilibrium system favors the reaction which produces more total moles of gas. This is summarized below.

TABLE 19.3:

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:

$$\mathrm{CaCO_3}(s) \rightleftarrows \mathrm{CaO}(s) + \mathrm{O_2}(g)$$

Oxygen is the only gas in the system. An increase in the pressure of the system slows the rate of decomposition of $CaCO_3$ because the reverse reaction is favored. 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.

$$\mathrm{H_2}(g) + \mathrm{Cl_2}(g) \rightleftarrows 2\mathrm{HCl}(g)$$

Summary

- The influence of pressure on an equilibrium system is described.

Practice

Read the material on pressure at the link below and answer the following questions:

http://www.chemguide.co.uk/physical/equilibria/change.html

1. How is pressure directly related to an equilibrium constant?
2. What is done to related pressures to moles?

19.9 Nonreversible Reactions

- Define a non-reversible reaction.
- List the generic products of non-reversible reactions.

Where's the fire?

Fires are a part of life. Some fires clear the land and allow new growth. Other fires provide warmth on a cold night. Unfortunately, many fires are destructive, leaving damage in their wake. All fires leave the environment changed, never to revert back to the original situation. The carbon dioxide and water generated by a fire go off into the atmosphere and do not return. The change is permanent and irreversible.

Going to Completion

When one of the products of a reaction is removed from the chemical equilibrium system as soon as it is produced, the reverse reaction cannot establish itself and equilibrium is never reached. Reactions such as these are said to go to completion. These processes are often referred to as **non-reversible reactions**. Reactions which go to completion tend to produce one of three types of products: (1) an insoluble precipitate, (2) a gas, (3) a molecular compound such as water. Examples of these reactions are shown below.

1. Formation of a precipitate

   $$\mathrm{AgNO_3}(aq)+\mathrm{NaCl}(aq)\rightarrow \mathrm{NaNO_3}(aq)+\mathrm{AgCl}(s)$$

2. Formation of a gas

   $$\mathrm{Mg}(s)+2\mathrm{HCl}(aq)\rightarrow \mathrm{MgCl_2}(aq)+\mathrm{H_2}(g)$$

3. Formation of water

   $$\mathrm{HCl}(aq)+\mathrm{NaOH}(aq)\rightarrow \mathrm{NaCl}(aq)+\mathrm{H_2O}(l)$$

If we look at these reactions in more detail, we can see some things that are not apparent the way the equations are written. Looking at the first equation, we do not see a double arrow between reactants and products because the reaction is considered essentially irreversible. However if we consider the half-reaction $\mathrm{Ag^+}+\mathrm{Cl^-}\rightarrow\mathrm{AgCl}$, then the reverse reaction would be $\mathrm{AgCl}\rightarrow\mathrm{Ag^+}+\mathrm{Cl^-}$. The K_{eq} for the reverse reaction is 1.8×10^{-10}. For all practical purposes, the reaction goes to completion.

Formation of a gas in an open system is essentially irreversible since the gas escapes into the atmosphere. Looking at the activity series we see that Mg is much higher in the series than hydrogen. So the reaction would be expected to go strongly in the indicated direction.

The third reaction gets a little more complicated. In solution, the reactants HCl and NaOH will be ionize completely as does the NaCl product. Water exists in an equilibrium with $\mathrm{H^+}$ and $\mathrm{OH^-}$, with the dissociation constant for water being 1×10^{-14}. So, in the solution resulting from the reaction given here, the $[\mathrm{H^+}]$ is 1×10^{-7} M, a very insignificant amount. For all practical purposes, this reaction can be said to go to completion.

Summary

- Non-reversible reactions are those that go to completion.

Practice

Read the material at the link below and answer the following questions:

http://onlinehomework.zohosites.com/Irreversible-Reactions.html

1. How do we represent a reversible reaction?
2. How do we represent an irreversible reaction?
3. Why is the decomposition of potassium chlorate an irreversible reaction?
4. Why is the reaction between barium chloride and sulfuric acid irreversible?

Review

1. List the three situations for non-reversible reactions.
2. Silver nitrate also forms a precipitate with NaI. What would this precipitate be?
3. Would the reaction between HBr and KOH also be considered irreversible?

- **non-reversible reaction:** A reaction that never reaches equilibrium because the reverse reaction cannot establish itself.

19.10 LeChâtelier's Principle and the Equilibrium Constant

- Describe the relationship between Le Châtelier's principle and the equilibrium constant.

How much is in savings this month?

With on-line banking, management of your personal finances can become less complicated in some ways. You can automatically deposit paychecks, pay bills, and designate how much goes into savings or other special accounts each month. If you want to maintain 10% of your bank account in savings, you can set up a program that moves money in and out of the account when you get a paycheck or pay bills. The amount of money in savings will change as the money comes in and out of the bank, but the ratio of savings to checking will always be constant.

LeChâtelier's Principle and the Equilibrium Constant

Occasionally, when students apply LeChatelier's principle to an equilibrium problem involving a change in concentration, they assume that K_{eq} must change. This seems logical since we talk about "shifting" the equilibrium in one direction or the other. However, K_{eq} is a constant, for a given equilibrium at a given temperature, so it must not change. Here is an example of how this works. Consider the simplified equilibrium below:

$$A \rightleftarrows B$$

Let's say we have a 1.0 liter container. At equilibrium the following amounts are measured.

$$A = 0.50 \text{ mol}$$
$$B = 1.0 \text{ mol}$$

The value of K_{eq} is given by:

$$K_{eq} = \frac{[B]}{[A]} = \frac{1.0 \text{ M}}{0.50 \text{ M}} = 2.0$$

Now we will disturb the equilibrium by adding 0.50 mole of A to the mixture. The equilibrium will shift towards the right, forming more B. Immediately after the addition of A and before any response, we now have 1.0 mol of A and 1.0 mol of B. The equilibrium then shifts in the forward direction. We will introduce a variable (x), which will represent the change in concentrations as the reaction proceeds. Since the mole ratio of $A : B$ is 1:1, as $[A]$ decreases by the amount x, the $[B]$ increases by the amount x. We set up an analysis called *ICE*, which stands for Initial, Change, and Equilibrium. The values in the table represent molar concentrations.

	A	B
Initial	1.0	1.0
Change	$-x$	$+x$
Equilibrium	$1.0-x$	$1.0+x$

At the new equilibrium position, the values for A and B as a function of x can be set equal to the value of the K_{eq}. Then, one can solve for x.

$$K_{eq} = 2.0 = \frac{[B]}{[A]} = \frac{1.0+x}{1.0-x}$$

Solving for x:

$$\begin{aligned}2.0(1.0-x) &= 1.0+x\\ 2.0-2.0x &= 1.0+x\\ 3.0x &= 1.0\\ x &= 0.33\end{aligned}$$

This value for x is now plugged back in to the Equilibrium line of the table and the final concentrations of A and B after the reaction is calculated.

$$\begin{aligned}[A] &= 1.0-x = 0.67 \text{ M}\\ [B] &= 1.0+x = 1.33 \text{ M}\end{aligned}$$

The value of K_{eq} has been maintained since $\frac{1.33}{0.67} = 2.0$. This shows that even though a change in concentration of one of the substances in equilibrium causes a shift in the equilibrium position, the value of the equilibrium constant does not change.

Summary

- Maintenance of the constant K_{eq} for a reaction is described.

Practice

Read the material at the link below and answer the following questions:

http://www.chem.purdue.edu/gchelp/howtosolveit/Equilibrium/ICEchart.htm

1. What concentration units should be used?
2. What quantities should you use for equilibrium problems?
3. What must the change in each quantity agree with?
4. What is “*x*”?

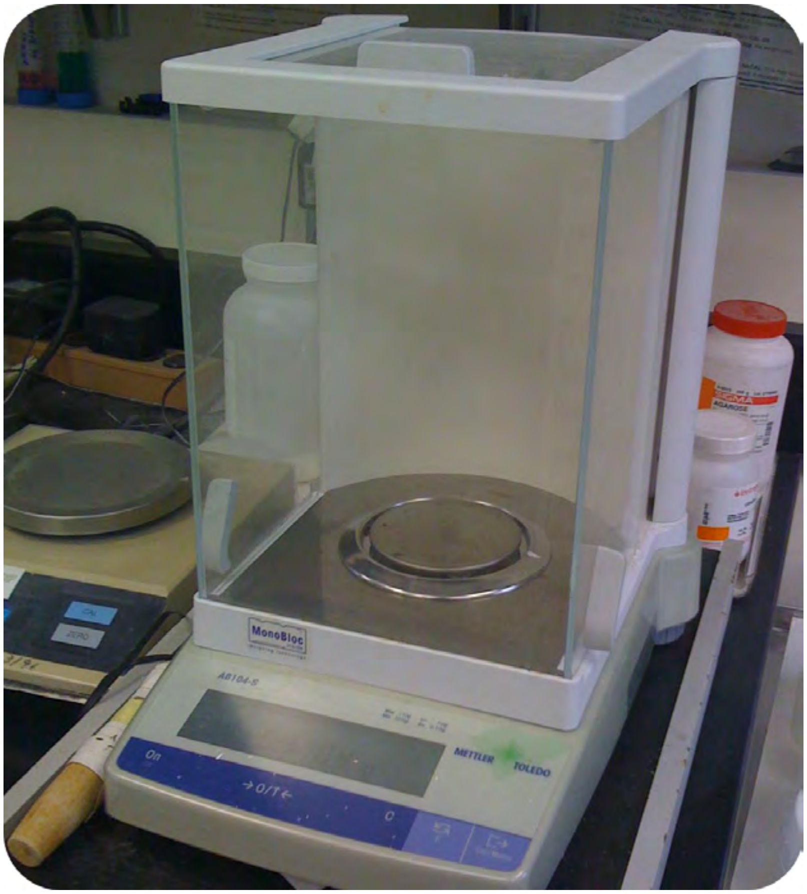
Review

1. Does K_{eq} change for a given reaction at a given temperature?
2. What does ICE stand for?
3. Will the equilibrium position change if materials are added to or removed from the reaction?
4. How does addition or removal of materials affect the K_{eq}?

- **Initial Change Equilibrium (ICE):** A calculation that looks at the initial conditions, change, and new equilibrium in a reaction.

19.11 Solubility Product Constant (Ksp)

- Define solubility product constant.
- Perform calculations involving solubility product constants.



No more weighing

At one time, a major analytical technique was gravimetric analysis. An ion would be precipitated out of solution, purified, and weighed to determine the amount of that ion in the original material. As an example, measurement of Ca^{2+} involved dissolving the sample in water, precipitating the calcium as calcium oxalate, purifying the precipitate, drying it, and weighing the final product. Although this approach can be very accurate (atomic weights for many elements were determined this way), the process is slow, tedious, and prone to a number of errors in technique. Newer methods are now available that measure minute amounts of calcium ions in solution without the long, involved gravimetric approach.

Solubility Product Constant

Ionic compounds have widely differing solubilities. Sodium chloride has a solubility of about 360 g per liter of water at 25°C. Salts of alkali metals tend to be quite soluble. On the other end of the spectrum, the solubility of zinc hydroxide is only 4.2×10^{-4} g/L of water at the same temperature. Many ionic compounds containing hydroxide are relatively insoluble.

Most ionic compounds that are considered to be insoluble will still dissolve to a small extent in water. These "mostly insoluble" compounds are considered to be strong electrolytes because whatever portion of the compound that dissolved also dissociates. As an example, silver chloride dissociates to a small extent into silver ions and chloride ions upon being added to water.

$$\text{AgCl}(s) \rightleftarrows \text{Ag}^+(aq) + \text{Cl}^-(aq)$$

The process is written as an equilibrium because the dissociation occurs only to a small extent. Therefore, an equilibrium expression can be written for the process. Keep in mind that the solid silver chloride does not have a variable concentration and so is not included in the expression.

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$

This equilibrium constant is called the **solubility product constant**, (K_{sp}) and is equal to the mathematical product of the ions each raised to the power of the coefficient of the ion in the dissociation equation.

The stoichiometry of the formula of the ionic compound dictates the form of the K_{sp} expression. For example the formula of calcium phosphate is $Ca_3(PO_4)_2$. The dissociation equation and K_{sp} expression are shown below:

$$\text{Ca}_3(\text{PO}_4)_2(s) \rightleftarrows 3\text{Ca}^{2+}(aq) + 2\text{PO}_4^{3-}(aq) \quad K_{sp} = [\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2$$

The **Table** 19.4 lists solubility product constants for some common nearly insoluble ionic compounds.

TABLE 19.4: **Solubility Product Constants (25 °C)**

Compound	K_{sp}	Compound	K_{sp}
AgBr	5.0×10^{-13}	CuS	8.0×10^{-37}
AgCl	1.8×10^{-10}	$Fe(OH)_2$	7.9×10^{-16}
$Al(OH)_3$	3.0×10^{-34}	$Mg(OH)_2$	7.1×10^{-12}
$BaCO_3$	5.0×10^{-9}	$PbCl_2$	1.7×10^{-5}
$BaSO_4$	1.1×10^{-10}	$PbCO_3$	7.4×10^{-14}
$CaCO_3$	4.5×10^{-9}	PbI_2	7.1×10^{-9}
$Ca(OH)_2$	6.5×10^{-6}	$PbSO_4$	6.3×10^{-7}
$Ca_3(PO_4)_2$	1.2×10^{-26}	$Zn(OH)_2$	3.0×10^{-16}
$CaSO_4$	2.4×10^{-5}	ZnS	3.0×10^{-23}

Summary

- The solubility product constant is defined.
- Calculations using solubility product constants are illustrated.

Practice

Read the material at the link below and solve the problems at the end of the reading:

http://www.tonywhiddon.org/lhs/apchemistry/studyguides/solubility/ksp.htm

Review

1. What does the K_{sp} tell us?
2. Which of the lead salts listed in the table above is the most soluble?
3. What is the exponent for an ion in the equation?

- **solubility product constant,** (K_{sp})**:** The mathematical product of the ions each raised to the power of the coefficient of the ion in the dissociation equation.

19.12 Conversion of Solubility to Ksp

- Define molar solubility.
- Perform calculations involving molar solubility and K_{sp}.

How is baking soda made?

Baking soda (sodium bicarbonate) is prepared by bubbling carbon dioxide gas through a solution of ammonia and sodium chloride. Ammonium carbonate is first formed which then reacts with the NaCl to form sodium bicarbonate and ammonium chloride. The sodium bicarbonate is less soluble than the other materials, so it will precipitate out of solution.

Conversion of Solubility to K_{sp}

Solubility is normally expressed in g/L of saturated solution. However, solubility can also be expressed as the moles per liter. Molar solubility is the number of moles of solute in one liter of saturated solution. In other words, the molar solubility of a given compound represents the highest molarity solution that is possible for that compound. The molar mass of a compound is the conversion factor between solubility and molar solubility. Given that the solubility of $Zn(OH)_2$ is 4.2×10^{-4} g/L, the molar solubility can be calculated as shown below:

$$\frac{4.2 \times 10^{-4}\ \cancel{\text{g}}}{\text{L}} \times \frac{1\ \text{mol}}{99.41\ \cancel{\text{g}}} = 4.2 \times 10^{-6}\ \text{mol/L (M)}$$

Solubility data can be used to calculate the K_{sp} for a given compound. The following steps need to be taken.

1. Convert form solubility to molar solubility.
2. Use the dissociation equation to determine the concentration of each of the ions in mol/L.
3. Apply the K_{sp} equation.

Sample Problem: Calculating K_{sp} from Solubility

The solubility of lead(II) is found experimentally to be 0.533 g/L. Calculate the K_{sp} for lead(II) fluoride.

Step 1: List the known quantities and plan the problem.

Known

- solubility of PbF_2 = 0.533 g/L
- molar mass = 245.20 g/mol

Unknown

- K_{sp} of PbF_2 = ?

The dissociation equation for PbF_2 and the corresponding K_{sp} expression

$$\text{PbF}_2(s) \rightleftarrows \text{Pb}^{2+}(aq) + 2\text{F}^-(aq) \qquad\qquad K_{sp} = [\text{Pb}^{2+}][\text{F}^-]^2$$

The steps above will be followed to calculate the K_{sp} for PbF_2.

Step 2: Solve.

$$\text{molar solubility} \qquad \frac{0.533\ \cancel{\text{g}}}{\text{L}} \times \frac{1\ \text{mol}}{245.20\ \cancel{\text{g}}} = 2.17 \times 10^{-3}\ \text{M}$$

The dissociation equation shows that for every mole of PbF_2 that dissociates, 1 mol of Pb^{2+} and 2 mol of F^- are produced. Therefore, at equilibrium the concentrations of the ions are:

$$[\text{Pb}^{2+}] = 2.17 \times 10^{-3}\ \text{M} \quad \text{and} \quad [\text{F}^-] = 2 \times 2.17 \times 10^{-3} = 4.35 \times 10^{-3}\ \text{M}$$

Substitute into the expression and solve for the K_{sp}.

$$K_{sp} = (2.17 \times 10^{-3})(4.35 \times 10^{-3})^2 = 4.11 \times 10^{-8}$$

Step 3: Think about your result.

The solubility product constant is significantly less than 1 for a nearly insoluble compound such as PbF_2.

Summary

- Molar solubility calculations are described.
- Calculations of K_{sp} using molar solubility are described.

Practice

Read the material at the link below and do the problems at the end:

http://www.chemteam.info/Equilibrium/Calc-Ksp-FromMolSolub.html

Review

1. What are the solution requirements for determining molar solubility?
2. Why do we need to convert mass to molarity to determine K_{sp}?
3. What K_{sp} values would you expect for very insoluble compounds?

- **molar solubility:** The number of moles of solute in one liter of saturated solution.

19.13 Conversion of Ksp to Solubility

- Perform calculations converting K_{sp} to solubility.

How do you purify water?

Purification of water for drinking and other uses is a complicated process. Heavy metals need to be removed, a process accomplished by addition of carbonates and sulfates. Lead contamination can present major health problems, especially for younger children. Lead sulfates and carbonates are very insoluble, so will precipitate out of solution very easily.

Conversion of K_{sp} to Solubility

TABLE 19.5: **Solubility Product Constants (25°C)**

Compound	K_{sp}	Compound	K_{sp}
AgBr	5.0×10^{-13}	CuS	8.0×10^{-37}
AgCl	1.8×10^{-10}	$Fe(OH)_2$	7.9×10^{-16}
$Al(OH)_3$	3.0×10^{-34}	$Mg(OH)_2$	7.1×10^{-12}
$BaCO_3$	5.0×10^{-9}	$PbCl_2$	1.7×10^{-5}
$BaSO_4$	1.1×10^{-10}	$PbCO_3$	7.4×10^{-14}
$CaCO_3$	4.5×10^{-9}	PbI_2	7.1×10^{-9}
$Ca(OH)_2$	6.5×10^{-6}	$PbSO_4$	6.3×10^{-7}
$Ca_3(PO_4)_2$	1.2×10^{-26}	$Zn(OH)_2$	3.0×10^{-16}
$CaSO_4$	2.4×10^{-5}	ZnS	3.0×10^{-23}

The known K_{sp} values from the **Table** 19.5 can be used to calculate the solubility of a given compound by following the steps listed below.

1. Set up an ICE problem (Initial, Change, Equilibrium) in order to use the K_{sp} value to calculate the concentration of each of the ions.
2. The concentration of the ions leads to the molar solubility of the compound.
3. Use the molar mass to convert from molar solubility to solubility.

The K_{sp} of calcium carbonate is 4.5×10^{-9}. We begin by setting up an ICE table showing the dissociation of $CaCO_3$ into calcium ions and carbonate ions. The variable s will be used to represent the molar solubility of $CaCO_3$. In this case, each formula unit of $CaCO_3$ yields one Ca^{2+} ion and one ${CO_3}^{2-}$ ion. Therefore, the equilibrium concentrations of each ion are equal to s.

$$\begin{array}{rccc} & \mathrm{CaCO_3}(s) & \rightleftarrows & \mathrm{Ca^{2+}}(aq) + \mathrm{CO_3^{2-}}(aq) \\ \text{Initial (M)} & & & 0.00 \qquad 0.00 \\ \text{Change (M)} & & & +s \qquad +s \\ \text{Equilibrium (M)} & & & s \qquad s \end{array}$$

The K_{sp} expression can be written in terms of s and then used to solve for s.

$$\begin{aligned} K_{sp} &= [\mathrm{Ca^{2+}}][\mathrm{CO_3^{2-}}] = (s)(s) = s^2 \\ s &= \sqrt{K_{sp}} = \sqrt{4.5 \times 10^{-9}} = 6.7 \times 10^{-5}\ \mathrm{M} \end{aligned}$$

The concentration of each of the ions at equilibrium is 6.7×10^{-5} M. We can use the molar mass to convert from molar solubility to solubility.

$$\frac{6.7 \times 10^{-5}\ \cancel{\mathrm{mol}}}{\mathrm{L}} \times \frac{100.09\ \mathrm{g}}{1\ \cancel{\mathrm{mol}}} = 6.7 \times 10^{-3}\ \mathrm{g/L}$$

So the maximum amount of calcium carbonate that is capable of dissolving in 1 liter of water at 25°C is 6.7×10^{-3} grams. Note that in the case above, the 1:1 ratio of the ions upon dissociation led to the K_{sp} being equal to s^2. This is referred to as a formula of the type AB, where A is the cation and B is the anion. Now let's consider a formula of the type AB_2, such as $Fe(OH)_2$. In this case the setup of the ICE table would look like the following:

$$\begin{array}{rccc} & \mathrm{Fe(OH)_2}(s) & \rightleftarrows & \mathrm{Fe^{2+}}(aq) + 2\mathrm{OH^-}(aq) \\ \text{Initial (M)} & & & 0.00 \qquad 0.00 \\ \text{Change (M)} & & & +s \qquad +2s \\ \text{Equilibrium (M)} & & & s \qquad 2s \end{array}$$

When the K_{sp} expression is written in terms of s, we get the following result for the molar solubility.

$$\begin{aligned} K_{sp} &= [\mathrm{Fe^{2+}}][\mathrm{OH^-}]^2 = (s)(2s)^2 = 4s^3 \\ s &= \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{7.9 \times 10^{-16}}{4}} = 5.8 \times 10^{-6}\ \mathrm{M} \end{aligned}$$

The **Table** 19.6 shows the relationship between K_{sp} and molar solubility based on the formula.

TABLE 19.6:

Compound Type	**Example**	K_{sp} **Expression**	**Cation**	**Anion**	K_{sp} **in Terms of** s
AB	CuS	$[Cu^{2+}][S^{2-}]$	s	s	s^2
AB_2 or A_2B	Ag_2CrO_4	$[Ag^+]^2[CrO_4{}^{2-}]$	$2s$	s	$4s^3$
AB_3 or A_3B	$Al(OH)_3$	$[Al^{3+}][OH^-]^3$	s	$3s$	$27s^4$
A_2B_3 or A_3B_2	$Ba_3(PO_4)_2$	$[Ba^{2+}]^3[PO_4{}^{3-}]^2$	$3s$	$2s$	$108s^5$

The K_{sp} expressions in terms of s can be used to solve problems in which the K_{sp} is used to calculate the molar solubility as in the examples above. Molar solubility can then be converted to solubility.

Summary

- The process of determining solubilities using K_{sp} values is described.

Practice

Read the material at the link below and do the problems at the end.

http://www.tonywhiddon.org/lhs/apchemistry/studyguides/solubility/ksp.htm

Review

1. What information is needed to carry out these calculations?
2. What allows the calculation of molar solubility?
3. How is solubility determined?

19.14 Predicting Precipitates

- Predict solubility of a compound based on the comparison between the ion product and the K_{sp}.

What do you see?

The invention of the X-ray machine had radically improved medical diagnosis and treatment. For the first time, it was possible to see inside a person's body to detect broken bones, tumors, obstructions, and other types of problems. Barium sulfate is often used to examine patients with problems of the esophagus, stomach, and intestines. This insoluble compound coats the inside of the tissues and absorbs X-rays, allowing a clear picture of the interior structure of these organs.

Predicting Precipitates

Knowledge of K_{sp} values will allow you to be able to predict whether or not a precipitate will form when two solutions are mixed together. For example, suppose that a known solution of barium chloride is mixed with a known solution of sodium sulfate. Barium sulfate is a mostly insoluble compound and so could potentially precipitate from the mixture. However, it is first necessary to calculate the **ion product**, $[Ba^{2+}][SO_4{}^{2-}]$ for the solution. If the value of the ion product is less than the value of the K_{sp}, then the solution will remain unsaturated. No precipitate will form because the concentrations are not high enough to begin the precipitation process. If the value of the ion product is greater than the value of the K_{sp}, then a precipitate will form. The formation of the precipitate lowers the concentration of each of the ions until the ion product is exactly equal to the K_{sp}, at which point precipitation ceases.

Sample Problem: Predicting Precipitates

Will a precipitate of barium sulfate form when 10.0 mL of 0.0050 M $BaCl_2$ is mixed with 20.0 mL of 0.0020 M Na_2SO_4?

FIGURE 19.6

Barium sulfate is used as a component of white pigment for paints and as an agent in certain x-ray imaging processes.

Step 1: List the known quantities and plan the problem.

Known

- concentration of $BaCl_2$ = 0.0050 M
- volume of $BaCl_2$ = 10.0 mL
- concentration of Na_2SO_4 = 0.0020 M
- volume of Na_2SO_4 = 20.0 mL
- K_{sp} of $BaSO_4 = 1.1 \times 10^{-10}$

Unknown

- ion product $[Ba^{2+}][SO_4{}^{2-}]$
- if a precipitate forms

The concentration and volume of each solution that is mixed together must be used to calculate the $[Ba^{2+}]$ and the $[SO_4{}^{2-}]$. Each individual solution is diluted when they are mixed together. The ion product is calculated and compared to the K_{sp} to determine if a precipitate forms.

Step 2: Solve.

The moles of each ion from the original solutions are calculated by multiplying the molarity by the volume in liters.

$$\begin{aligned}\text{mol Ba}^{2+} &= 0.0050\text{ M} \times 0.010\text{ L} = 5.0 \times 10^{-5}\text{ mol Ba}^{2+}\\ \text{mol SO}_4^{2-} &= 0.0020\text{ M} \times 0.020\text{ L} = 4.0 \times 10^{-5}\text{ mol SO}_4^{2-}\end{aligned}$$

The concentration of each ion after dilution is then calculated by dividing the moles by the final solution volume of 0.030 L.

$$\begin{aligned}[\text{Ba}^{2+}] &= \frac{5.0 \times 10^{-5}\text{ mol}}{0.030\text{ L}} = 1.7 \times 10^{-3}\text{ M}\\ \left[\text{SO}_4^{2-}\right] &= \frac{4.0 \times 10^{-5}\text{ mol}}{0.030\text{ L}} = 1.3 \times 10^{-3}\text{ M}\end{aligned}$$

Now the ion product is calculated.

$$[\text{Ba}^{2+}][\text{SO}_4^{2-}] = (1.7 \times 10^{-3})(1.3 \times 10^{-3}) = 2.2 \times 10^{-6}$$

Since the ion product is greater than the K_{sp}, a precipitate of barium sulfate will form.

Step 3: Think about your result.

Two significant figures are appropriate for the calculated value of the ion product.

Summary

- Calculations are shown which allow the prediction of precipitate formation based on K_{sp}.

Practice

Work the problems at the link below:

http://misterguch.brinkster.net/jan2002.pdf

A useful table for constants can be found at http://users.stlcc.edu/gkrishnan/ksptable.html

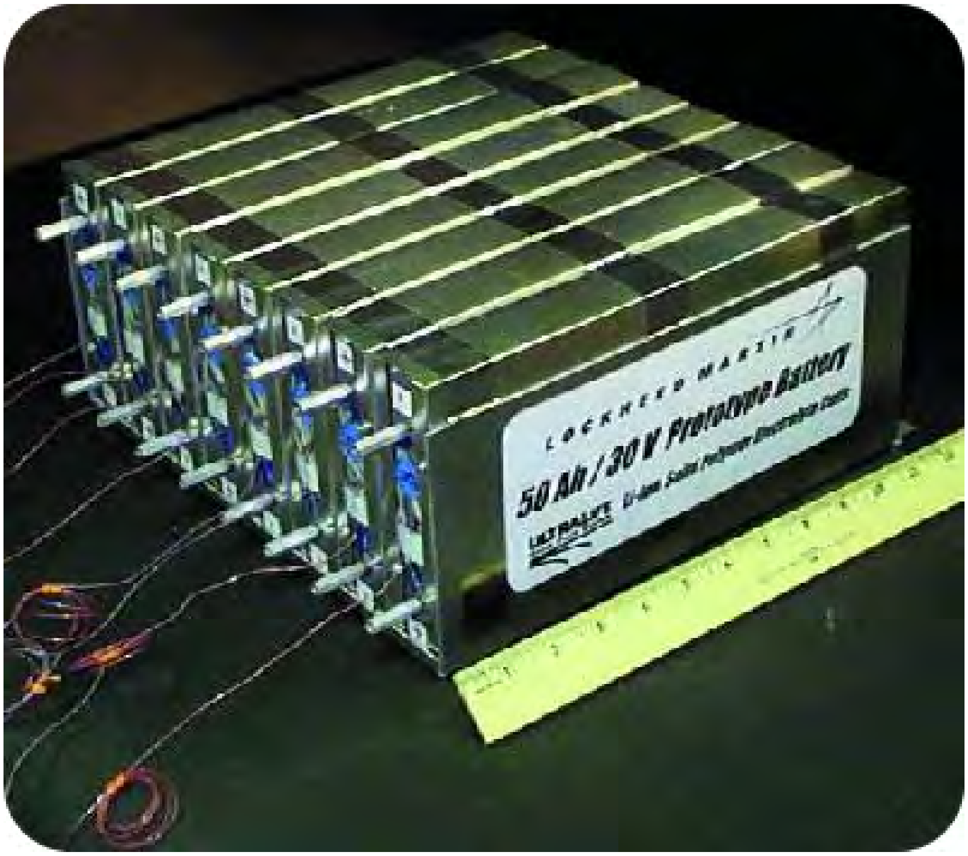
Review

1. What would be the equation for the ion product of $BaCl_2$?
2. What happens if the ion product is less than the K_{sp}?
3. Why did we not need to calculate an ion product for NaCl?

- **ion product:** The product of the concentrations of ions in a solution.

19.15 Common Ion Effect

- Define common ion.
- Define common ion effect.
- Perform calculations involving the common ion effect.



Quite a charge

Lithium carbonate is an essential component of lithium batteries, which tend to be longer-lasting than regular alkaline batteries. The material is obtained from lithium ores by adding CO_2 under high pressure to form the more soluble $LiHCO_3$. The mixture is then depressurized to remove the carbon dioxide and the lithium carbonate precipitates out of solution.

Common Ion Effect

In a saturated solution of calcium sulfate, an equilibrium exists between the solid calcium sulfate and its ions in solution.

$$\mathrm{CaSO_4}(s) \rightleftarrows \mathrm{Ca^{2+}}(aq) + \mathrm{SO_4^{2-}}(aq) \qquad K_{sp} = 2.4 \times 10^{-5}$$

Suppose that some calcium nitrate were added to this saturated solution. Immediately, the concentration of the calcium ion in the solution would increase. As a result, the ion product of the $[\mathrm{Ca^{2+}}]$ times the $[\mathrm{SO_4}^{2-}]$ would increase and now be greater than the K_{sp}. According to LeChâtelier's principle, the equilibrium above would shift to the left in order to relieve the stress of the added calcium ion. Additional calcium sulfate would precipitate out of the solution until the ion product once again becomes equal to the K_{sp}. Note that in the new equilibrium the concentrations of the calcium ion and the sulfate ion would no longer be equal to each other. The calcium ion concentration would be larger than the sulfate ion concentration.

This situation describes the common ion effect. A **common ion** is an ion that is in common to both salts in a solution. In the above example, the common ion is Ca^{2+}. The **common ion effect** is a decrease in the solubility of an ionic compound as a result of the addition of a common ion. Adding calcium ion to the saturated solution of calcium sulfate causes additional $CaSO_4$ to precipitate from the solution, lowering its solubility. The addition of a solution containing sulfate ion, such as potassium sulfate, would result in the same common ion effect.

Sample Problem: The Common Ion Effect

What is the concentration of zinc ion in 1.00 L of a saturated solution of zinc hydroxide to which 0.040 mol of NaOH has been added?

Step 1: List the known quantities and plan the problem.

Known

- $K_{sp} = 3.0 \times 10^{-16}$ (from table in the concept Conversion of Ksp to Solubility
- moles of added NaOH = 0.040 mol
- volumes of solution = 1.00 L

Unknown

- $[Zn^{2+}]$ = ? M

Express the concentrations of the two ions relative to the variable s. The concentration of the zinc ion will be equal to s, while the concentration of the hydroxide ion will be equal to $0.040+2s$.

Step 2: Solve.

The K_{sp} expression can be written in terms of the variable s.

$$K_{sp} = [\mathrm{Zn}^{2+}][\mathrm{OH}^-]^2 = (s)(0.040+2s)^2$$

Because the value of the K_{sp} is so small, we can make the assumption that the value of s will be very small compared to 0.040. This simplifies the mathematics involved in solving for s.

$$K_{sp} = (s)(0.040)^2 = 0.0016\,s = 3.0 \times 10^{-16}$$
$$s = \frac{K_{sp}}{\left[\mathrm{OH}^-\right]^2} = \frac{3.0 \times 10^{-16}}{0.0016} = 1.9 \times 10^{-13}\ \mathrm{M}$$

The concentration of the zinc ion is equal to s and so $[Zn^{2+}]$ = 1.9×10^{-13} M.

Step 3: Think about your result.

The relatively high concentration of the common ion, OH^-, results in a very low concentration of zinc ion. The molar solubility of the zinc hydroxide is less in the presence of the common ion than it would be in water.

Summary

- The common ion and common ion effect are described.
- Calculations involving the common ion effect are described.

Practice

Work the problems at the link below:

http://science.widener.edu/svb/tutorial/saltcomioncsn7.html

Review

1. How is Le Châtelier's principle involved in the common-ion effect?
2. Could the common ion effect ever increase the solubility of a compound?
3. In the sample problem, what would the effect be of adding $Zn(NO_3)_2$?

- **common ion:** An ion that is in common to both salts in a solution.
- **common ion effect:** A decrease in the solubility of an ionic compound as a result of the addition of a common ion.

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CHAPTER 20 Entropy and Free Energy

Chapter Outline

20.1 Entropy

- Define entropy.
- List factors that influence the entropy of a system.
- List situations that illustrate the concept of entropy.

What will it look like?

When the pieces of a jigsaw puzzle are dumped from the box, the pieces naturally hit the table in a very random state. In order to put the puzzle together, a great deal of work must be done in order to overcome the natural disorder of the pieces. The pieces need to be turned right-side up, then sorted by color or edge (some people like to put the border together first). Then comes the challenge of finding the exact spot of each piece of the puzzle in order to get the final organized picture.

Entropy

There is a tendency in nature for systems to proceed toward a state of greater disorder or randomness. **Entropy** is a measure of the degree of randomness or disorder of a system. Entropy is an easy concept to understand when thinking about everyday situations. The entropy of a room that has been recently cleaned and organized is low. As time goes by, it likely will become more disordered and thus its entropy will increase (see **Figure** 20.1). The natural tendency of a system is for its entropy to increase.

Chemical reactions also tend to proceed in such a way as to increase the total entropy of the system. How can you tell if a certain reaction shows an increase or a decrease in entropy? The molecular state of the reactants and products provide certain clues. The general cases below illustrate entropy at the molecular level.

1. For a given substance, the entropy of the liquid state is greater than the entropy of the solid state. Likewise, the entropy of the gas is greater than the entropy of the liquid. Therefore, entropy increases in processes in

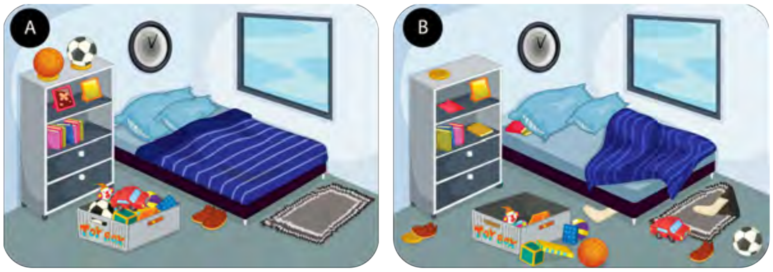


FIGURE 20.1
The messy room on the right has more entropy than the highly ordered room on the left.

which solid or liquid reactants form gaseous products. Entropy also increases when solid reactants form liquid products.

2. Entropy increases when a substance is broken up into multiple parts. The process of dissolving increases entropy because the solute particles become separated from one another when a solution is formed.
3. Entropy increases as temperature increases. An increase in temperature means that the particles of the substance have greater kinetic energy. The faster moving particles have more disorder than particles, which are moving more slowly at a lower temperature.
4. Entropy generally increases in reactions in which the total number of product molecules is greater than the total number of reactant molecules. An exception to this rule is when a gas is being produced from nongaseous reactants.

The examples below will serve to illustrate how the entropy change in a reaction can be predicted.

$Cl_2(g) \rightarrow Cl_2(l)$

The entropy is decreasing because a gas is becoming a liquid.

$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

The entropy is increasing because a gas is being produced and the number of molecules is increasing.

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

The entropy is decreasing because four total reactant molecules are forming two total product molecules. All are gases.

$AgNO_3(aq) + NaCl(aq) \rightarrow NaNO_3(aq) + AgCl(s)$

The entropy is decreasing because a solid is formed from aqueous reactants.

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

The entropy change is unknown (but likely not zero), because there are equal numbers of molecules on both sides of the equation and all are gases.

Summary

- Entropy is defined.
- Situations involving entropy changes are described.

Practice

Read the material at the link below and answer the questions:

http://www.kentchemistry.com/links/Kinetics/entropy.htm

Review

Indicate whether entropy increases or decreases in each of the following situations:

1. The jigsaw puzzle is taken apart and put back in the box.
2. Clothes are folded and put away.
3. ice → steam.
4. $\mathrm{Pb(NO_3)_2}(aq) + 2\mathrm{KI}(aq) \rightarrow \mathrm{PbI_2}(s) + 2\mathrm{KNO_3}$.

- **entropy:** A measure of the degree of randomness or disorder of a system.

20.2 Standard Entropy

- Perform change in entropy calculations involving standard entropy.

How much energy is available?

As scientists explore energy supplies, geothermal sources look very appealing. The natural geysers that exist in some parts of the world could possibly be harnessed to provide power for many purposes. The change in energy content and the release of energy as steam condenses to liquid can help fill some of our growing energy needs.

Standard Entropy

All molecular motion ceases at absolute zero (0 K). Therefore, the entropy of a pure crystalline substance at absolute zero is defined to be equal to zero. As the temperature of the substance increases, its entropy increases because of an increase in molecular motion. The absolute or **standard entropy** of substances can be measured. The symbol for entropy is S and the standard entropy of a substance is given by the symbol S°, indicating that the standard entropy is determined under standard conditions. The units for entropy are J/K • mol. Standard entropies for a few substances are shown in the **Table** 20.1.

TABLE 20.1: **Standard Entropy Values at 25°C**

Substance	S° (J/K · mol)
$H_2(g)$	131.0
$O_2(g)$	205.0
$H_2O(l)$	69.9
$H_2O(g)$	188.7
C(graphite)	5.69
C(diamond)	2.4

The knowledge of the absolute entropies of substances allows us to calculate the entropy change (ΔS°) for a reaction. For example, the entropy change for the vaporization of water can be found as follows.

$$\begin{aligned}\Delta S^\circ &= S^\circ(H_2O(g)) - S^\circ(H_2O(l)) \\ &= 188.7 \text{ J/K}\cdot\text{mol} - 69.9 \text{ J/K}\cdot\text{mol} = 118.8 \text{ J/K}\cdot\text{mol}\end{aligned}$$

The entropy change for the vaporization of water is positive because the gas state has higher entropy than the liquid state.

In general, the entropy change for a reaction can be determined if the standard entropies of each substance are known. The equation below can be applied.

$$\Delta S^\circ = \sum nS^\circ(\text{products}) - \sum nS^\circ(\text{reactants})$$

The standard entropy change is equal to the sum of all the standard entropies of the products minus the sum of all the standard entropies of the reactants. The symbol "*n*" signifies that each entropy must first be multiplied by its coefficient in the balanced equation. The entropy change for the formation of liquid water from gaseous hydrogen and oxygen can be calculated using this equation.

$$\begin{aligned}&2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \\ &\Delta S^\circ = 2(69.9) - [2(131.0) + 1(205.0)] = -327 \text{ J/K}\cdot\text{mol}\end{aligned}$$

The entropy change for this reaction is highly negative because three gaseous molecules are being converted into two liquid molecules. According to the drive towards higher entropy, the formation of water from hydrogen and oxygen is an unfavorable reaction. In this case, the reaction is highly exothermic and the drive towards a decrease in energy allows the reaction to occur.

Summary

- Calculations of change in entropy using standard entropy are described.

Practice

Read the material at the link below and do the problems:

http://www.science.uwaterloo.ca/ cchieh/cact/applychem/entropy.html

Review

1. When is the entropy of any material at its lowest?
2. In the reaction involving the formation of water from hydrogen and oxygen, why is the entropy value negative?
3. Why would diamond have a lower standard entropy value than graphite?

- **standard entropy:** The entropy of one mole of substance under standard conditions.

20.3 Spontaneous and Nonspontaneous Reactions

- Define spontaneous reaction.
- Define nonspontaneous reaction.
- Give examples of spontaneous and nonspontaneous reactions.

Watch that nitro!

Nitroglycerin is tricky stuff. An active ingredient in dynamite (where it is stabilized), "raw" nitroglycerin is very unstable. Physical shock will cause the material to explode. The reaction is shown below:

$$4C_3H_5(ONO_2)_3 \rightarrow 12CO_2 + 10H_2O + 6N_2 + O_2$$

The explosion of nitroglycerin releases large volumes of gases and is very exothermic.

Spontaneous Reactions

Reactions are favorable when they result in a decrease in enthalpy and an increase in entropy of the system. When both of these conditions are met, the reaction occurs naturally. A **spontaneous reaction** is a reaction that favors the formation of products at the conditions under which the reaction is occurring. A roaring bonfire is an example of a spontaneous reaction, being exothermic (a decrease in the energy of the system as energy is released to the surroundings as heat). The products of a fire are composed partly of gases such as carbon dioxide and water vapor. The entropy of the system increases during a combustion reaction. The combination of energy decrease and entropy increase dictates that combustion reactions are spontaneous reactions.

A **nonspontaneous reaction** is a reaction that does not favor the formation of products at the given set of conditions. In order for a reaction to be nonspontaneous, it must be endothermic, accompanied by a decrease in entropy, or both.

FIGURE 20.2

Bonfire.

Our atmosphere is composed primarily of a mixture of nitrogen and oxygen gases. One could write an equation showing these gases undergoing a chemical reaction to form nitrogen monoxide.

$$N_2(g) + O_2(g) \rightarrow 2NO(g)$$

Fortunately, this reaction is nonspontaneous at normal temperatures and pressures. It is a highly endothermic reaction with a slightly positive entropy change (ΔS). Nitrogen monoxide is capable of being produced at very high temperatures and been observed to form as a result of lightning strikes.

One must be careful not to confuse the term spontaneous with the notion that a reaction occurs rapidly. A spontaneous reaction is one in which product formation is favored, even if the reaction is extremely slow. A piece of paper will not suddenly burst into flames, although its combustion is a spontaneous reaction. What is missing is the required activation energy to get the reaction started. If the paper were to be heated to a high enough temperature, it would begin to burn, at which point the reaction would proceed spontaneously until completion.

In a reversible reaction, one reaction direction may be favored over the other. Carbonic acid is present in carbonated beverages. It decomposes spontaneously to carbon dioxide and water according to the following reaction.

$$H_2CO_3(aq) \rightleftarrows CO_2(g) + H_2O(l)$$

If you were to start with pure carbonic acid in water and allow the system to come to equilibrium, more than 99% of the carbonic acid would be converted into carbon dioxide and water. The forward reaction is spontaneous because the products of the forward reaction are favored at equilibrium. In the reverse reaction, carbon dioxide and water are the reactants and carbonic acid is the product. When carbon dioxide is bubbled into water, less than 1% is converted to carbonic acid when the reaction reaches equilibrium. The reverse reaction as written above is not spontaneous.

Summary

- Spontaneous and nonspontaneous reactions are defined.
- Examples of both types of reactions are given.

Practice

Read the material at the link below and answer the following questions:

http://chemistry.about.com/od/workedchemistryproblems/a/Entropy-And-Reaction-Spontaneity-Example-Problem.htm

1. Why is system I a spontaneous reaction?
2. Why is system II not spontaneous?
3. Why is system III spontaneous?

Review

1. Why is a combustion reaction spontaneous?
2. Is NO formation spontaneous at room temperature?
3. How do we know that the equilibrium between carbonic acid and CO_2 goes strongly to the right?

- **nonspontaneous reaction:** A reaction that does not favor the formation of products at the given set of conditions.
- **spontaneous reaction:** A reaction that favors the formation of products at the conditions under which the reaction is occurring.

20.4 Free Energy

- Define free energy.
- Describe how changes in ΔH and ΔS affect ΔG.

All aboard!

The steam engine picture above is slowly going out of style, but is still a pictures que part of modern railroading. The water in a boiler would be heated by a fire (usually coal) and turned to steam. This steam would then push the pistons that drove the wheels of the train. Converting coal to heat and then to steam and pressure allowed work to be done in moving the train.

Free Energy

Many chemical reactions and physical processes release energy that can be used to do other things. When the fuel in a car is burned, some of the released energy is used to power the vehicle. **Free energy** is energy that is available to do work. Spontaneous reactions release free energy as they proceed. Recall that the determining factors for spontaneity of a reaction are the enthalpy and entropy changes that occur for the system. The free energy change of a reaction is a mathematical combination of the enthalpy change and the entropy change.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

The symbol for free energy is G, in honor of American scientist Josiah Gibbs (1839-1903), who made many contributions to thermodynamics. The change in Gibbs free energy is equal to the change in enthalpy minus the mathematical product of the change in entropy multiplied by the Kelvin temperature. Each thermodynamic quantity in the equation is for substances in their standard states. The usual units for ΔH is kJ/mol, while ΔS is often reported in J/K • mol. It is necessary to change the units for ΔS to kJ/K • mol, so that the calculation of ΔG is in kJ/mol.

A spontaneous reaction is one that releases free energy, and so the sign of ΔG must be negative. Since both ΔH and ΔS can be either positive or negative, depending on the characteristics of the particular reaction, there are four different general outcomes for ΔG and these are outlined in the table below.

TABLE 20.2: **Enthalpy, Entropy, and Free Energy Changes**

ΔH	ΔS	ΔG
− value (exothermic)	+ value (disordering)	always negative
+ value (endothermic)	+ value (disordering)	negative at higher temperatures
− value (exothermic)	− value (ordering)	negative at lower temperatures
+ value (endothermic)	− value (ordering)	never negative

Keep in mind that the temperature in the Gibbs free energy equation is the Kelvin temperature and so can only be positive. When ΔH is negative and ΔS is positive, the sign of ΔG will always be negative, and the reaction will be spontaneous at all temperatures. This corresponds to both driving forces being in favor of product formation. When ΔH is positive and ΔS is negative, the sign of ΔG will always be positive, and the reaction can never be spontaneous. This corresponds to both driving forces working against product formation.

Summary

- Free energy is defined.
- Relationships between enthalpy, entropy, and free energy are described.

Practice

Watch the video at the link and answer the following questions:

MEDIA

Click image to the left for more content.

http://www.youtube.com/watch?v=DPjMPeU5OeM

1. What is another term for free energy?
2. What happens to the total energy when the ball rolls down the slide?
3. How does H change in a spontaneous reaction?
4. How does S change in a spontaneous reaction?

Review

1. What do spontaneous reactions do?
2. What are the units for ΔH?

3. What are the units for ΔS?

- **free energy:** Energy that is available to do work.

20.5 Calculating Free Energy Change (ΔG°)

- Perform free energy calculations using enthalpy, entropy, and temperature values.

Time for dessert!

When you are baking something, you heat the oven to the temperature indicated in the recipe. Then you mix all the ingredients, put them in the proper baking dish, and place them in the oven for a specified amount of time. If you had mixed the ingredients and left them out at room temperature, not much would change. The materials need to be heated to a given temperature for a set time in order for the ingredients to react with one another and produce a delicious final product.

Calculating Free Energy (ΔG°)

The free energy change of a reaction can be calculated using the following expression.

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

where $\Delta G =$ free energy change (kJ/mol)

$\Delta H =$ change in enthalpy (kJ/mol)

$\Delta S =$ change in entropy ($\text{J/K} \cdot \text{mol}$)

$T =$ temperature (Kelvin)

Note that all values are for substances in their standard state. In performing calculations, it is necessary to change the units for ΔS to kJ/K • mol, so that the calculation of ΔG is in kJ/mol.

Sample Problem: Gibbs Free Energy

Methane gas reacts with water vapor to produce a mixture of carbon monoxide and hydrogen according to the balanced equation below.

$$\text{CH}_4(g) + \text{H}_2\text{O}(g) \rightarrow \text{CO}(g) + 3\text{H}_2(g)$$

The ΔH° for the reaction is +206.1 kJ/mol, while the ΔS° is +215 J/K • molΔG° at 25°C and determine if the reaction is spontaneous at that temperature.

Step 1: List the known values and plan the problem.

Known

- $\Delta H^\circ = 206.1$ *kJ/mol*
- $\Delta S^\circ = 215\ \text{J/K} \cdot \text{mol} = 0.215\ \text{kJ/K} \cdot \text{mol}$
- $T = 25°\text{C} = 298\ \text{K}$

Unknown

- $\Delta G^\circ =?$ kJ/mol

Prior to substitution into the Gibbs free energy equation, the entropy change is converted to kJ/K • mol

Step 2: Solve.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 206.1\ \text{kJ/mol} - 298\ \text{K}(0.215\ \text{kJ/K} \cdot \text{mol}) = +142.0\ \text{kJ/mol}$$

The resulting positive value of ΔG indicates that the reaction is not spontaneous at 25°C.

Step 3: Think about your result.

The unfavorable driving force of increasing enthalpy outweighed the favorable increase in entropy. The reaction will be spontaneous only at some elevated temperature.

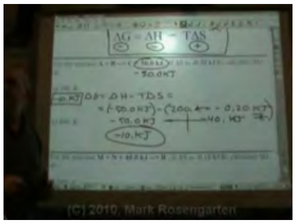
Available values for enthalpy and entropy changes are generally measured at the standard conditions of 25°C and 1 atm pressure. They are slightly temperature dependent and so we must use caution when calculating specific ΔG values at temperatures other than 25°C, as in the practice problem above. However, since the values for ΔH and ΔS do not change a great deal, the tabulated values can safely be used when making general predictions about the spontaneity of a reaction at various temperatures.

Summary

- Calculations of free energy changes are described.

Practice

Watch the video at the link below and answer the following questions:



MEDIA

Click image to the left for more content.

http://www.youtube.com/watch?v=Jw2G5UQqZXg

1. Why is ΔH negative in this example?
2. What would happen if you forgot to change the sign of the $T\Delta S$ value in the first calculation?
3. What indicates that the reaction is spontaneous?

Review

1. What would happen to ΔH if you forgot to change the units for ΔS to kJ/K • mol
2. What are standard conditions for enthalpy and entropy changes?
3. At what temperature would the reaction become spontaneous?

20.6 Temperature and Free Energy

- Describe the effect of temperature on ΔG.

How is steel produced?

Iron ore (Fe_2O_3) and coke (an impure form of carbon) are heated together to make iron and carbon dioxide. The reaction is non-spontaneous at room temperature, but becomes spontaneous at temperature above 842 K. The iron can then be treated with small amounts of other materials to make a variety of steel products.

Temperature and Free Energy

Consider the reversible reaction in which calcium carbonate decomposes into calcium oxide and carbon dioxide gas. The production of CaO (called quicklime) has been an important reaction for centuries.

$$\mathrm{CaCO_3}(s) \rightleftarrows \mathrm{CaO}(s) + \mathrm{CO_2}(g)$$

The ΔH° for the reaction is 177.8 kJ/mol, while the ΔS° is 160.5 J/K • mol. The reaction is endothermic with an increase in entropy due to the production of a gas. We can first calculate the ΔG° at 25°C in order to determine if the reaction is spontaneous at room temperature.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 177.8 \text{ kJ/mol} - 298\ K(0.1605 \text{ kJ/K} \cdot \text{mol}) = 130.0 \text{ kJ/mol}$$

Since the ΔG° is a large positive quantity, the reaction strongly favors the reactants and very little products would be formed. In order to determine a temperature at which ΔG° will become negative, we can first solve the equation for the temperature when ΔG° is equal to zero.

$$0 = \Delta H^\circ - T\Delta S^\circ$$
$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{177.8 \text{ kJ/mol}}{0.1605 \text{ kJ/K} \cdot \text{mol}} = 1108 \text{ K} = 835^\circ \text{ C}$$

So at any temperature higher than 835°C, the value of ΔG° will be negative and the decomposition reaction will be spontaneous.

FIGURE 20.3

This lime kiln in Cornwall was used to produce quicklime (calcium oxide), an important ingredient in mortar and cement.

Recall that the assumption that ΔH° and ΔS° are independent of temperature means that the temperature at which the sign of ΔG° switches from being positive to negative (835°C) is an approximation. It is also important to point out that one should not assume that absolutely no products are formed below 835°C and that at that temperature decomposition suddenly begins. Rather, at lower temperatures, the amount of products formed is simply not great enough to say that the products are favored. When this reaction is performed, the amount of products can be detected by monitoring the pressure of the CO_2 gas that is produced. Above about 700°C, measurable amounts of CO_2 are produced. The pressure of CO_2 at equilibrium gradually increases with increasing temperature. Above 835°C, the pressure of CO_2 at equilibrium begins to exceed 1 atm, the standard-state pressure. This is an indication that the products of the reaction are now favored above that temperature. When quicklime is manufactured, the CO_2 is constantly removed from the reaction mixture as it is produced. This causes the reaction to be driven towards the products according to LeChâtelier's principle.

Summary

- The influence of temperature on free energy is described.

Practice

Read the material at the link below and answer the following questions:

http://www.chem1.com/acad/webtext/thermeq/TE4.html#2B

1. Is an exothermic reaction where entropy increases spontaneous or nonspontaneous?

2. Give an example of a process where a process proceeds spontaneously only below a certain temperature.
3. If $\Delta H > 0$ and $\Delta S < 0$, can the reaction ever be spontaneous?

Review

1. If you increased the pressure of CO_2 in the quicklime reaction, what would happen to the equilibrium?
2. Why do we calculate the situation where ΔG is zero?
3. At temperatures below 835°C, is any product formed?

20.7 Changes of State and Free Energy

- Describe how a change of state influences free energy.

In hot water

Energy in a body of water can be gained or lost depending on conditions. When water is heated, if the temperature is hot enough, steam is generated. The increase in heat energy creates a higher level of disorder in the water molecules as they boil off and leave the liquid.

Changes of State and Free Energy

At the temperature at which a change of state occurs, the two states are in equilibrium with one another. For an ice-water system, equilibrium takes place at 0°C, so ΔG° is equal to 0 at that temperature. The heat of fusion of water is known to be equal to 6.01 kJ/mol, and so the Gibbs free energy equation can be solved for the entropy change that occurs during the melting of ice. The symbol ΔS_{fus} represents the entropy change during the melting process, while T_{f} is the freezing point of water.

$$\begin{aligned}\Delta G &= 0 = \Delta H - T\Delta S\\ \Delta S_{\text{fus}} &= \frac{\Delta H_{\text{fus}}}{T_{\text{f}}} = \frac{6.01 \text{ kJ/mol}}{273 \text{ K}} = 0.0220 \text{ kJ/K}\cdot\text{mol} = 22.0 \text{ J/K}\cdot\text{mol}\end{aligned}$$

The entropy change is positive as the solid state changes into the liquid state. If the transition went from the liquid to the solid state, the numerical value for ΔS would be the same, but the sign would be reversed since we are going from a less ordered to a more ordered situation.

A similar calculation can be performed for the vaporization of liquid to gas. In this case we would use the molar heat of vaporization. This value would be 40.79 kJ/mol. The ΔS_{vap} would then be as follows:

$$\Delta S = \frac{40.79 \text{ kJ/mol}}{373 \text{ K}} = 0.1094 \text{ kJ/K} \cdot \text{mol} = 109.4 \text{ J/K} \cdot \text{mol}$$

The value is positive, again reflecting the increase in disorder going from liquid to vapor. Condensation from vapor to liquid would give a negative value for ΔS.

Summary

- Calculations are shown for determining entropy changes at transition temperatures (ice → water or water → vapor and reverse).

Practice

Read the material on the link below and answer the following questions:

http://www.everyscience.com/Chemistry/Physical/Entropy/f.1311.php

1. Is the transfer of heat reversible or irreversible at the transition temperature?
2. If the phase transition is exothermic, is the entropy change positive or negative?
3. What is Trouton's Rule?

Review

1. What precautions need to be taken in selecting a value for ΔH?
2. Why is temperature selection important?
3. Why would the entropy of vaporization be so much larger than the entropy of fusion?

20.8 Calculations of Free Energy and Keq

- Describe the relationship between ΔG° and K_{eq}.
- Perform calculations involving these two parameters.

What are these called when they point down?

Formation of stalactites (pointing down) and stalagmites (pointing up) is a complex process. Solutions of minerals drip down and absorb carbon dioxide as the water flows. Calcium carbonate dissolves in this liquid and redeposits on the rock as the carbon dioxide is dissipated into the environment.

Equilibrium Constant and ΔG

At equilibrium the ΔG for a reversible reaction is equal to zero. K_{eq} relates the concentrations of all substances in the reaction at equilibrium. Therefore we can write (through a more advanced treatment of thermodynamics) the following equation:

$$\Delta G^\circ = -RT \ln K_{eq}$$

The variable R is the ideal gas constant (8.314 J/K • mol), T is the Kelvin temperature, and $\ln K_{eq}$ is the natural logarithm of the equilibrium constant.

When K_{eq} is large, the products of the reaction are favored and the negative sign in the equation means that the ΔG° is negative. When K_{eq} is small, the reactants of the reaction are favored. The natural logarithm of a number less than one is negative and so the sign of ΔG° is positive. The table below summarizes the relationship of ΔG° to K_{eq}.

TABLE 20.3: Relationship of and

K_{eq}	$\ln K_{eq}$	ΔG°	**Description**
>1	positive	negative	Products are favored at equilibrium.
1	0	0	Reactants and products are equally favored.
<1	negative	positive	Reactants are favored at equilibrium.

Knowledge of either the standard free energy change or the equilibrium constant for a reaction allows for the calculation of the other. The following two sample problems illustrate each case.

Sample Problem: Gibbs Free Energy and the Equilibrium Constant

The formation of nitrogen monoxide from nitrogen and oxygen gases is a reaction that strongly favors the reactants at 25°C.

$$\mathrm{N_2}(g) + \mathrm{O_2}(g) \rightleftarrows 2\mathrm{NO}(g)$$

The actual concentrations of each gas would be difficult to measure, and so the K_{eq} for the reaction can more easily calculated from the ΔG°, which is equal to 173.4 kJ/mol.

Step 1: List the known values and plan the problem.

Known

- $\Delta G^\circ = +173.4\ kJ/mol$
- $R = 8.314\ \mathrm{J/K \cdot mol}$
- $T = 25^\circ\mathrm{C} = 298\ \mathrm{K}$

Unknown

- $K_{eq} = ?$

In order to make the units agree, the value of ΔG° will need to be converted to J/mol (173,400 J/mol). To solve for K_{eq}, the inverse of the natural logarithm, e^x, will be used.

Step 2: Solve.

$$\Delta G^\circ = -RT \ln K_{eq}$$
$$\ln K_{eq} = \frac{-\Delta G^\circ}{RT}$$
$$K_{eq} = e^{\frac{-\Delta G^\circ}{RT}} = e^{\frac{-173{,}400\ \mathrm{J/mol}}{8.314\ \mathrm{J/K \cdot mol}(298\ \mathrm{K})}} = 4.0 \times 10^{-31}$$

Step 3: Think about your result.

The large positive free energy change leads to a K_{eq} value that is extremely small. Both lead to the conclusion that the reactants are highly favored and very few product molecules are present at equilibrium.

Sample Problem: Free Energy from K_{sp}

The solubility product constant (K_{sp}) of lead(II) iodide is 1.4×10^{-8} at 25°C. Calculate ΔG° for the dissociation of lead(II) iodide in water.

$$\text{PbI}_2(s) \rightleftarrows \text{Pb}^{2+}(aq) + 2\text{I}^-(aq)$$

Step 1: List the known values and plan the problem.

Known

- $K_{eq} = K_{sp} = 1.4 \times 10^{-8}$
- $R = 8.314 \text{ J/K} \cdot \text{mol}$
- $T = 25°\text{C} = 298 \text{ K}$

Unknown

- $\Delta G^\circ = ? \text{ kJ/mol}$

The equation relating ΔG° to K_{eq} can be solved directly.

Step 2: Solve.

$$\begin{aligned}\Delta G^\circ &= -RT \ln K_{eq} \\ &= -8.314 \text{ J/K} \cdot \text{mol}(298 \text{ K}) \ln(1.4 \times 10^{-8}) \\ &= 45,000 \text{ J/mol} \\ &= 45 \text{ kJ/mol}\end{aligned}$$

Step 3: Think about your result.

The large, positive ΔG° indicates that the solid lead(II) iodide is nearly insoluble and most is present as the solid at equilibrium.

Summary

- The relationship between ΔG and K_{eq} is described.
- Calculations involving these two parameters are shown.

Practice

Read the material at the link below and answer the following questions:

http://www.chem1.com/acad/webtext/thermeq/TE5.html

1. What is the difference between ΔG and ΔG°?
2. At equilibrium, why does the equation between free energy and equilibrium constant reduce to $\Delta G^\circ = -RT \ln K_{eq}$?
3. What other equilibrium units could we use?

Review

1. When K_{eq} is large, what will be the sign of ΔG?
2. When K_{eq} is small, are reactants or products favored?
3. What does R stand for?

20.9 References

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CHAPTER 21 Acids and Bases

Chapter Outline

21.1 Properties of Acids

- List characteristics of acids.

Is the coffee ready yet?

Many people enjoy drinking coffee. A cup first thing in the morning helps start the day. But keeping the coffee maker clean can be a problem. Lime deposits build up after a while and slow down the brewing process. The best cure for this is to put vinegar (dilute acetic acid) in the pot and run it through the brewing cycle. The vinegar dissolves the deposits and cleans the maker, once again speeding up the brewing process. Just be sure to run water through the process after the vinegar, or you will get some really horrible coffee for a while.

Acids

Acids are very common in some of the foods that we eat. Citrus fruits such as oranges and lemons contain citric acid and ascorbic acid, which is better known as vitamin C. Carbonated sodas contain phosphoric acid. Vinegar contains acetic acid. Your own stomach utilizes hydrochloric acid to digest food.

Acids are a distinct class of compounds because of the properties of their aqueous solutions. Those properties are outlined below.

1. Aqueous solutions of acids are electrolytes, meaning that they conduct an electrical current. Some acids are strong electrolytes because they ionize completely in water, yielding a great many ions. Other acids are weak electrolytes that exist primarily in a non-ionized form when dissolved in water.
2. Acids have a sour taste. Lemons, vinegar, and sour candies all contain acids.
3. Acids change the color of certain acid-base indicators. Two common indicators are litmus and phenolphthalein. Blue litmus turns red in the presence of an acid, while phenolphthalein is colorless.
4. Acids react with active metals to yield hydrogen gas. Recall that an activity series is a list of metals in descending order of reactivity. Metals that are above hydrogen in the activity series will replace the hydrogen from an acid in a single-replacement reaction, as shown below.

$$\text{Zn}(s) + \text{H}_2\text{SO}_4(aq) \rightarrow \text{ZnSO}_4(aq) + \text{H}_2(g)$$

5. Acids react with bases to produce a salt and water. When equal moles of an acid and a base are combined, the acid is neutralized by the base. Water and an ionic compound called a salt are produced.

Summary

- Properties of acids are described.

Practice

Watch the video at the link below and answer the following questions:

MEDIA

Click image to the left for more content.

http://www.youtube.com/watch?v=uahCEZf831c

1. Which of the four solutions are acids?
2. Stop the video at 0:30 minutes and predict conductivities.
3. What color did the acids turn when universal indicator was added?

Review

1. Are all acids electrolytes in water?
2. What color does blue litmus turn in the presence of an acid?
3. What does the reaction of an acid and a base produce?

21.2 Properties of Bases

- List the properties of bases.

Have you ever had acid indigestion?

Maybe you ate too much pizza and felt very uncomfortable hours later. This feeling is due to excess stomach acid being produced. The discomfort can be dealt with by taking an antacid. The base in the antacid will react with the HCl in the stomach and neutralize it, taking care of that unpleasant feeling.

Bases

Bases have properties that mostly contrast with those of acids.

1. Aqueous solutions of bases are also electrolytes. Bases can be either strong or weak, just as acids can.
2. Bases often have a bitter taste and are found in foods less frequently than acids. Many bases, like soaps, are slippery to the touch.

3. Bases also change the color of indicators. Litmus turns blue in the presence of a base while phenolphthalein turns pink.
4. Bases do not react with metals in the way that acids do.
5. Bases react with acids to produce a salt and water.

FIGURE 21.1

Phenolphthalein indicator in presence of base.

Please note that tasting chemicals and touching them are NOT good lab practices and should be avoided – in other words, don't do this at home.

Bases are less common as foods, but they are nonetheless present in many household products. Many cleaners contain ammonia, a base. Sodium hydroxide is found in drain cleaner. **Antacids**, which combat excess stomach acid, are comprised of bases such as magnesium hydroxide or sodium hydrogen carbonate.

Summary

- The properties of bases are listed.

Practice

Read the material at the site below and answer the following questions:

https://sites.google.com/site/sodiumhydroxsite/Acidsandbasesbasics/chemical-properties-of-bases

1. What does the reaction between an acid and a base produce?
2. What is this reaction called?
3. What does the reaction of a base with an ammonium salt form?

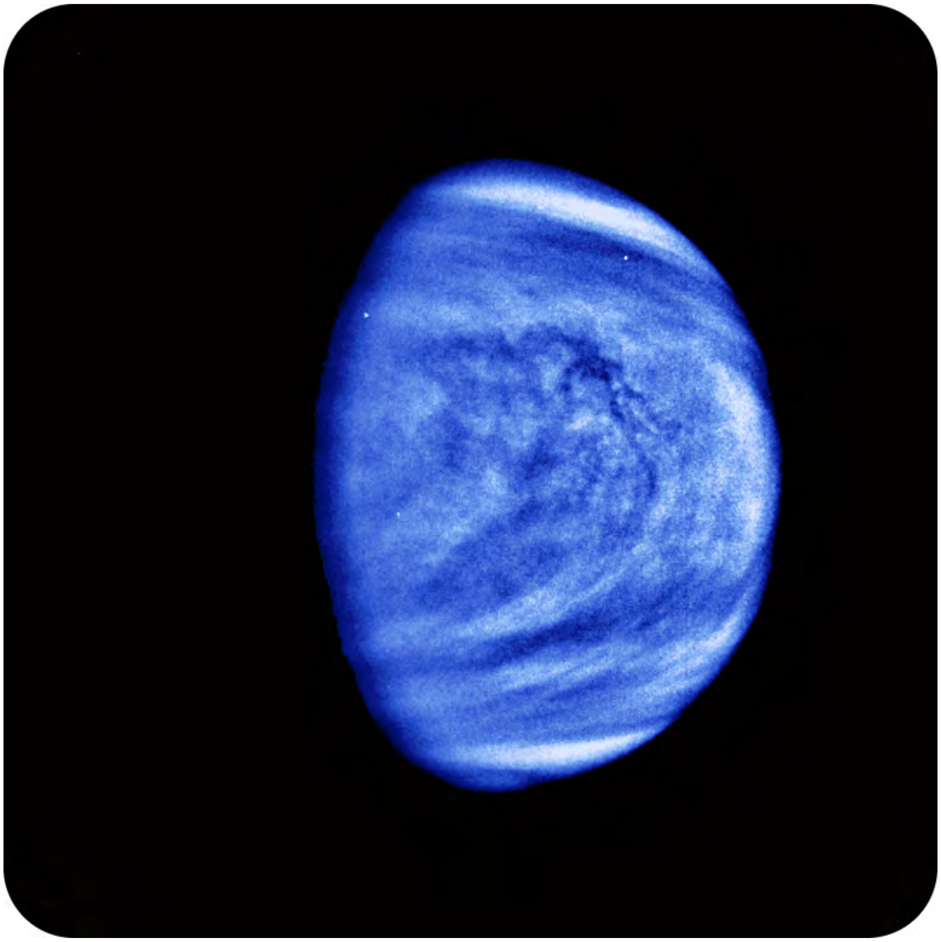
Review

1. Are bases electrolytes?
2. What color does a base turn phenolphthalein?
3. Do bases react with metals the same way that acids do?

- **antacid:** A commercial preparation that neutralizes stomach acid.

21.3 Arrhenius Acids

- Define Arrhenius acid.
- Give examples of Arrhenius acids.
- Describe the hydronium ion.



Don't breathe too deeply.

Venus (pictured above) is the planet nearest us, but has a very different and hostile environment. It has a surface temperature that averages around 450°C. The atmosphere is composed of carbon dioxide, but clouds of sulfuric acid move through the upper atmosphere, helping to create the extremely unfriendly conditions. Not a place you want to visit on vacation.

Arrhenius Acids

Swedish chemist Svante Arrhenius (1859-1927) was the first to propose a theory to explain the observed behavior of acids and bases. Because of their ability to conduct a current, he knew that both acids and bases contained ions in solution. An **Arrhenius acid** is a compound, which ionizes to yield hydrogen ions (H^+) in aqueous solution.

Acids are molecular compounds with ionizable hydrogen atoms. Only hydrogen atoms that are part of a highly polar covalent bond are ionizable. Hydrogen chloride (HCl) is a gas at room temperature and pressure. The H-Cl bond in hydrogen chloride is a polar bond. The hydrogen atom is electron deficient because of the higher electronegativity of the chlorine atom. Consequently, the hydrogen atom is attracted to the lone pair of electrons in a water molecule when HCl is dissolved in water. The result is that the H-Cl bond breaks, with both bonding electrons remaining with the Cl, forming a chloride ion. The H^+ ion attaches to the water molecule, forming a polyatomic ion called the hydronium ion. The **hydronium ion (H_3O^+)** can be thought of as a water molecule with an attached hydrogen ion.

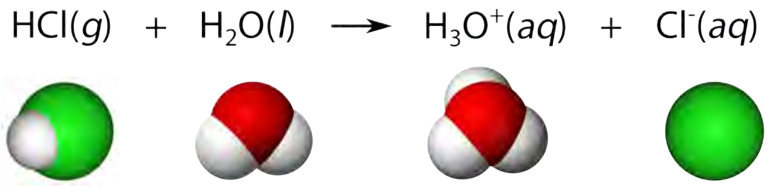


FIGURE 21.2

Formation of a hydronium ion.

Equations showing the ionization of an acid in water are frequently simplified by omitting the water molecule:

$$HCl(g) \rightarrow H^+(aq) + Cl^-$$

This is merely a simplification of the previous equation, but it is commonly used. Any hydrogen ions in an aqueous solution will be attached to water molecules as hydronium ions.

Not all hydrogen atoms in molecular compounds are ionizable. In methane (CH_4), the hydrogen atoms are covalently bonded to carbon in bonds that are only slightly polar. The hydrogen atoms are not capable of ionizing and methane has no acidic properties. Acetic acid (CH_3COOH) belongs to a class of acids called organic acids. There are four hydrogen atoms in the molecule, but only the one hydrogen that is bonded to an oxygen atom is ionizable.

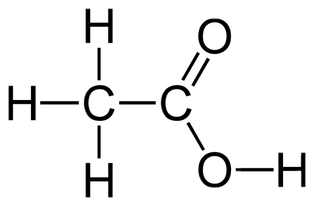


FIGURE 21.3

The O-H bond can be ionized to yield the H^+ ion and the acetate ion. The other hydrogen atoms in this molecule are not acidic.

The **Table** 21.1 lists some of the more common acids:

TABLE 21.1: **Common Acids**

Acid Name	**Formula**
Hydrochloric acid	HCl
Nitric acid	HNO_3
Sulfuric acid	H_2SO_4
Phosphoric acid	H_3PO_4
Acetic acid	CH_3COOH
Hypochlorous acid	$HClO$

A **monoprotic acid** is an acid that contains only one ionizable hydrogen. Hydrochloric acid and acetic acid are monoprotic acids. A **polyprotic acid** is an acid that contains multiple ionizable hydrogens. Most common polyprotic acids are either diprotic (such as H_2SO_4) or triprotic (such as H_3PO_4).

Summary

- Arrhenius acid is defined.
- Examples of Arrhenius acids are given.

Practice

Read the material at the link below and answer the following questions:

http://dwb4.unl.edu/Chem/CHEM869R/CHEM869RLinks/www.nidlink.com/7Ejfromm/arrhenius.htm

1. What was Arrhenius' first scientific idea?
2. What did his Ph.D committee think about it?
3. What did he win for this idea?
4. Write the generic equation for dissociation of an Arrhenius acid.

Review

1. What is an Arrhenius acid?
2. What is a hydronium ion?
3. Is H_2SO_4 a monoprotic or a polyprotic acid?

- **Arrhenius acid:** Acompound which ionizes to yield hydrogen ions (H^+) in aqueous solution.
- **hydronium ion (H_3O^+):** A water molecule with an attached hydrogen ion.
- **monoprotic acid:** An acid that contains only one ionizable hydrogen.
- **polyprotic acid:** An acid that contains multiple ionizable hydrogens.

21.4 Arrhenius Bases

- Define Arrhenius base.
- Give examples of Arrhenius bases.

What can this be used for?

Sodium hydroxide is a versatile chemical. It can be used for such mundane purposes as cleaning clogged drains. Several commercial preparations contain sodium hydroxide for this purpose. It has a number of applications in the food processing field. Ice cream is thickened using NaOH. If olives are soaked in a solution containing sodium hydroxide and other chemicals, the olives will turn black. Soft pretzels are made chewy by the application of sodium hydroxide to the food. This compound has been widely used in the synthesis of plastics, for etching aluminum, for paint removal, and is employed in the dehorning of cattle (in case that is a need you have).

Arrhenius Bases

An **Arrhenius base** is a compound, which ionizes to yield hydroxide ions (OH^-) in aqueous solution. The **Table** 21.2 lists several of the more common bases.

TABLE 21.2: **Common Bases**

Base Name	**Formula**
Sodium hydroxide	NaOH
Potassium hydroxide	KOH

TABLE 21.2: (continued)

Magnesium hydroxide	$Mg(OH)_2$
Calcium hydroxide	$Ca(OH)_2$

All of the bases listed in the table are solids at room temperature. Upon dissolving in water, each dissociates into a metal cation and the hydroxide ion.

$$\text{NaOH}(s) \xrightarrow{\text{H}_2\text{O}} \text{Na}^+(aq) + \text{OH}^-(aq)$$

Sodium hydroxide is a very caustic substance also known as lye. Lye is used as a rigorous cleaner and is an ingredient in the manufacture of soaps. Care must be taken with strong bases like sodium hydroxide, as exposure can lead to severe burns (see **Figure** 21.4).

FIGURE 21.4

This foot has severe burns due to prolonged contact with a solution of sodium hydroxide, also known as lye.

Sodium belongs to the group of elements called the alkali metals. An **alkaline solution** is another name for a solution that is basic. All alkali metals react readily with water to produce the metal hydroxide and hydrogen gas. The resulting solutions are basic.

$$2\text{K}(s) + 2\text{H}_2\text{O}(l) \rightarrow 2\text{KOH}(aq) + \text{H}_2(g)$$

Bases that consist of an alkali metal cation and the hydroxide anion are all very soluble in water. Compounds of the Group 2 metals (the alkaline earth metals) are also basic. However, these compounds are generally not as soluble in water. Therefore the dissociation reactions for these compounds are shown as equilibrium reactions.

$$\text{Mg(OH)}_2(s) \overset{\text{H}_2\text{O}}{\rightleftharpoons} \text{Mg}^{2+}(aq) + 2\text{OH}^-(aq)$$

These relatively insoluble hydroxides were some of the compounds discussed in the context of the solubility product constant (K_{sp}). The solubility of magnesium hydroxide is 0.0084 g per liter of water at 25°C. Because of its low solubility, magnesium hydroxide is not as dangerous as sodium hydroxide. In fact, magnesium hydroxide is the active ingredient in a product called milk of magnesia, which is used as an antacid or a mild laxative.

Summary

- Arrhenius base is defined.
- Examples of Arrhenius bases are given.

Practice

Read the material at the link below and then take the quiz:

http://flatworldknowledge.lardbucket.org/books/introductory-chemistry/section_16_01.html

Review

1. What is an Arrhenius base?
2. What is one reaction that will form an Arrhenius base?
3. Are alkaline earth bases very water-soluble?

- **alkaline solution:** Another name for a solution that is basic.
- **Arrhenius base:** A compound which ionizes to yield hydroxide ions (OH^-) in aqueous solution.

21.5 Brønsted-Lowry Acids and Bases

- Define Brønsted-Lowry acid.
- Define Brønsted-Lowry base.
- Give examples of Brønsted-Lowry acids and bases.

A new theory

The Arrhenius concept of acids and bases was a significant contribution to our understanding of acids and bases. It replaced and expanded the original idea of Lavoisier that all acids contained oxygen. However, the Arrhenius theory had its shortcomings also. It did not take into account the role of the solvent. In addition, this concept did not deal with acid-base behavior in solvents such as benzene where there could be no ionization. So it was time for a new idea, building on the findings of Arrhenius but also going beyond them.

Brønsted-Lowry Acids and Bases

The Arrhenius definition of acids and bases is somewhat limited. There are some compounds whose properties suggest that they are either acidic or basic, but which do not qualify according to the Arrhenius definition. An example is ammonia (NH_3). Its aqueous solution turns litmus blue, it reacts with acids, and displays all the other properties of a base. However, it does not contain the hydroxide ion. In 1923, a broader definition of acids and bases was independently proposed by Danish chemist Johannes Brønsted (1879-1947) and English chemist Thomas Lowry (1874-1936). A **Brønsted-Lowry acid** is a molecule or ion that donates a hydrogen ion in a reaction. A **Brønsted-Lowry base** is a molecule or ion that accepts a hydrogen ion in a reaction. A hydrogen ion is commonly referred to as a proton, and so acids and bases are proton donors and proton acceptors respectively according to the Brønsted-Lowry definition. All substances that are categorized as acids and bases under the Arrhenius definition are also defined as such under the Brønsted-Lowry definition. The new definition, however, includes some substances that are left out according to the Arrhenius definition.

What kind of molecule would qualify as a Brønsted-Lowry base? These molecules need to be able to accept a hydrogen ion (or proton). Two possibilities come to mind: an anion that can form a neural compound with a proton, or a molecule in which one or more atoms has lone-pair electrons. The most obvious anion is the Arrhenius base OH^-. This ion can forma water molecule with a proton by accepting the proton. The acetate anion CH_3COO^- is another anion that can combine with a proton to form acetic acid. Lone-pair electron groups would include the nitrogen atom (see **Figure** 21.5). The two electrons at the top of the nitrogen atom are not connected in any type of bond, but they do interact readily with a bare proton.

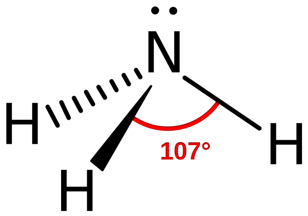


FIGURE 21.5

Lone pair electrons on nitrogen.

Oxygen is another atom with lone pair electrons that can function as Brønsted-Lowry bases.

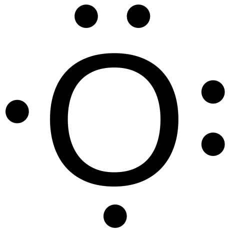


FIGURE 21.6

Electrons in an oxygen atom.

The two single electrons (to the left and bottom of the atom) can form single covalent bonds with other atoms while the two pairs of double electrons (top and right) are available to interact with a hydrogen ion.

Summary

- Brønsted-Lowry acids and bases are defined.

Practice

Read the material at the link below and answer the following questions:

http://www.chemteam.info/AcidBase/Bronsted-Lowry-AcidBase.html

1. Why is water considered a base in the reaction between water and HCl?
2. Why is H_3O^+ considered an acid?
3. Why is the chloride anion considered a base?

Review

1. What is a Brønsted-Lowry acid?
2. What is a Brønsted-Lowry base?
3. How does ammonia function as a Brønsted-Lowry base?

- **Brønsted-Lowry acid:** A molecule or ion that donates a hydrogen ion in a reaction.
- **Brønsted-Lowry base:** A molecule or ion that accepts a hydrogen ion in a reaction.

21.6 Brønsted-Lowry Acid-Base Reactions

- Define amphoterism.
- Define conjugate acid.
- Define conjugate base.
- Write reactions that illustrate the idea of conjugate acid-base pairs.

Which direction?

The Roman god Janus was considered the god of gates and doors, beginnings and endings. He is portrayed with two faces, looking in two directions at once. Janus would have been in a good position to look at the acid-base reactions we see in this concept, since they are equilibrium reactions involving two different forms of both acids and bases.

Brønsted-Lowry Acid-Base Reactions

An acid-base reaction according to the Brønsted-Lowry definition is a transfer of a proton from one molecule or ion to another. When ammonia is dissolved in water, it undergoes the following reversible reaction.

$$\underset{\text{base}}{\mathrm{NH_3}(aq)} + \underset{\text{acid}}{\mathrm{H_2O}(l)} \rightleftarrows \underset{\text{acid}}{\mathrm{NH_4^+}(aq)} + \underset{\text{base}}{\mathrm{OH^-}(aq)}$$

In this reaction, the water molecule is donating a proton to the ammonia molecule. The resulting products are the ammonium ion and the hydroxide ion. The water is acting as a Brønsted-Lowry acid, while the ammonia is acting as a Brønsted-Lowry base. The hydroxide ion that is produced causes the solution to be basic.

We can also consider the reverse reaction in the above equation. In that reaction, the ammonium ion donates a proton to the hydroxide ion. The ammonium ion is a Brønsted-Lowry acid, while the hydroxide ion is a Brønsted-Lowry base. Most Brønsted-Lowry acid-base reactions can be analyzed in this way. There is one acid and one base as reactants, and one acid and one base as products.

In the above reaction, water acted as an acid, which may seem a bit unexpected. Water can also act as a base in a Brønsted-Lowry acid-base reaction, as long as it reacts with a substance that is a better proton donor. Shown below is the reaction of water with the hydrogen sulfate ion.

$$\underset{\text{acid}}{\mathrm{HSO_4^-}(aq)} + \underset{\text{base}}{\mathrm{H_2O}(l)} \rightleftarrows \underset{\text{acid}}{\mathrm{H_3O^+}(aq)} + \underset{\text{base}}{\mathrm{SO_4^{2-}}(aq)}$$

So water is capable of being either an acid or a base, a characteristic called amphoterism. An **amphoteric substance** is one that is capable of acting as either an acid or a base by donating or accepting hydrogen ions.

Conjugate Acids and Bases

When a substance that is acting as a Brønsted-Lowry acid donates its proton, it becomes a base in the reverse reaction. In the reaction above, the hydrogen sulfate ion (HSO_4^-) donates a proton to water and becomes a sulfate ion (SO_4^{2-}). The HSO_4^- and the SO_4^{2-} are linked to one another by the presence or absence of the H^+ ion. A **conjugate acid-base pair** is a pair of substances related by the loss or gain of a single hydrogen ion. A **conjugate acid** is the particle produced when a base accepts a proton. The hydrogen sulfate ion is the conjugate acid of the sulfate ion. A **conjugate base** is the particle produced when an acid donates a proton. The sulfate ion is the conjugate base of the hydrogen sulfate ion.

In the reaction illustrated below, water serves both as acid and base simultaneously. One water molecule serves as an acid and donates a proton. The other water molecule functions as a base by accepting the proton.

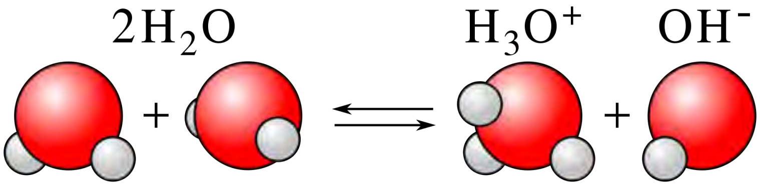


FIGURE 21.7
Water molecules as a conjugate acid-base pair.

A typical Brønsted-Lowry acid-base reaction contains two conjugate acid-base pairs as shown below.

$$\mathrm{HNO_2}(aq) + \mathrm{PO_4^{3-}}(aq) \rightleftarrows \mathrm{NO_2^-}(aq) + \mathrm{HPO_4^{2-}}(aq)$$

One conjugate acid-base pair is HNO_2 / NO_2^-, while the other pair is HPO_4^{2-} / PO_4^{3-}.

Summary

- Conjugate acids and bases are defined.
- Examples of conjugate acid-base pairs are given.

Practice

Read the material at the link below and do the problems at the end of the selection:

http://s-owl.cengage.com/ebooks/vining_owlbook_prototype/ebook/ch16/Sect16-1-b.html

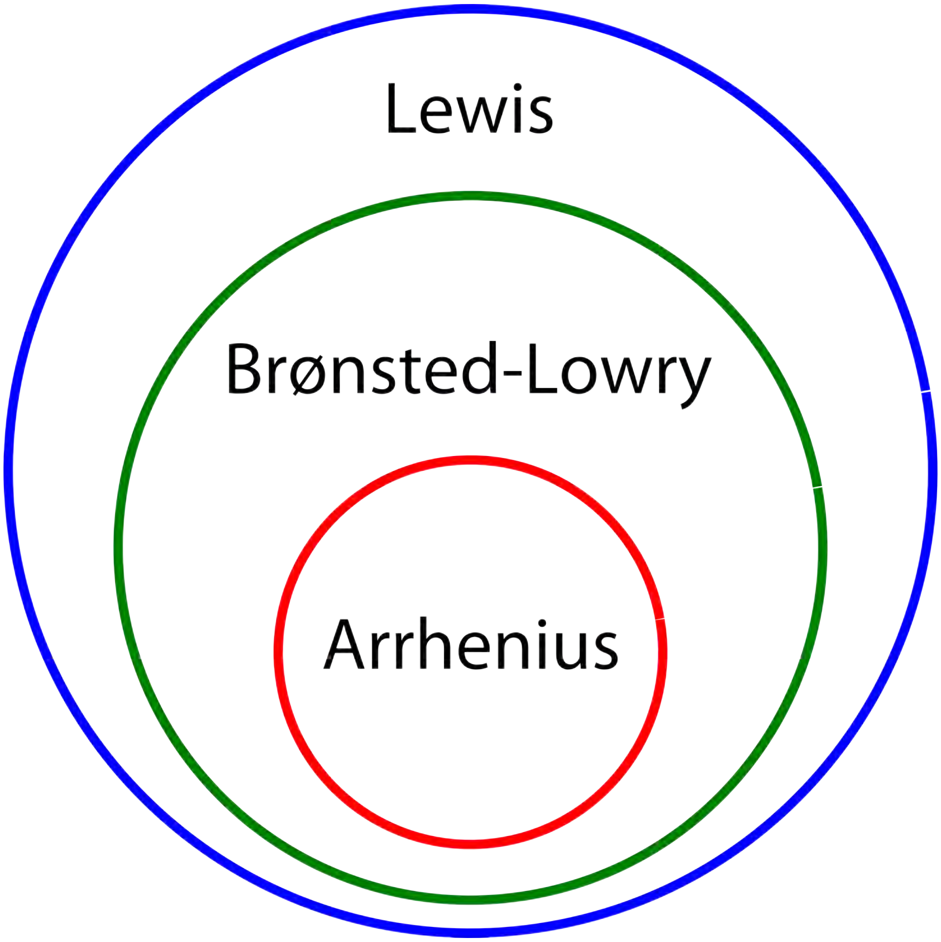
Review

1. In the reaction between ammonia and water, how does the ammonia serve as a base on the left-hand side of the equation?
2. How does the ammonium ion serve as an acid on the right-hand side of the equation?
3. Write the conjugate acid-base pairs for the reaction between two water molecules illustrated above.

- **amphoteric substance:** One that is capable of acting as either an acid or a base by donating or accepting hydrogen ions.
- **conjugate acid:** The particle produced when a base accepts a proton.
- **conjugate acid-base pair:** A pair of substances related by the loss or gain of a single hydrogen ion.
- **conjugate base:** The particle produced when an acid donates a proton.

21.7 Lewis Acids and Bases

- Define Lewis acids and bases.
- Give examples of Lewis acids and bases.



The big picture gets bigger

Ideas in science never stay static. One discovery builds on another. Our concepts of acids and bases have grown from the fundamental ideas of Arrhenius to Brønsted-Lowry to Lewis. Each step adds to our understanding of the world around us and makes the "big picture" even bigger.

Lewis Acids and Bases

Gilbert Lewis (1875-1946) proposed a third theory of acids and bases that is even more general than either the Arrhenius or Brønsted-Lowry theories. A **Lewis acid** is a substance that accepts a pair of electrons to form a covalent bond. A **Lewis base** is a substance that donates a pair of electrons to form a covalent bond. So a Lewis acid-base reaction is represented by the transfer of a pair of electrons from a base to an acid. A hydrogen ion, which lacks any electrons accept a pair of electrons. It is an acid under both the Brønsted-Lowry and Lewis definitions. Ammonia consists of a nitrogen atom as the central atom with a lone pair of electrons. The reaction between ammonia and the hydrogen ion can be depicted as shown in the **Figure** 21.8.

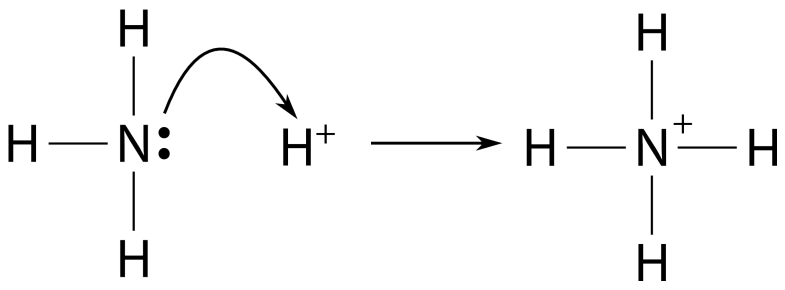


FIGURE 21.8

Reaction between ammonia and proton.

The lone pair on the nitrogen atom is transferred to the hydrogen ion, making the NH_3 a Lewis base while the H^+ is a Lewis acid.

Some reactions that do not qualify as acid-base reactions under the other definitions do so under only the Lewis definition. An example is the reaction of ammonia with boron trifluoride.

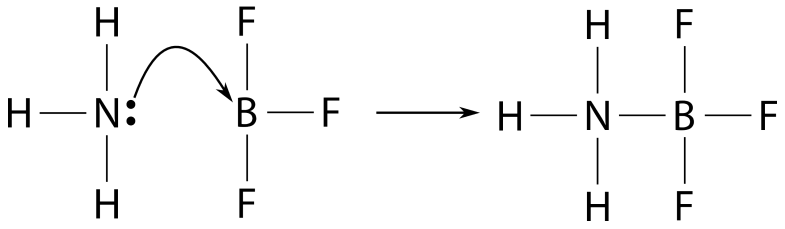


FIGURE 21.9

Ammonia and boron trifluoride.

Boron trifluoride is the Lewis acid, while ammonia is again the Lewis base. As there is no hydrogen ion involved in this reaction, it qualifies as an acid-base reaction only under the Lewis definition. The **Table** 21.3 summarizes the three acid-base theories.

TABLE 21.3: **Acid-Base Definitions**

Type	**Acid**	**Base**
Arrhenius	H^+ ions in solution	OH^- ions in solution
Brønsted-Lowry	H^+ donor	H^+ acceptor
Lewis	electron-pair acceptor	electron-pair donor

Summary

- Lewis acids and bases are defined.
- Examples of Lewis acids and bases are given.

Practice

Do the practice problems associated with Section 3 Lewis Theory at the link below:

http://staarhelper.com/Mr_B_Science/daily_lessons/cacid.htm

Review

1. What is the difference between a Lewis acid or base and a Brønsted Lowry acid or base?
2. What is required to happen in Lewis acid-base reactions?
3. Do all Lewis acid-base reactions involve protons?

- **Lewis acid:** A substance that accepts a pair of electrons to form a covalent bond.

21.8 Ion-Product of Water

- Define the ion-product constant of water.
- Define acidic solution.
- Define basic solution.
- Use the constant to calculate $[H^+]$ or $[OH^-]$ when the other is known.

What's inside?

At one time you could take the little caps off the top of a car battery and check the condition of the sulfuric acid inside. If it got low, you could add more acid. But sulfuric acid is hazardous stuff, so the batteries are now sealed to protect people. It's not a good idea to cut into a battery to see what it looks like – you could get acid burns.

The Ion-Product of Water

The **self-ionization of water** (the process in which water ionizes to hydronium ions and hydroxide ions) occurs to a very limited extent. When two molecules of water collide, there can be a transfer of a hydrogen ion from one molecule to the other. The products are a positively charged hydronium ion and a negatively charged hydroxide ion.

$$H_2O(l) + H_2O(l) \rightleftarrows H_3O^+(aq) + OH^-(aq)$$

We often use the simplified form of the reaction:

$$H_2O(l) \rightleftarrows H^+(aq) + OH^-(aq)$$

The equilibrium constant for the self-ionization of water is referred to as the ion-product for water and is given the symbol K_w.

$$K_w = [H^+][OH^-]$$

The **ion-product of water** (K_w) is the mathematical product of the concentration of hydrogen ions and hydroxide ions. Note that H_2O is not included in the ion-product expression because it is a pure liquid. The value of K_w is very small, in accordance with a reaction that favors the reactants. At 25°C, the experimentally determined value of K_w in pure water is 1.0×10^{-14}.

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$$

In pure water, the concentrations of hydrogen and hydroxide ions are equal to one another. Pure water or any other aqueous solution in which that is the case is said to be neutral. To find the molarity of each ion, the square root of K_w is taken.

$$[H^+] = [OH^-] = 1.0 \times 10^{-7}\ \text{M}$$

An **acidic solution** is a solution in which the concentration of hydrogen ions is greater than the concentration of hydroxide ions. For example, hydrogen chloride ionizes to produce H^+ and Cl^- ions upon dissolving in water.

$$HCl(g) \rightarrow H^+(aq) + Cl^-(aq)$$

This increases the concentration of H^+ ions in the solution. According to LeChâtelier's principle, the equilibrium represented by $H_2O(l) \rightleftarrows H^+(aq) + OH^-(aq)$ is forced to the left, towards the reactant. As a result the concentration of the hydroxide ion decreases.

A **basic solution** is a solution in which the concentration of hydroxide ions is greater than the concentration of hydrogen ions. Solid potassium hydroxide dissociates in water to yield potassium ions and hydroxide ions.

$$KOH(s) \rightarrow K^+(aq) + OH^-(aq)$$

Now the increase in concentration of the OH^- ions causes a decrease in the concentration of the H^+ ions and the ion-product of $[H^+][OH^-]$ remains constant

Sample Problem: Use of K_w for an Aqueous Solution

Hydrochloric acid (HCl) is a strong acid, meaning it is 100% ionized in solution. What is the $[H^+]$ and the $[OH^-]$ in a solution of 2.0×10^3 M HCl?

Step 1: List the known values and plan the problem.

Known

- [HCl] = 2.0×10^{-3} M
- $K_w = 1.0 \times 10^{-14}$

Unknown

- [H^+] = ? M
- [OH^-] = ? M

Because HCl is 100% ionized, the concentration of H^+ ions in solution will be equal to the original concentration of HCl. Each HCl molecule that was originally present ionizes into one H^+ ion and one Cl^- ion. The concentration of OH^- can then be determined from the [H^+] and K_w.

Step 2: Solve.

$$\begin{aligned}\left[H^+\right] &= 2.0 \times 10^{-3}\text{ M}\\ K_w &= \left[H^+\right]\left[OH^-\right] = 1.0 \times 10^{-14}\\ \left[OH^-\right] &= \frac{K_w}{\left[H^+\right]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-3}} = 5.0 \times 10^{-12}\text{ M}\end{aligned}$$

Step 3: Think about your result.

The [H^+] is much higher than the [OH^-] because the solution is acidic. As with other equilibrium constants, the unit for K_w is customarily omitted.

Summary

- The self-ionization of water is described and an ionization constant for the process is stated.
- Acidic and basic solutions are defined.
- Calculations using K_w are illustrated.

Practice

Read the material on the first two pages of the link below and do those practice problems:

http://www.vigoschools.org/ mmc3/Chem%201/Lecture%20Notes/L2%20-%20Hydrogen%20Ions%20and%20pH%20-%2015.1.pdf

Review

1. What is an acidic solution?
2. What is a basic solution?
3. What is the [OH^-] of a solution which has a [H^+] of 1×10^{-5} M?

- **acidic solution:** A solution in which the concentration of hydrogen ions is greater than the concentration of hydroxide ions.
- **basic solution:** A solution in which the concentration of hydroxide ions is greater than the concentration of hydrogen ions.
- **ion-product of water (K_w):** The mathematical product of the concentration of hydrogen ions and hydroxide ions.
- **self-ionization of water:** The process in which water ionizes to hydronium ions and hydroxide ions.

21.9 The pH Scale

- Define pH.
- List pH values of common materials.

Why is grapefruit juice acidic?

Grapefruit juice has a pH of somewhere between 2.9-3.3, depending on the specific product. Excessive exposure to this juice can cause erosion of tooth enamel and produce tooth damage. The acids in grapefruit juice are carbon-based, with citric acid being one of the major constituents. This compound has three ionizable hydrogens on each molecule which contribute to the relatively low pH of the juice. Another component of grape juice is malic acid, containing two ionizable hydrogens per molecule.

The pH Scale

Expressing the acidity of a solution by using the molarity of the hydrogen ion is cumbersome because the quantities are generally very small. Danish scientist Søren Sørenson (1868-1939) proposed an easier system for indicating the concentration of H^+ called the pH scale. The letters pH stand for the power of the hydrogen ion. The **pH** of a solution is the negative logarithm of the hydrogen-ion concentration.

$\text{pH} = -\log[H^+]$

In pure water or a neutral solution the $[H^+] = 1.0 \times 10^{-7}$ M. Substituting into the pH expression:

$\text{pH} = -\log[1.0 \times 10^{-7}] = -(-7.00) = 7.00$

The pH of pure water or any neutral solution is thus 7.00. For significant figure purposes, the numbers to the right of the decimal point in the pH value are the significant figures. Since 1.0×10^{-7} has two significant figures, the pH can be reported as 7.00.

A logarithmic scale condenses the range of acidity to numbers that are easy to use. Consider a solution with $[H^+] = 1.0 \times 10^{-4}$ M. That is a hydrogen-ion concentration that is 1000 times higher than in pure water. The pH of such a solution is 4.00, a difference of just 3 pH units. Notice that when the $[H^+]$ is written in scientific notation and the coefficient is 1, the pH is simply the exponent with the sign changed. The pH of a solution with the $[H^+] = 1 \times 10^{-2}$ M is 2 and the pH of a solution with the $[H^+] = 1 \times 10^{-10}$ M is 10.

As we saw earlier, a solution with the $[H^+]$ higher than 1.0×10^{-7} is acidic, while a solution with the $[H^+]$ lower than is basic. Consequently, solutions whose pH is less than 7 are acidic, while those with a pH higher than 7 are basic. The **Figure** 21.10 illustrates this relationship, along with some examples of various solutions.

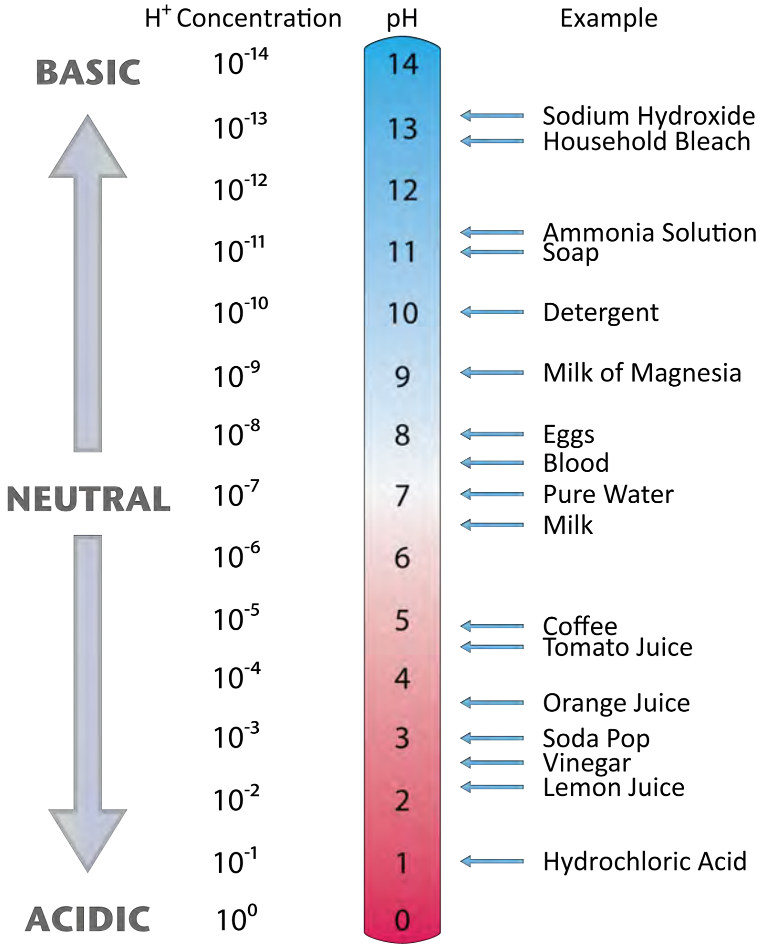


FIGURE 21.10

The pH values for several common materials.

Summary

- The concept of pH is defined.
- pH values for several common materials are listed.

Practice

Read the material at the link below and answer the following questions:

http://staff.jccc.net/pdecell/chemistry/phscale.html

- What is a buffer?
- How much more acidic is vinegar than grapefruit?
- How much more basic is soapy water than milk of magnesia?

Review

1. What is one value of using pH instead of molar concentrations?
2. Is coffee an acidic or a basic substance?
3. If a material has a pH of 9.3, is it acidic or basic?

- **pH:** The negative logarithm of the hydrogen-ion concentration.

21.10 Calculating pH of Acids and Bases

- Perform pH calculations for acidic and basic solutions.

Raising tropical fish

Many people enjoy having tropical fish in their homes or businesses. These brightly-colored creatures are relaxing to watch, but do require a certain amount of maintenance in order to survive. Tap water is usually too alkaline when it comes out of the faucet, so some adjustments need to be made. The pH of the water will change over time while it is in the tank, which means you need to test it every so often. Then you get to be a chemist for your fish.

Calculating pH of Acids and Bases

Calculation of pH is simple when there is a 1×10^{power} problem. However, in real life that is rarely the situation. If the coefficient is not equal to 1, a calculator must be used to find the pH. For example, the pH of a solution with $[H^+] = 2.3 \times 10^{-5}$ M can be found as shown below.

pH = $-\log[2.3 \times 10^{-5}] = 4.64$

When the pH of a solution is known, the concentration of the hydrogen ion can be calculated. The inverse of the logarithm (or antilog) is the 10^x key on a calculator.

$[H^+] = 10^{-pH}$

For example, suppose that you have a solution with a pH of 9.14. To find the $[H^+]$ use the 10^x key.

$[H^+] = 10^{-pH} = 10^{-9.14} = 7.24 \times 10^{-10}$ M

Hydroxide Ion Concentration and pH

As we saw earlier, the hydroxide ion concentration of any aqueous solution is related to the hydrogen ion concentration through the value of K_w. We can use that relationship to calculate the pH of a solution of a base.

Sample Problem: The pH of a Base

Sodium hydroxide is a strong base. Find the pH of a solution prepared by dissolving 1.0 g of NaOH into enough water to make 1.0 L of solution.

Step 1: List the known values and plan the problem.

Known

- mass NaOH = 1.0 g
- molar mass NaOH = 40.00 g/mol
- volume solution = 1.0 L
- $K_w = 1.0 \times 10^{-14}$

Unknown

- pH of solution = ?

First, convert the mass of NaOH to moles. Second, calculate the molarity of the NaOH solution. Because NaOH is a strong base and is soluble, the $[\text{OH}^-]$ will be equal to the concentration of the NaOH. Third, use K_w to calculate the $[\text{H}^+]$ in the solution. Lastly, calculate the pH.

Step 2: Solve.

$$1.00\ \cancel{\text{g NaOH}} \times \frac{1\text{ mol NaOH}}{40.00\ \cancel{\text{g NaOH}}} = 0.025\text{ mol NaOH}$$

$$\text{Molarity} = \frac{0.025\text{ mol NaOH}}{1.00\text{ L}} = 0.025\text{ M NaOH} = 0.025\text{ M OH}^-$$

$$\left[\text{H}^+\right] = \frac{K_w}{\left[\text{OH}^-\right]} = \frac{1.0 \times 10^{-14}}{0.025\text{ M}} = 4.0 \times 10^{-13}\text{ M}$$

$$\text{pH} = -\log\left[\text{H}^+\right] = -\log(4.0 \times 10^{-13}) = 12.40$$

Step 3: Think about your result.

The solution is basic and so its pH is greater than 7. The reported pH is rounded to two decimal places because the original mass and volume has two significant figures.

Summary

- Calculations of pH for acidic and basic solutions are described.

Practice

Carry out the requested calculations at the link below:

http://www.sciencegeek.net/APchemistry/APtaters/pHcalculations.htm

Review

1. What is the pH of a 4.5×10^{-3} M HI solution?
2. What is the pH of a 3.67×10^{-5} M NaBr solution?
3. If we have a weak base with a low ionization constant, can we assume that the $[OH^-]$ in the solution is equal to the concentration of the base?

21.11 The pOH Concept

- Define pOH.
- Perform calculations of pOH.

Soap Lake has a long history as a healing place. Indian tribes would put aside their rivalries when they came to the lake to enjoy the high mineral content of the water. Thousands of visitors in the days before good antibiotics would come and enjoy the soothing waters of the lake. Soap Lake is alkaline, with water quality thought to be similar to that of the moons of the planet Jupiter.

The pOH Concept

As with the hydrogen-ion concentration, the concentration of the hydroxide ion can be expressed logarithmically by the pOH. The **pOH** of a solution is the negative logarithm of the hydroxide-ion concentration.

$\text{pOH} = -\log[\text{OH}^-]$

The pH of a solution can be related to the pOH. Consider a solution with a pH = 4.0. The $[\text{H}^+]$ of the solution would be 1.0×10^{-4} M. Dividing K_w by this yields a $[\text{OH}^-]$ of 1.0×10^{-10} M. Finally the pOH of the solution equals $-\log(1.0 \times 10^{-10}) = 10$. This example illustrates the following relationship.

$\text{pH} + \text{pOH} = 14$

The pOH scale is similar to the pH scale in that a pOH of 7 is indicative of a neutral solution. A basic solution has a pOH of less than 7, while an acidic solution has a pOH of greater than 7. The pOH is convenient to use when finding the hydroxide ion concentration from a solution with a known pH.

Sample Problem: Using pOH

Find the hydroxide concentration of a solution with a pH of 4.42.

Step 1: List the known values and plan the problem.

Known

- pH = 4.42
- pH + pOH = 14

Unknown [OH-] = ? M

First, the pOH is calculated, followed by the $[OH^-]$.

Step 2: Solve.

$$\begin{gathered} \text{pOH} = 14 - \text{pH} = 14 - 4.42 = 9.58 \\ \left[\text{OH}^-\right] = 10^{-\text{pOH}} = 10^{-9.58} = 2.6 \times 10^{-10}\ \text{M} \end{gathered}$$

Step 3: Think about your result.

The pH is that of an acidic solution, and the resulting hydroxide-ion concentration is less than 1×10^{-7} M. The answer has two significant figures because the given pH has two decimal places.

The diagram below shows all of the interrelationships between $[H^+]$, $[OH^-]$, pH, and pOH.

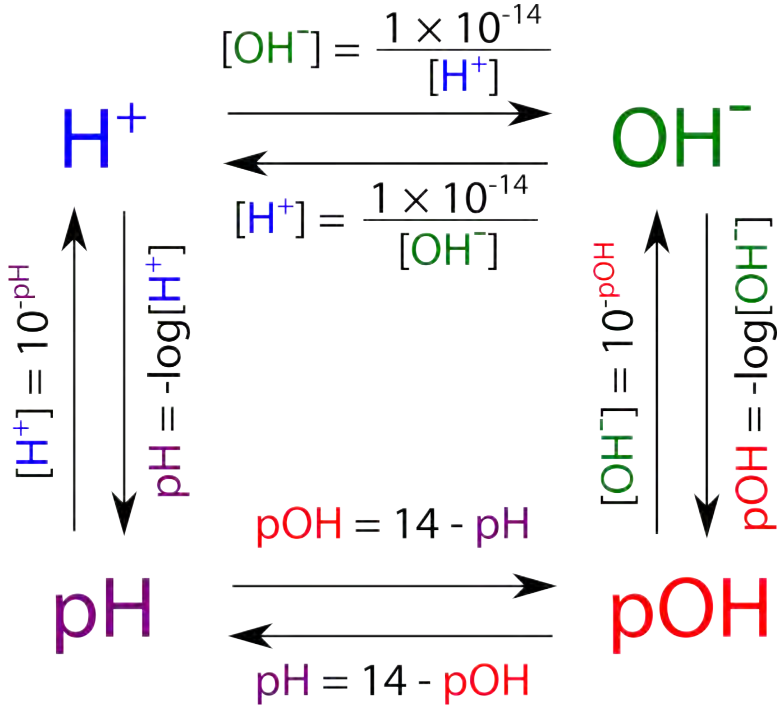


FIGURE 21.11

Relationships between hydrogen ion concentration, hydroxide ion concentration, pH, and pOH.

Summary

- pOH is defined.
- Calculations involving pOH are described.

Practice

Do all calculations at the link below that involve pOH:

http://www.sciencegeek.net/APchemistry/APtaters/pHcalculations.htm

Review

1. What is the formula for calculating pOH?
2. What pOH value is indicative of an acidic solution?
3. A pOH value of 3 would indicate what type of solution?

- **pOH:** The negative logarithm of the hydroxide-ion concentration.

21.12 Strong and Weak Acids and Acid Ionization Constant (Ka)

- Define a strong acid.
- List some strong acids.
- Define a weak acid.
- List some weak acids.
- Write the expression for the acid ionization constant.

How do they etch glass?

Etching of glass is a slow process that can produce beautiful artwork. Traditionally, the glass has been treated with dilute hydrofluoric acid which gradually dissolves the glass under it. Parts of the piece that should not be etched are covered with wax or some other non-reactive material. In more recent times, compounds such as ammonium bifluoride have been used. Whichever chemical is employed, the artist must be very careful not to get any on the skin.

Strong and Weak Acids and Acid Ionization Constant

Acids are classified as either strong or weak, based on their ionization in water. A **strong acid** is an acid which is completely ionized in aqueous solution. Hydrogen chloride (HCl) ionizes completely into hydrogen ions and chloride ions in water.

$$\text{HCl}(g) \rightarrow \text{H}^+(aq) + \text{Cl}^-(aq)$$

A **weak acid** is an acid that ionizes only slightly in aqueous solution. Acetic acid (found in vinegar) is a very common weak acid. Its ionization is shown below.

$$\text{CH}_3\text{COOH}(aq) \rightleftarrows \text{H}^+(aq) + \text{CH}_3\text{COO}^-(aq)$$

The ionization of acetic acid is incomplete, and so the equation is shown with a double arrow. The extent of ionization of weak acids varies, but is generally less than 10%. A 0.10 M solution of acetic acid is only about 1.3% ionized, meaning that the equilibrium strongly favors the reactants.

Weak acids, like strong acids, ionize to yield the H^+ ion and a conjugate base. Because HCl is a strong acid, its conjugate base (Cl^-) is extremely weak. The chloride ion is incapable of accepting the H^+ ion and becoming HCl again. In general, the stronger the acid, the weaker its conjugate base. Likewise, the weaker the acid, the stronger its conjugate base.

TABLE 21.4: **Relative Strengths of Acids and their Conjugate Bases**

Acid	Conjugate Base
Strong Acids	
HCl (hydrochloric acid) (strongest)	Cl^- (chloride ion) (weakest)
H_2SO_4 (sulfuric acid)	$\text{HSO}_4{}^-$ (hydrogen sulfate ion)
HNO_3 (nitric acid)	$\text{NO}_3{}^-$ (nitrate ion)
Weak Acids	
H_3PO_4 (phosphoric acid)	$\text{H}_2\text{PO}_4{}^-$ (dihydrogen phosphate ion)
CH_3COOH (acetic acid)	CH_3COO^- (acetate ion)
H_2CO_3 (carbonic acid)	$\text{HCO}_3{}^-$ (hydrogen carbonate ion)
HCN (hydrocyanic acid) (weakest)	CN^- (cyanide ion) (strongest)

Strong acids are 100% ionized in solution. Weak acids are only slightly ionized. Phosphoric acid is stronger than acetic acid and so is ionized to a greater extent. Acetic acid is stronger than carbonic acid, and so on.

The Acid Ionization Constant, K_a

The ionization for a general weak acid, HA, can be written as follows:

$$\text{HA}(aq) \rightarrow \text{H}^+(aq) + \text{A}^-(aq)$$

Because the acid is weak, an equilibrium expression can be written. An **acid ionization constant** (K_a) is the equilibrium constant for the ionization of an acid.

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

The acid ionization represents the fraction of the original acid that has been ionized in solution. Therefore, the numerical value of K_a is a reflection of the strength of the acid. Weak acids with relatively higher K_a values are stronger than acids with relatively lower K_a values. Because strong acids are essentially 100% ionized, the concentration of the acid in the denominator is nearly zero and the K_a value approaches infinity. For this reason, K_a values are generally reported for weak acids only.

The **Table** 21.5 is a listing of acid ionization constants for several acids. Note that polyprotic acids have a distinct ionization constant for each ionization step, with each successive ionization constant being smaller than the previous one.

TABLE 21.5: **Acid Ionization Constants at 25°C**

Name of Acid	**Ionization Equation**	K_a
Sulfuric acid	$H_2SO_4 \rightleftarrows H^+ + HSO_4^-$ $HSO_4^- \rightleftarrows H^+ + SO_4^{2-}$	very large 1.3×10^{-2}
Oxalic acid	$H_2C_2O_4 \rightleftarrows H^+ + HC_2O_4^-$ $HC_2O_4^- \rightleftarrows H^+ + C_2O_4^{2-}$	6.5×10^{-2} 6.1×10^{-5}
Phosphoric acid	$H_3PO_4 \rightleftarrows H^+ + H_2PO_4^-$ $H_2PO_4^- \rightleftarrows H^+ + HPO_4^{2-}$ $HPO_4^{2-} \rightleftarrows H^+ + PO_4^{3-}$	7.5×10^{-3} 6.2×10^{-8} 4.8×10^{-13}
Hydrofluoric acid	$HF \rightleftarrows H^+ + F^-$	7.1×10^{-4}
Nitrous acid	$HNO_2 \rightleftarrows H^+ + NO_2^-$	4.5×10^{-4}
Benzoic acid	$C_6H_5COOH \rightleftarrows H^+ + C_6H_5COO^-$	6.5×10^{-5}
Acetic acid	$CH_3COOH \rightleftarrows H^+ + CH_3COO^-$	1.8×10^{-5}
Carbonic acid	$H_2CO_3 \rightleftarrows H^+ + HCO_3^-$ $HCO_3^- \rightleftarrows H^+ + CO_3^{2-}$	4.2×10^{-7} 4.8×10^{-11}
Hydrocyanic acid	$HCN \rightleftarrows H^+ + CN^-$	4.9×10^{-10}

Summary

- Strong and weak acids are defined.
- The acid ionization constant (K_a) is defined.

Practice

Read the material at the link below and answer the following questions:

http://www.chemguide.co.uk/physical/acidbaseeqia/acids.html

1. Why is the $[H_2O]$ factor not included in the expression for K_a?
2. When we write H^+, what are we really talking about?
3. Which is the weaker acid: methanoic or ethanoic acid?

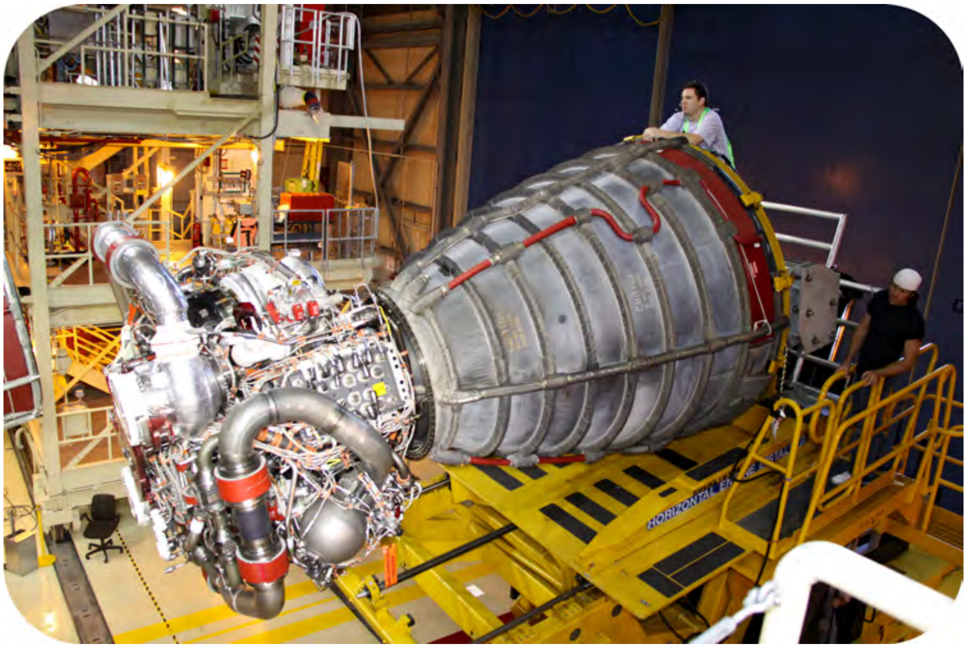
Review

1. Why is the chloride ion the weakest conjugate base?
2. What is the percent ionization in a 0.1 M solution of acetic acid?
3. Which is the stronger acid: HF or benzoic acid?

- **acid ionization constant** (K_a)**:** The equilibrium constant for the ionization of an acid.
- **strong acid:** An acid that is completely ionized in aqueous solution.
- **weak acid:** An acid that ionizes only slightly in aqueous solution.

21.13 Strong and Weak Bases and Base Ionization Constant (Kb)

- Define strong and weak bases.
- Give examples of strong and weak bases.
- Write the expression for the base ionization constant.



Ammonia for what?

All the complex electronics and apparatus in a space shuttle generate heat, as do the astronauts. The shuttles have a complex arrangement of systems to dissipate that heat into outer space. One of the components of this system is a series of coils filled with ammonia that are located on the outside of the shuttle. Ammonia absorbs the heat and then releases it into space as the gas circulates through the coils. This approach is both inexpensive and effective.

Strong and Weak Bases and Base Ionization Constant, K_b

As with acids, bases can either be strong or weak, depending on their extent of ionization. A **strong base** is a base, which ionizes completely in aqueous solution. The most common strong bases are soluble metal hydroxide compounds such as potassium hydroxide. Some metal hydroxides are not as strong simply because they are not as soluble. Calcium hydroxide is only slightly soluble in water, but what portion that does dissolve also dissociates into ions.

A **weak base** is a base that ionizes only slightly in aqueous solution. Recall that a base can be defined as a substance, which accepts a hydrogen ion from another substance. When a weak base such as ammonia is dissolved in water, it accepts an H$^+$ ion from water, forming the hydroxide ion and the conjugate acid of the base, the ammonium ion.

$$NH_3(aq) + H_2O(l) \rightleftarrows NH_4^+(aq) + OH^-(aq)$$

The equilibrium greatly favors the reactants and the extent of ionization of the ammonia molecule is very small.

An equilibrium expression can be written for the reactions of weak bases with water. Because the concentration of water is extremely large and virtually constant, the water is not included in the expression. A **base ionization constant** (K_b) is the equilibrium constant for the ionization of a base. For ammonia the expression is:

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

The numerical value of K_b is a reflection of the strength of the base. Weak bases with relatively higher K_b values are stronger than bases with relatively lower K_b values. The table below is a listing of base ionization constants for several weak bases.

TABLE 21.6: Base Ionization Constants at 25°C

Name of Base	**Ionization Equation**	K_b
Methylamine	$CH_3NH_2 + H_2O \rightleftarrows CH_3NH_3^+ + OH^-$	5.6×10^{-4}
Ammonia	$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$	1.8×10^{-5}
Pyridine	$C_5H_5N + H_2O \rightleftarrows C_2H_5NH^+ + OH^-$	1.7×10^{-9}
Acetate ion	$CH_3COO^- + H_2O \rightleftarrows CH_3COOH + OH^-$	5.6×10^{-10}
Fluoride ion	$F + H_2O \rightleftarrows HF + OH^-$	1.4×10^{-11}
Urea	$H_2NCONH_2 + H_2O \rightleftarrows H_2NCONH_3^+ + OH^-$	1.5×10^{-14}

Notice that the conjugate base of a weak acid is also a weak base. For example, the acetate ion has a small tendency to accept a hydrogen ion from water to form acetic acid and the hydroxide ion.

Summary

- Strong and weak bases are defined.
- The base equilibrium constant is stated.

Practice

Read the material at the link below and answer the following questions:

http://www.chemguide.co.uk/physical/acidbaseeqia/bases.html

1. In the presence of hydroxide ions, which way does the equilibrium shift for the equation showing the dissociation of water?
2. What percentage of ammonia in solution actually produces hydroxide ions?
3. How does the position of equilibrium relate to the strength of a weak base?

Review

1. Define a strong base.
2. Define a weak base.
3. Which is the stronger base: pyridine or urea?

- **base ionization constant** (K_b)**:** The equilibrium constant for the ionization of a base.
- **strong base:** A base which ionizes completely in aqueous solution.
- **weak base:** A base that ionizes only slightly in aqueous solution.

21.14 Calculating Ka and Kb

- Perform calculations of acid and base ionization constants.

Who invented the pH meter?

The pH meter came about because Florida orange growers need a way to test the acidity of their fruit. The first meter was invented by Arnold Beckman, who went on to form Beckman Instruments. Beckman's business was very successful and he used much of his fortune to fund science education and research. The Beckman family donated $40 million to build the Beckman Institute at the University of Illinois, seen above.

Calculating K_a and K_b

The numerical value of K_a or K_b can be determined from an experiment. A solution of known concentration is prepared and its pH is measured with an instrument called a **pH meter**.

Sample Problem: Calculation of an Acid Ionization Constant

A 0.500 M solution of formic acid is prepared and its pH is measured to be 2.04. Determine the K_a for formic acid.

Step 1: List the known values and plan the problem.

Known

- initial [HCOOH] = 0.500 M
- pH = 2.04

FIGURE 21.12
A pH meter is a laboratory device that provides quick, accurate measurements of the pH of solutions.

Unknown

- $K_a = ?$

First, the pH is used to calculate the $[H^+]$ at equilibrium. An ICE table is set up in order to determine the concentrations of HCOOH and $HCOO^-$ at equilibrium. All concentrations are then substituted into the K_a expression and the K_a value is calculated.

Step 2: Solve.

$$[H^+] = 10^{-pH} = 10^{-2.04} = 9.12 \times 10^{-3} \text{ M}$$

Since each formic acid molecule that ionizes yields one H^+ ion and one formate ion ($HCOO^-$), the concentrations of H^+ and $HCOO^-$ are equal at equilibrium. We assume that the initial concentrations of each ion are zero, resulting in the following ICE table.

TABLE 21.7:

Concentrations	**[HCOOH]**	**$[H^+]$**	**$[HCOO^-]$**
Initial	0.500	0	0
Change	-9.12×10^{-3}	$+9.12 \times 10^{-3}$	$+9.12 \times 10^{-3}$
Equilibrium	0.491	9.12×10^{-3}	9.12×10^{-3}

Now substituting into the K_a expression gives:

$$K_a = \frac{[H^+][HCOO^-]}{[HCOOH]} = \frac{(9.12 \times 10^{-3})(9.12 \times 10^{-3})}{0.491} = 1.7 \times 10^{-4}$$

Substituting into the K_b expression yields the K_b for ethylamine.

$$K_b = \frac{[C_2H_5NH_3^+][OH^-]}{[C_2H_5NH_2]} = \frac{(2.04 \times 10^{-2})(2.04 \times 10^{-2})}{0.730} = 5.7 \times 10^{-4}$$

Summary

- Calculations of K_a and K_b are described.

Practice

Read the material at the link below and answer the following questions:

http://www.ausetute.com.au/kb.html

1. What does an Arrhenius base dissociate to?
2. What does a Brønsted-Lowry base form in water?
3. How is percent ionization determined?

Review

1. What approach is used for calculation of ionization constants?
2. What initial assumptions are made?
3. What equilibrium assumptions are made?

- **pH meter:** A device for accurate measurement of pH.

21.15 Calculating pH of Weak Acid and Base Solutions

- Perform calculations to determine the pH of a weak acid or base solution.

Ouch, that hurts!

Bess are beautiful creatures that help plants flourish. They carry pollen from one plant to another to facilitate plant growth and development. But they can also be troublesome when they sting you. For people who are allergic to bee venom, this can be a serious, life-threatening problem. For the rest of us, it can be a painful experience. When stung by a bee, one first-aid treatment is to apply a paste of baking soda (sodium bicarbonate) to the stung area. This weak base helps with the itching and swelling that accompanies the bee sting.

Calculating pH of Weak Acid and Base Solutions

The K_a and K_b values have been determined for a great many acids and bases, as shown in Tables 21.5 and 21.6. These can be used to calculate the pH of any solution of a weak acid or base whose ionization constant is known.

Sample Problem: Calculating the pH of a Weak Acid

Calculate the pH of a 2.00 M solution of nitrous acid (HNO_2). The K_a for nitrous acid is 4.5×10^{-4}.

Step 1: List the known values and plan the problem.

Known

- initial $[HNO_2] = 2.00$ M

- $K_a = 4.5 \times 10^{-4}$

Unknown

- pH = ?

First, an ICE table is set up with the variable x used to signify the change in concentration of the substance due to ionization of the acid. Then the K_a expression is used to solve for x and calculate the pH.

Step 2: Solve.

TABLE 21.9:

Concentrations	**[HNO_2]**	**[H^+]**	**[$NO_2{}^-$]**
Initial	2.00	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$2.00-x$	x	x

The K_a expression and value is used to set up an equation to solve for x.

$$K_a = 4.5 \times 10^{-4} = \frac{(x)(x)}{2.00-x} = \frac{x^2}{2.00-x}$$

The quadratic equation is required to solve this equation for x. However, a simplification can be made because of the fact that the extent of ionization of weak acids is small. The value of x will be very much less than 2.00, so the "$-x$" in the denominator can be dropped.

$$\begin{aligned} 4.5 \times 10^{-4} &= \frac{x^2}{2.00-x} \approx \frac{x^2}{2.00} \\ x &= \sqrt{4.5 \times 10^{-4}(2.00)} = 2.9 \times 10^{-2}\ \text{M} = \left[H^+\right] \end{aligned}$$

Since the variable x represents the hydrogen-ion concentration, the pH of the solution can now be calculated.

$$pH = -\log[\text{H}^+] = -\log[2.9 \times 10^{-2}] = 1.54$$

Step 3: Think about your result.

The pH of a 2.00 M solution of a strong acid would be equal to $-\log(2.00) = -0.30$. The higher pH of the 2.00 M nitrous acid is consistent with it being a weak acid and therefore not as acidic as a strong acid would be.

The procedure for calculating the pH of a solution of a weak base is similar to that of the weak acid in the sample problem. However, the variable x will represent the concentration of the hydroxide ion. The pH is found by taking the negative logarithm to get the pOH, followed by subtracting from 14 to get the pH.

Summary

- The procedure or calculating the pH of a weak acid or base is illustrated.

Practice

Perform the calculations at the site below:

http://www.sciencegeek.net/APchemistry/APtaters/pHcalculations.htm

Review

1. What does x stand for in the equation?
2. What simplifying assumption is made?
3. What would x stand for if we were calculating pOH?

21.16 Neutralization Reaction and Net Ionic Equations for Neutralization Reactions

- Define neutralizations reaction.
- Write balanced equations for neutralization reactions.
- Write net ionic equations for neutralization reactions.

Pouring concrete

Who cleans up afterwards?

Pouring concrete and working it are messy jobs. In the process, a lot of wastewater with an alkaline pH is generated. Often, regulations require that this wastewater be cleaned up at the site. One practical way to neutralize the basic pH is the bubble CO_2 into the water. The carbon dioxide forms a weak acid (carbonic acid, H_2CO_3) in solution which serves to bring the alkaline pH down to something closer to neutral.

Neutralization Reactions and Net Ionic Equations for Neutralization Reactions

A **neutralization reaction** is a reaction in which an acid and a base react in an aqueous solution to produce a salt and water. The aqueous sodium chloride that is produced in the reaction is called a salt. A **salt** is an ionic compound composed of a cation from a base and an anion from an acid. A salt is essentially any ionic compound that is neither an acid nor a base.

Strong Acid-Strong Base Reactions

When equal amounts of a strong acid such as hydrochloric acid are mixed with a strong base such as sodium hydroxide, the result is a neutral solution. The products of the reaction do not have the characteristics of either an acid or a base. Here is the balanced molecular equation.

$$\text{HCl}(aq) + \text{NaOH}(aq) \rightarrow \text{NaCl}(aq) + \text{H}_2\text{O}(l)$$

Chemical reactions occurring in aqueous solution are more accurately represented with a net ionic equation. The full ionic equation for the neutralization of hydrochloric acid by sodium hydroxide is written as follows:

$$\text{H}^+(aq) + \text{Cl}^-(aq) + \text{Na}^+(aq) + \text{OH}^-(aq) \rightarrow \text{Na}^+(aq) + \text{Cl}^-(aq) + \text{H}_2\text{O}(l)$$

Since the acid and base are both strong, they are fully ionized and so are written as ions, as is the NaCl formed as a product. The sodium and chloride ions are spectator ions in the reaction, leaving the following as the net ionic reaction.

$$\mathrm{H^+}(aq) + \mathrm{OH^-}(aq) \rightarrow \mathrm{H_2O}(l)$$

All neutralization reactions of a strong acid with a strong base simplify to the net ionic reaction of hydrogen ion combining with hydroxide ion to produce water.

What if the acid is a diprotic acid such as sulfuric acid? The balanced molecular equation now involves a 1:2 ratio between acid and base.

$$\mathrm{H_2SO_4}(aq) + 2\mathrm{NaOH}(aq) \rightarrow \mathrm{Na_2SO_4}(aq) + 2\mathrm{H_2O}(l)$$

In order for the reaction to be a full neutralization, twice as many moles of NaOH must react with the H_2SO_4. The sodium sulfate salt is soluble, and so the net ionic reaction is again the same. Different mole ratios occur for other polyprotic acids or bases with multiple hydroxides such as $Ca(OH)_2$.

Reactions Involving a Weak Acid or Weak Base

Reactions where at least one of the components is weak do not generally result in a neutral solution. The reaction between weak nitrous acid and strong potassium hydroxide is shown below.

$$\mathrm{HNO_2}(aq) + \mathrm{KOH}(aq) \rightarrow \mathrm{KNO_2}(aq) + \mathrm{H_2O}(l)$$

In order to write the net ionic equation, the weak acid must be written as a molecule since it does not ionize to a great extent in water. The base and the salt are fully dissociated.

$$\mathrm{HNO_2}(aq) + \mathrm{K^+}(aq) + \mathrm{OH^-}(aq) \rightarrow \mathrm{K^+}(aq) + \mathrm{NO_2^-}(aq) + \mathrm{H_2O}(l)$$

The only spectator ion is the potassium ion, resulting in the net ionic equation:

$$\mathrm{HNO_2}(aq) + \mathrm{OH^-}(aq) \rightarrow \mathrm{NO_2^-}(aq) + \mathrm{H_2O}(l)$$

The strong hydroxide ion essentially "forces" the weak nitrous acid to become ionized. The hydrogen ion from the acid combines with the hydroxide ion to form water, leaving the nitrite ion as the other product. The resulting solution is not neutral (pH = 7), but instead is slightly basic.

Reactions can also involve a weak base and strong acid, resulting in a solution that is slightly acidic. The molecular and net ionic equations for the reaction of hydrochloric acid and ammonia are shown below.

$$\begin{aligned}&\mathrm{HCl}(aq) + \mathrm{NH_3}(aq) \rightarrow \mathrm{NH_4Cl}(aq) \\ &\mathrm{H^+}(aq) + \mathrm{NH_3}(aq) \rightarrow \mathrm{NH_4^+}(aq) \qquad (\mathrm{Cl^-}\text{ is spectator ion})\end{aligned}$$

Reactions between acids and bases that are both weak may result in solutions that are neutral, acidic, or basic.

Summary

- Neutralization is defined.
- Equations for acid-base neutralizations are given.
- Net ionic equations for neutralization reactions are given.

Practice

Do the problems on the sheet at the link below:

http://www.bbc.co.uk/bitesize/standard/chemistry/acids/reactions/revision/4/

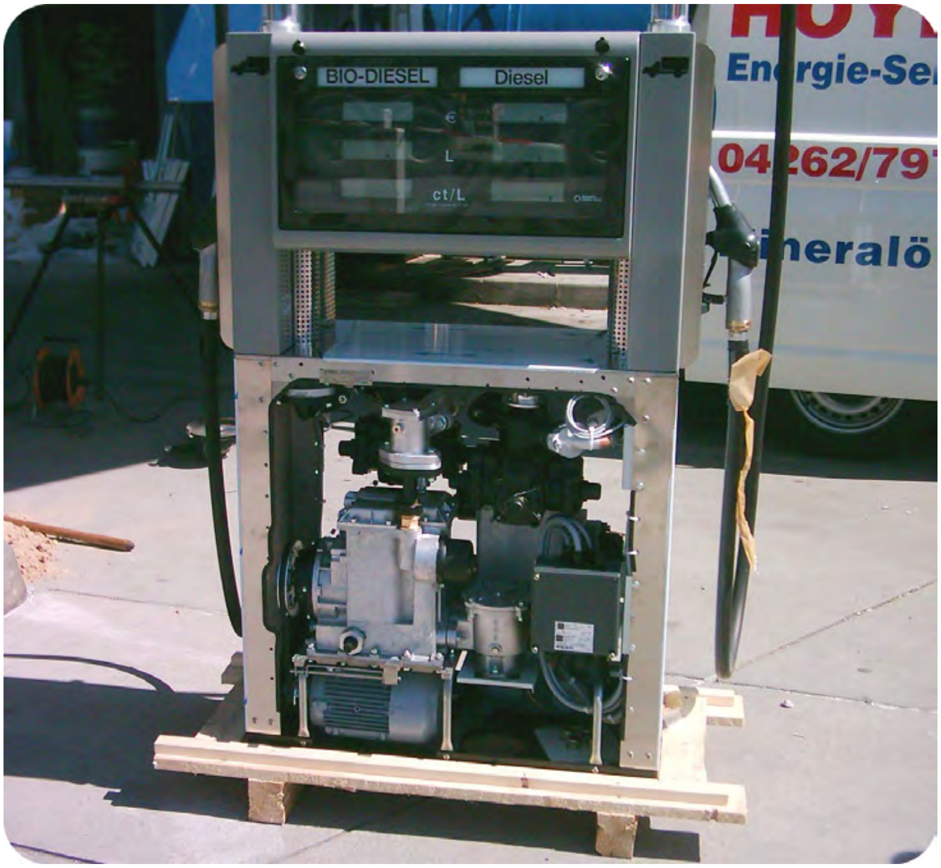
Review

1. What is a neutralization reaction?
2. What is a salt?
3. Write the net ionic equation for the neutralization of a strong acid and a strong base.

- **neutralization reaction:** A reaction in which an acid and a base react in an aqueous solution to produce a salt and water.
- **salt:** An ionic compound composed of a cation from a base and an anion from an acid.

21.17 Titration Experiment

- Define equivalence point.
- Describe how to perform a titration experiment.



Didn't that used to be French fries?

A lot of research is going on these days involving the development of biodiesel fuels. Often this material can be made from used vegetable oils. The vegetable oil is treated with lye to create the biofuel. In the oils is a variable amount of acid that needs to be determined so the workers will know how much lye to add to make the final fuel. Before the lye is added, the native vegetable oil is titrated to find out how much free acid is present. Then the amount of lye added can be adjusted to take into account the amount needed to neutralize these free acids.

Titration Experiment

In the neutralization of hydrochloric acid by sodium hydroxide, the mole ratio of acid to base is 1:1.

$$\mathrm{HCl}(aq) + \mathrm{NaOH}(aq) \rightarrow \mathrm{NaCl}(aq) + \mathrm{H_2O}(l)$$

One mole of HCl would be fully neutralized by one mole of NaOH. If instead the hydrochloric acid was reacted with barium hydroxide, the mole ratio would be 2:1.

$$2HCl(aq) + Ba(OH)_2(aq) \rightarrow BaCl_2(aq) + 2H_2O(l)$$

Now two moles of HCl would be required to neutralize one mole of $Ba(OH)_2$. The mole ratio insures that the number of moles of H^+ ions supplied by the acid is equal to the number of OH^- ions supplied by the base. This must be the case for neutralization to occur. The **equivalence point** is the point in a neutralization reaction where the number of moles of hydrogen ions is equal to the number of moles of hydroxide ions.

In the laboratory, it is useful to have an experiment where the unknown concentration of an acid or a base can be determined. This can be accomplished by performing a controlled neutralization reaction. A **titration** is 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. Many titrations are acid-base neutralization reactions, though other types of titrations can also be performed.

In order to perform an acid-base titration, the chemist must have a way to visually detect that the neutralization reaction has occurred. An **indicator** is a substance that has a distinctly different color when in an acidic or basic solution. A commonly used indicator for strong acid-strong base titrations is phenolphthalein. Solutions in which a few drops of phenolphthalein have been added turn from colorless to brilliant pink as the solution turns from acidic to basic. The steps in a titration reaction are outlined below.

1. A measured volume of an acid of unknown concentration is added to an Erlenmeyer flask.
2. Several drops of an indicator are added to the acid and mixed by swirling the flask.
3. A buret is filled with the base solution of unknown molarity.
4. The stopcock of the buret is opened and base is slowly added to the acid while the flask is constantly swirled to insure mixing. The stopcock is closed at the exact point at which the indicator just changes color.

The **standard solution** is the solution in a titration whose concentration is known. In the titration described above the base solution is the standard solution. It is very important in a titration to add the solution from the buret slowly so that the point at which the indicator changes color can be found accurately. The **end point** of a titration is the point at which the indicator changes color. When phenolphthalein is the indicator, the end point will be signified by a faint pink color.

FIGURE 21.13

Phenolphthalein in basic solution.

Summary

- Definitions are given for equivalence point, titration and indicator.
- The process for carrying out a titration is described.

Practice

Watch the video at the link below and answer the following questions:

MEDIA

Click image to the left for more content.

http://www.youtube.com/watch?v=g8jdCWC10vQ

1. What is the indicator used?
2. What color is it in acid solution?
3. What is the glass tube called that contains the known concentration of sodium hydroxide?
4. What other method can be used to determine the end-point of the titration?

Review

1. What is the standard solution?
2. How do you know you have reached the end-point?
3. What is the reaction that occurs during a titration?

- **end point:** The point at which the indicator changes color.
- **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.
- **indicator:** A substance that has a distinctly different color when in an acidic or basic solution.
- **standard solution:** The solution in a titration whose concentration is known.
- **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.

21.18 Titration Calculations

- Perform calculations to determine concentration of unknown acid or base.

How is soap made?

The manufacture of soap requires a number of chemistry techniques. One necessary piece of information is the saponification number, the amount of base needed to hydrolyze a certain amount of fat to produce the free fatty acids that are an essential part of the final product. The fat is heated with a known amount of base (usually NaOH or KOH). After hydrolysis is complete, the left-over base is titrated to determine how much was needed to hydrolyze the fat sample.

Titration Calculations

At the equivalence point in a neutralization, the moles of acid are equal to the moles of base.

$$\text{moles acid} = \text{moles base}$$

Recall that the molarity (M) of a solution is defined as the moles of the solute divided by the liters of solution (L). So the moles of solute are therefore equal to the molarity of a solution multiplied by the volume in liters.

$$\text{moles solute} = M \times L$$

We can then set the moles of acid equal to the moles of base.

$$M_A \times V_A = M_B \times V_B$$

M_A is the molarity of the acid, while M_B is the molarity of the base. V_A and V_B are the volumes of the acid and base, respectively.

Suppose that a titration is performed and 20.70 mL of 0.500 M NaOH is required to reach the end point when titrated against 15.00 mL of HCl of unknown concentration. The above equation can be used to solve for the molarity of the acid.

$$M_A = \frac{M_B \times V_B}{V_A} = \frac{0.500 \text{ M} \times 20.70 \text{ mL}}{15.00 \text{ mL}} = 0.690 \text{ M}$$

The higher molarity of the acid compared to the base in this case means that a smaller volume of the acid is required to reach the equivalence point.

The above equation works only for neutralizations in which there is a 1:1 ratio between the acid and the base. The sample problem below demonstrates the technique to solve a titration problem for a titration of sulfuric acid with sodium hydroxide.

Sample Problem: Titration

In a titration of sulfuric acid against sodium hydroxide, 32.20 mL of 0.250 M NaOH is required to neutralize 26.60 mL of H_2SO_4. Calculate the molarity of the sulfuric acid.

Step 1: List the known values and plan the problem.

Known

- molarity NaOH = 0.250 M
- volume NaOH = 32.20 mL
- volume H_2SO_4 = 26.60 mL

Unkonwn

- molarity H_2SO_4 = ?

$$\text{equation} \qquad \text{H}_2\text{SO}_4(aq) + 2\text{NaOH}(aq) \rightarrow \text{Na}_2\text{SO}_4(aq) + 2\text{H}_2\text{O}(l)$$

First determine the moles of NaOH in the reaction. From the mole ratio, calculate the moles of H_2SO_4 that reacted. Finally, divide the moles H_2SO_4 by its volume to get the molarity.

Step 2: Solve.

$$\text{mol NaOH} = M \times L = 0.250 \text{ M} \times 0.03220 \text{ L} = 8.05 \times 10^{-3} \text{ mol } NaOH$$

$$8.05 \times 10^{-3} \text{ mol NaOH} \times \frac{1 \text{ mol H}_2\text{SO}_4}{2 \text{ mol NaOH}} = 4.03 \times 10^{-3} \text{ mol H}_2\text{SO}_4$$

$$\frac{4.03 \times 10^{-3} \text{ mol H}_2\text{SO}_4}{0.02660 \text{ L}} = 0.151 \text{ M H}_2\text{SO}_4$$

Step 3: Think about your result.

The volume of H_2SO_4 required is smaller than the volume of NaOH because of the two hydrogen ions contributed by each molecule.

Summary

- The process of calculating concentration from titration data is described and illustrated.

Practice

Do the problems at the link below:

http://www.sophia.org/acidbase-titration-calculations-concept

Review

1. What assumption is made about the amounts of materials at the neutral point?
2. What is different about the calculation using sulfuric acid?
3. Why is the mole ratio important?

21.19 Titration Curves

- Describe titration curves of acid-base neutralization reactions.

Where did graphs come from?

The $x-y$ plot that we know of as a graph was the brainchild of the French mathematician-philosopher Rene Descartes (1596-1650). His studies in mathematics led him to develop what was known as "Cartesian geometry", including the idea of our current graphs. The coordinates re often referred to as Cartesian coordinates.

Titration Curves

As base is added to acid at the beginning of a titration, the pH rises very slowly. Nearer to the equivalence point, the pH begins to rapidly increase. If the titration is a strong acid with a strong base, the pH at the equivalence point is equal to 7. A bit past the equivalence point, the rate of change of the pH again slows down. A **titration curve** is a graphical representation of the pH of a solution during a titration. The **Figure** below shows two different examples of a strong acid-strong base titration curve. On the left is a titration in which the base is added to the acid and so the pH progresses from low to high. On the right is a titration in which the acid is added to the base. In this case, the pH starts out high and decreases during the titration. In both cases, the equivalence point is reached when the moles of acid and base are equal and the pH is 7. This also corresponds to the color change of the indicator.

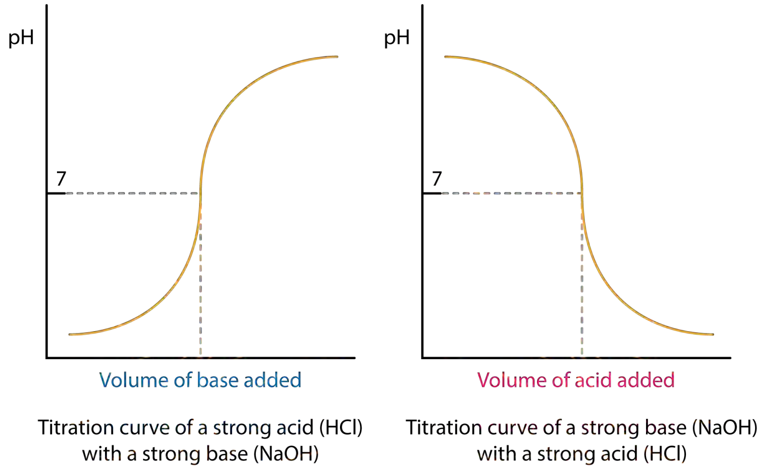


FIGURE 21.14
A titration curve shows the pH changes that occur during the titration of an acid with a base. On the left, base is being added to acid. On the right, acid is being added to base. In both cases, the equivalence point is at pH 7.

Titration curves can also be generated in the case of a weak acid-strong base titration or a strong base-weak acid titration. The general shape of the titration curve is the same, but the pH at the equivalence point is different. In a weak acid-strong base titration, the pH is greater than 7 at the equivalence point. In a strong acid-weak base titration, the pH is less than 7 at the equivalence point.

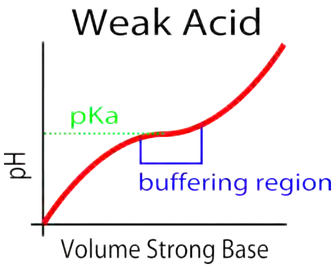


FIGURE 21.15
Titration curve of weak acid and strong base.

Summary

- Acid-base titration curves are described.

Practice

Read the material at the link below and answer the following questions:

http://www.chemguide.co.uk/physical/acidbaseeqia/phcurves.html

1. Why is the equivalence point less than pH 7 for the titration of ammonia with HCl?
2. Why is it difficult to do a titration of a weak acid and a weak base?
3. Why do we get two inflection points for the titration of ethanedioic acid?

Review

1. What does a titration curve tell us?
2. At what pH are the moles of acid and base equal?
3. Is the equivalence point for a weak acid-strong base titration the same as for a strong-acid-strong base titration?

- **titration curve:** A graphical representation of the pH of a solution during a titration.

21.20 Indicators

- Define indicator.
- Describe the use of indicators in acid-base experiments.

Who would write a song about a cabbage?

There's an old bluegrass song known as "Boil Them Cabbage Down" (check out a great performance on this link: http://www.youtube.com/watch?v=xT9TTlh5jgA). Many people enjoy the music, but chemistry students also enjoy the product of the cabbage boiling. Extracting the anthocyanin dye for cabbage leaves with boiling water give a solution that is red in acidic solution, purple in neutral solutions, and green to yellow in basic solution (pictured above).

Indicators

An **acid-base indicator** is a substance that displays different colors when in the presence of an acid or a base. How does that work? An indicator is a weak acid that ionizes within a known pH range, usually about 2 pH units. We can represent the protonated form of the indicator molecule as HIn and the deprotonated form as In^-. The following equilibrium exists for the indicator.

$$\mathrm{HIn}(aq) \rightleftarrows \mathrm{H}^+(aq) + \mathrm{In}^-(aq)$$

According to LeChâtelier's principle, the addition of H^+ ions (as in a low pH solution) drives the equilibrium to the left and the protonated HIn predominates. The addition of OH^- (as in a high pH solution) decreases the H^+

concentration and drives the equilibrium to the right and the deprotonated In^- predominates. To be useful as an indicator, the two forms must be different colors. In the case of phenolphthalein, the protonated form is colorless, while the deprotonated form is pink. The **Figure** 21.16 shows a variety of acid-base indicators that can be used in titration experiments.

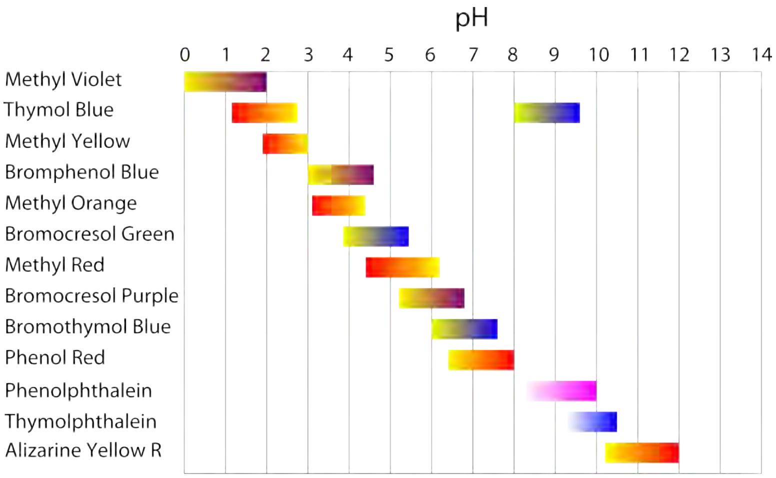


FIGURE 21.16

pH indicators.

Depending on the pH at the equivalence point, the appropriate indicator must be chosen. For example, bromphenol blue has a yellow color below a pH of about 3 and a blue-violet color above a pH of about 4. Bromphenol blue would not be a good choice as the indicator for a strong acid-strong base titration, because the pH is 7 at the equivalence point. Instead, it could be used for a strong acid-weak base titration, where the pH at the equivalence point is lower.

Most indicators have two colored forms. Universal indicator displays the entire rainbow of colors from low pH to high pH (see **Figure** 21.17). Universal indicator is used to make pH paper, which can be used to quickly test solutions for their approximate pH.

FIGURE 21.17

Universal indicator tape.

Summary

- Acid-base indicator is defined.
- Examples of acid-base indicators are given.

Practice

Watch the video at the link below and answer the following questions:

MEDIA

Click image to the left for more content.

http://www.youtube.com/watch?v=6Y4Y-__ME60

1. What was the acid used?
2. What was the base used?
3. What color was methyl orange in acid? in base?
4. What color did indigo carmine turn in acid? in base?

Review

1. What is an indicator?
2. What would be the best indicator to use around pH 1?
3. What indicator besides phenolphthalein might you use for a pH 7 experiment?

- **acid-base indicator:** A substance that displays different colors when in the presence of an acid or a base.

21.21 Hydrolysis of Salts: Equations

- Define salt hydrolysis.
- Write equations for salts that form basic solutions.
- Write equations for salts that form acidic solutions.
- Write equations for salts that form neutral solutions.

Baking better biscuits

Baking seems easy with all the pre-mixed items available ("just add water and stir"). But there is a good amount of chemistry involved in baking with ingredients that you measure out. One important ingredient is baking powder. The fluffiness in the final product of a non-yeast recipe is usually due to carbon dioxide formed from baking powder. One popular brand uses a mix of sodium bicarbonate and sodium aluminum sulfate to produce the CO_2. The reaction is seen below:

$$3NaHCO_3 + NaAl(SO_4)_2 \rightarrow Al(OH)_3 + 2Na_2SO_4 + 3CO_2$$

If all goes well, the biscuits rise, the pancakes are fluffy, and everybody is happy.

Hydrolysis of Salts: Equations

A salt is an ionic compound that is formed when an acid and a base neutralize each other. While it may seem that salt solutions would always be neutral, they can frequently be either acidic or basic.

Consider the salt formed when the weak acid hydrofluoric acid is neutralized by the strong base sodium hydroxide. The molecular and net ionic equations are shown below.

$$\begin{gathered}\mathrm{HF}(aq)+\mathrm{NaOH}(aq)\rightarrow\mathrm{NaF}(aq)+\mathrm{H_2O}(l)\\ \mathrm{HF}(aq)+\mathrm{OH^-}(aq)\rightarrow\mathrm{F^-}(aq)+\mathrm{H_2O}(l)\end{gathered}$$

Since sodium fluoride is soluble, the sodium ion is a spectator ion in the neutralization reaction. The fluoride ion is capable of reacting to a small extent with water, accepting a proton.

$$\mathrm{F^-}(aq)+\mathrm{H_2O}(l)\rightleftarrows\mathrm{HF}(aq)+\mathrm{OH^-}(aq)$$

The fluoride ion is acting as a weak Brønsted-Lowry base. The hydroxide ion that is produced as a result of the above reaction makes the solution slightly basic. **Salt hydrolysis** is a reaction in which one of the ions from a salt reacts with water, forming either an acidic or basic solution.

Salts That Form Basic Solutions

When solid sodium fluoride is dissolved into water, it completely dissociates into sodium ions and fluoride ions. The sodium ions do not have any capability of hydrolyzing, but the fluoride ions hydrolyze to produce a small amount of hydrofluoric acid and hydroxide ion.

$$\mathrm{F^-}(aq)+\mathrm{H_2O}(l)\rightleftarrows\mathrm{HF}(aq)+\mathrm{OH^-}(aq)$$

Salts that are derived from the neutralization of a weak acid (HF) by a strong base (NaOH) will always produce salt solutions that are basic.

Salts That Form Acidic Solutions

Ammonium chloride (NH_4Cl) is a salt that is formed when the strong acid HCl is neutralized by the weak base NH_3. Ammonium chloride is soluble in water. The chloride ion produced is incapable of hydrolyzing because it is the conjugate base of the strong acid HCl. In other words, the Cl^- ion cannot accept a proton form water to form HCl and OH^-, as the fluoride ion did in the previous section. However, the ammonium ion is capable of reacting slightly with water, donating a proton and so acting as an acid.

$$\mathrm{NH_4^+}(aq)+\mathrm{H_2O}(l)\rightleftarrows\mathrm{H_3O^+}(aq)+\mathrm{NH_3}(aq)$$

Salts That Form Neutral Solutions

A salt that is derived from the reaction of a strong acid with a strong base forms a solution that has a pH of 7. An example is sodium chloride, formed from the neutralization of HCl by NaOH. A solution of NaCl in water has no acidic or basic properties, since neither ion is capable of hydrolyzing. Other salts that form neutral solutions include potassium nitrate (KNO_3) and lithium bromide (LiBr). The following summarizes how to determine the acidity or basicity of a salt solution.

TABLE 21.10:

Salt formed from:	Salt Solution
Strong acid + Strong base	Neutral
Strong acid + Weak base	Acidic
Weak acid + Strong base	Basic

Salts formed from the reaction of a weak acid and a weak base are more difficult to analyze because of competing hydrolysis reactions between the cation and the anion. These salts will not be considered in this concept.

Summary

- Salt hydrolysis is defined.
- Salt hydrolysis reactions resulting in acidic, basic, or neutral solutions are described.

Practice

Do problems 1, 2, 3, and 5 at the link below:

http://chemwiki.ucdavis.edu/Physical_Chemistry/Physical_Properties_of_Matter/Solubilty/Hydrolysis%3A_With_-Respect_to_Acids,_Bases,_and_Salt_Solutions

Review

1. How does F^- produce a basic solution?
2. How does the ammonium ion produce an acidic solution?
3. Why does dissolved NaCl produce a neutral solution?

- **salt hydrolysis:** A reaction in which one of the ions from a salt reacts with water, forming either an acidic or basic solution.

21.22 Calculating pH of Salt Solutions

- Perform calculations to determine pH of salt solutions if K_a or K_b are known.

Keeping things safe and healthy

We all enjoy a cool dip in a swimming pool on a hot day, but we may not realize the work needed to keep that water safe and healthy. The ideal pH for a swimming pool is around 7.2. The pH will change as a result of many factors. Adjustment can be accomplished with different chemicals depending on the tested pH. High pH can be lowered with liquid HCl (unsafe material) or sodium bisulfate. The bisulfate anion is a weak acid and can dissociate partially in solution. To increase pH, use sodium carbonate. The carbonate anion forms an equilibrium with protons that results in some formation of carbon dioxide.

Calculating pH of Salt Solutions

It is often helpful to be able to predict the effect a salt solution will have on the pH of that solution. Knowledge of the relevant acidity or basicity constants allows us to carry out the necessary calculations.

Sample Problem: Salt Hydrolysis

If we dissolve NaF in water, we get the following equilibrium:

$$\text{F}^-(aq) + \text{H}_2\text{O}(l) \rightleftarrows \text{HF}(aq) + \text{OH}^-(aq)$$

The pH of the resulting solution can be determined if the K_b of the fluoride ion is known.

20.0 g of sodium fluoride is dissolve in enough water to make 500.0 mL of solution. Calculate the pH of the solution. The K_b of the fluoride ion is 1.4×10^{-11}.

Step 1: List the known values and plan the problem.

Known

- mass NaF = 20.0 g
- molar mass NaF = 41.99 g/mol
- volume solution = 0.500 L
- K_b of F^- = 1.4×10^{-11}

Unknown

- pH of solution = ?

The molarity of the F^- solution can be calculated from the mass, molar mass, and solution volume. Since NaF completely dissociates, the molarity of the NaF is equal to the molarity of the F^- ion. An ICE table can be used to calculate the concentration of OH^- produced and then the pH of the solution.

Step 2: Solve.

$$20.0\ \cancel{\text{g NaF}} \times \frac{1\ \cancel{\text{mol NaF}}}{41.99\ \cancel{\text{g NaF}}} \times \frac{1\ \text{mol F}^-}{1\ \cancel{\text{mol NaF}}} = 0.476\ \text{mol F}^-$$

$$\frac{0.476\ \text{mol F}^-}{0.5000\ \text{L}} = 0.953\ \text{M F}^-$$

$$\text{Hydrolysis equation:} \qquad \text{F}^-(aq) + \text{H}_2\text{O}(l) \rightleftarrows \text{HF}(aq) + \text{OH}^-(aq)$$

TABLE 21.11:

Concentrations	**[F^-]**	**[HF]**	**[OH^-]**
Initial	0.953	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.953 - x$	x	x

$$K_b = 1.4 \times 10^{-11} = \frac{(x)(x)}{0.953 - x} = \frac{x^2}{0.953 - x} \approx \frac{x^2}{0.953}$$

$$x = [\text{OH}^-] = \sqrt{1.4 \times 10^{-11}(0.953)} = 3.65 \times 10^{-6}\ \text{M}$$

$$\text{pOH} = -\log(3.65 \times 10^{-6}) = 5.44$$

$$\text{pH} = 14 - 5.44 = 8.56$$

Step 3: Think about your result.

The solution is slightly basic due to the hydrolysis of the fluoride ion.

Salts That Form Acidic Solutions

When the ammonium ion dissolves in water, the following equilibrium exists:

$$\text{NH}_4^+(aq) + \text{H}_2\text{O}(l) \rightleftarrows \text{H}_3\text{O}^+(aq) + \text{NH}_3(aq)$$

The production of hydronium ions causes the resulting solution to be acidic. The pH of a solution of ammonium chloride can be found in a very similar way to the sodium fluoride solution in Sample Problem 21.7. However, since the ammonium chloride is acting as an acid, it is necessary to know the K_a of $NH_4{}^+$, which is 5.6×10^{-10}. We will find the pH of a 2.00 M solution of NH_4Cl. Because the NH_4Cl completely ionizes, the concentration of the ammonium ion is 2.00 M.

$$\text{NH}_4\text{Cl}(s) \rightarrow \text{NH}_4^+(aq) + \text{Cl}^-(aq)$$

Again, an ICE table is set up in order to solve for the concentration of the hydronium (or H^+) ion produced.

TABLE 21.12:

Concentrations	**[$NH_4{}^+$]**	**[H^+]**	**[NH_3]**
Initial	2.00	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$2.00-x$	x	x

Now substituting into the K_a expression gives:

$$K_a = 5.6 \times 10^{-10} = \frac{x^2}{2.00-x} \approx \frac{x^2}{2.00}$$

$$x = [\text{H}^+] = \sqrt{5.6 \times 10^{-10}(2.00)} = 3.3 \times 10^{-5}\ \text{M}$$

$$\text{pH} = -\log(3.3 \times 10^{-5}) = 4.48$$

A salt produced from a strong acid and a weak base yields a solution that is acidic.

Summary

- Calculations to determine pH of salt solutions are described.

Practice

Work the problems at the link below:

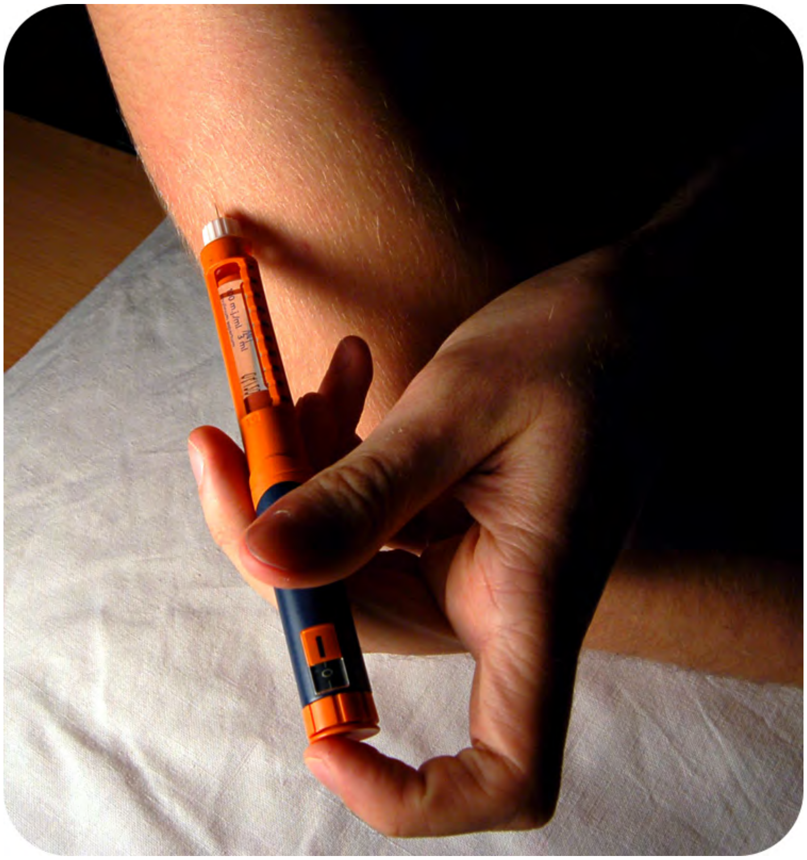
http://www.sparknotes.com/chemistry/acidsbases/phcalc/problems.html

Review

1. In the first example, how do we know that we can ignore x when determining [F^-]?
2. In example two, how do we know the ammonium ion concentration?
3. Could we write the equilibrium in example two as $NH_4^+ \rightleftarrows H^+ + NH_3$?

21.23 Buffers

- Define buffer.
- Define buffer capacity.
- Describe how a buffer controls pH.
- List some common buffer systems.



How does insulin work?

Diabetes mellitus is a disorder of glucose metabolism in which insulin production by the pancreas is impaired. Since insulin helps glucose enter the cells. A decrease of this hormone means that glucose cannot be used in its normal fashion. When this happens, the body begins to break down fats, producing a decrease in blood pH. Chemical systems in the body can balance this pH shift for a while, but excessive acid production can create serious problems if not corrected by administering insulin to restore normal glucose use.

Buffers

If only 1.0 mL of 0.10 M hydrochloric acid is added to 1.0 L of pure water the pH drops drastically from 7.0 to 4.0. This is a 1000-fold increase in the acidity of the solution. For many purposes, it is desirable to have a solution which is capable of resisting such large changes in pH when relatively small amounts of acid or base are added to them. Such a solution is called a buffer. A **buffer** is a solution of a weak acid or a base and its salt. Both components must be present for the system to act as a buffer to resist changes in pH. Commercial buffer solutions can be obtained and that have a wide variety of pH values.

Some common buffer systems are listed in the **Table** 21.13:

TABLE 21.13: **Some Common Buffers**

Buffer system	**Buffer components**	**pH of buffer (equal molarities of both components)**
Acetic acid / acetate ion	CH_3COOH / CH_3COO^-	4.74
Carbonic acid / hydrogen carbonate ion	H_2CO_3 / $HCO_3{}^-$	6.38
Dihydrogen phosphate ion / hydrogen phosphate ion	$H_2PO_4{}^-$ / $HPO_4{}^{2-}$	7.21
Ammonia / ammonium ion	NH_3 / $NH_4{}^+$	9.25

One example of a buffer is a solution made of acetic acid (the weak acid) and sodium acetate (the salt). The pH of a buffer consisting of 0.50 M CH_3COOH and 0.50 M CH_3COONa is 4.74. If 10.0 mL of 1.0 M HCl is added to 1.0 L of the buffer, the pH only decreases to 4.73. This ability to "soak up" the additional hydrogen ions from the HCl that was added is due to the reaction below.

$$\mathrm{CH_3COO^-}(aq) + \mathrm{H^+}(aq) \rightarrow \mathrm{CH_3COOH}(aq)$$

Since both the acetate ion and the acetic acid were already present in the buffer, the only thing that changes is the ratio of one to the other. Small changes in that ratio have only very minor effects on the pH.

If 10.0 mL of 1.0 M NaOH were added to another 1.0 L of the same buffer, the pH would only increase to 4.76. In this case the buffer takes up the additional hydroxide ions.

$$\mathrm{CH_3COOH}(aq) + \mathrm{OH^-}(aq) \rightarrow \mathrm{CH_3COO^-}(aq) + \mathrm{H_2O}(l)$$

Again the ration of acetate ion to acetic acid changes slightly, this time causing a very small increase in the pH.

It is possible to add so much acid or base to a buffer that its ability to resist a significant change in pH is overwhelmed. The **buffer capacity** is the amount of acid or base that can be added to buffer solution before a large change in pH occurs. The buffer capacity is exceed when the number of moles of H^+ or OH^- that are added to the buffer exceeds the number of moles of the buffer components.

Summary

- Buffer is defined.
- Reactions showing how buffers regulate pH are described.

Practice

Read the material at the link below and answer the following questions:

http://chemcollective.org/activities/tutorials/buffers/buffers3

1. What is a weak acid?

2. What does a conjugate base rarely do?
3. Write the generic equation for neutralization of a base by a weak acid.
4. Write the generic equation for neutralization of an acid by a weak base.

Review

1. What is a buffer?
2. How would the acetic acid/acetate buffer system neutralize added base?
3. If acid is added to the carbonic acid/carbonate buffer system, how is it neutralized?

- **buffer:** A solution of a weak acid or a base and its salt.
- **buffer capacity:** The amount of acid or base that can be added to buffer solution before a large change in pH occurs.

21.24 References

1. Image copyright Michael Pettigrew, 2013. http://www.shutterstock.com. Used under license from Shutterstock.com
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CHAPTER 22 Oxidation-Reduction Reactions

Chapter Outline

22.1 Oxygen in Reactions

- Define oxidation and reduction.
- Describe oxidation-reduction reactions involving oxygen.

FIGURE 22.1

Before (top) and after (bottom) teeth bleaching.

Are our teeth sparkling white? Are they attractive?

We worry a lot about our smiles. Over the years teeth do discolor some, so the procedure of teeth bleaching has become more and more popular. Best done in a dentist's office, various chemical preparations containing peroxides are used to whiten the teeth. Less effective, but easier to use. are "teeth-whitening" tooth pastes (also containing peroxides) that promise to give you a brighter smile and improve your life in every way.

Oxygen in Reactions

Many elements simply combine with oxygen to form the oxide of that element. The heating of magnesium in air allows it to combine with oxygen in the air to form magnesium oxide (see video below).

$$2\text{Mg}(s) + \text{O}_2(g) \rightarrow 2\text{MgO}(s)$$

MEDIA

Click image to the left for more content.

Compounds can also react with oxygen, possibly creating oxides of more than one element. When methane burns, carbon dioxide and water are produced.

$$\text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g)$$

Carbon dioxide is an oxide of carbon, while water is an oxide of hydrogen. Early scientists viewed **oxidation** as a process in which a substance was reacted with oxygen to produce one or more oxides. In the previous examples, magnesium and methane are being oxidized.

Oxidation is also defined as a loss of hydrogen atoms. In the following equation, ethanol is oxidized to acetaldehyde by the loss of two hydrogen atoms:

$$\mathrm{CH_3CH_2OH \rightarrow CH_3CHO + 2H\ atoms}$$

Oxidation does not necessarily require heating. Iron that is exposed to air and water slowly oxidizes in a process commonly known as rusting. Bleaches contain various compounds such as sodium hypochlorite (NaClO), which release oxygen that oxidizes stains. Hydrogen peroxide (H_2O_2) releases oxygen as it spontaneously decomposes. It acts as a bleach and an antiseptic that kills bacteria by oxidizing them.

The chemical reaction that is the opposite of oxidation is called reduction. Following from the notion that oxidation was originally thought to mean only the addition of oxygen, **reduction** was thought to be only the removal of oxygen from a substance. Many naturally occurring metal ores are present as oxides. The pure metals can be extracted by reduction. Iron is obtained from iron(III) oxide by reacting with carbon at high temperatures.

$$\mathrm{2Fe_2O_3}(s) + \mathrm{3C}(s) \rightarrow \mathrm{4Fe}(s) + \mathrm{3CO_2}(g)$$

The removal of oxygen from the Fe_2O_3 means that it is being reduced to Fe. Note that an oxidation process is simultaneously occurring. The carbon reactant is being oxidized to CO_2. This is an important concept. Oxidation and reduction must happen together. Neither can happen alone in a reaction.

Reduction can also be considered as a gain of hydrogen. The reverse of the ethanol → acetaldehyde reaction shown above is a reduction reaction:

$$\mathrm{CH_3CHO + 2H\ atoms \rightarrow CH_3CH_2OH}$$

Summary

- Oxidation and reduction are defined in terms of reactions with oxygen.
- Oxidation and reduction reactions must occur together.

Practice

Answer the questions at the following link:

http://www.chemguide.co.uk/inorganic/questions/q-redoxdefs.pdf

Review

1. Give a definition of oxidation in terms of oxygen.
2. Give a definition of reduction in terms of oxygen.
3. Characterize the following reaction in terms of the definitions of oxidation and reduction:

$$\mathrm{CH_4}(g) + \mathrm{2O_2}(g) \rightarrow \mathrm{CO_2}(g) + \mathrm{2H_2O}(g)$$

- **oxidation:** A process in which a substance was reacted with oxygen to produce one or more oxides or a reaction involving the loss of hydrogen.
- **reduction:** Removal of oxygen from a substance or the addition of hydrogen to a substance.

22.2 Oxidizing and Reducing Agents

- Define oxidizing agent.
- Define reducing agent.
- Identify oxidizing and reducing agents in a redox reaction.

Where do we get oxygen for breathing?

Life on planet Earth is a complicated and well-organized set of processes. Animals are designed to breathe oxygen and plants are designed to produce oxygen. Photosynthesis is the means by which we get the oxygen we need for life. Light striking a plant pigment known as chlorophyll initiates a complex series of reactions, many of which involve redox processes complete with movement of electrons. In this series of reactions, water is converted to oxygen gas, and we have something to sustain our lives.

Oxidizing and Reducing Agents

The reaction below is a redox reaction that produces zinc sulfide:

$$\text{Zn} + \text{S} \rightarrow \text{ZnS}$$

The half-reactions can be written:

$$\begin{aligned} &\text{Oxidation:} \quad \text{Zn} \rightarrow \text{Zn}^{2+} + 2e^- \\ &\text{Reduction:} \quad \text{S} + 2e^- \rightarrow \text{S}^{2-} \end{aligned}$$

In the reaction above, the zinc is being oxidized by losing electrons. However, there must be another substance present that gains those electrons and in this case that is the sulfur. In other words, the sulfur is causing the zinc to be oxidized. Sulfur is called the oxidizing agent. The zinc causes the sulfur to gain electrons and become reduced and so the zinc is called the reducing agent. The **oxidizing agent** is a substance that causes oxidation by accepting electrons. The **reducing agent** is a substance that causes reduction by losing electrons. The simplest way to think of this is that the oxidizing agent is the substance that is reduced, while the reducing agent is the substance that is oxidized. The sample problem below shows how to analyze a redox reaction.

Sample Problem: Oxidation-Reduction Reactions

When chlorine gas is bubbled into a solution of sodium bromide, a reaction occurs which produces aqueous sodium chloride and bromine. Determine what is being oxidized and what is being reduced. Identify the oxidizing and reducing agents.

$$\mathrm{Cl_2}(g) + 2\mathrm{NaBr}(aq) \rightarrow 2\mathrm{NaCl}(aq) + \mathrm{Br_2}(l)$$

Step 1: Plan the problem.

Break the reaction down into a net ionic equation and then into half-reactions. The substance that loses electrons is being oxidized and is the reducing agent. The substance that gains electrons is being reduced and is the oxidizing agent.

Step 2: Solve.

$$\begin{aligned} \mathrm{Cl_2}(g) + \cancel{2\mathrm{Na^+}(aq)} + 2\mathrm{Br^-}(aq) &\rightarrow \cancel{2\mathrm{Na^+}(aq)} + 2\mathrm{Cl^-}(aq) + \mathrm{Br_2}(l) \\ \mathrm{Cl_2}(g) + 2\mathrm{Br^-}(aq) &\rightarrow 2\mathrm{Cl^-}(aq) + \mathrm{Br_2}(l) \qquad \text{(net ionic reaction)} \end{aligned}$$

$$\begin{aligned} &\text{Oxidation:} \quad \mathrm{Cl_2}(g) + 2e^-(aq) \rightarrow 2\mathrm{Cl^-}(aq) \\ &\text{Reduction:} \quad 2\mathrm{Br^-}(aq) \rightarrow \mathrm{Br_2}(l) + 2e^- \end{aligned}$$

The $\mathrm{Cl_2}$ is being reduced and is the oxidizing agent. The $\mathrm{Br^-}$ is being oxidized and is the reducing agent.

Summary

- Oxidizing and reducing agents are described.
- Examples of oxidizing and reducing agents are shown.

Practice

Do problem one at the link below:

http://bhhs.bhusd.org/ourpages/auto/2010/6/28/55919701/Chapter%2020%20Worksheet%20Redox.pdf

Review

1. Define oxidizing agent.
2. Define reducing agent.

3. How does identifying the common ions help in the solution of a redox problem?

- **oxidizing agent:** A substance that causes oxidation by accepting electrons.
- **reducing agent:** A substance that causes reduction by losing electrons.

22.3 Molecular Redox Reactions

- Describe molecular redox reactions.

Cleaning your nails

Acetone is a versatile chemical, used in manufacture of plastics and as a solvent. It is a major constituent of such products as nail polish remover, paints, and cleaning fluids. The manufacture of acetone involves formation of an intermediate peroxide compound by oxidation, followed by formation of the final product.

Molecular Redox Reactions

The electron loss and gain is easy to see in a reaction in which ions are formed. However, in many reactions, no such electron transfer occurs. In a molecular compound, electrons are shared between atoms in a type of bond called a covalent bond. Yet it is still common for reactions involving molecular compounds to still be classified as redox reactions.

When hydrogen gas is reacted with oxygen gas, water is formed as the product.

$$2\text{H}_2(g)+\text{O}_2(g)\rightarrow 2\text{H}_2\text{O}(l)$$

In the individual hydrogen molecules, a pair of bonding electrons is shared equally between the hydrogen atoms (a nonpolar covalent bond). Likewise, the bonding electrons in the oxygen molecule are also shared equally between the two oxygen atoms. However, when the atoms are rearranged to form the water molecule, the electron sharing is no longer equal. In each hydrogen-oxygen bond in the water molecule, the bonding electrons are more attracted to the oxygen atom than they are to the hydrogen atom. We know this because oxygen has a higher electronegativity than hydrogen.

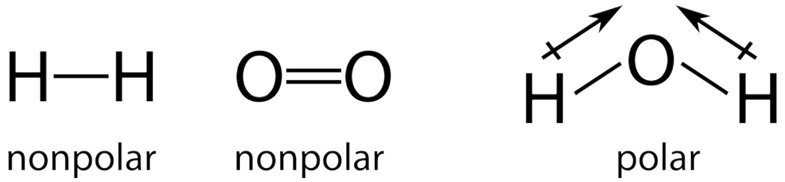

FIGURE 22.2

Bonding electrons in hydrogen, oxygen, and water.

In the course of this reaction, electrons are shifted away from each hydrogen atom and towards the oxygen atom. The hydrogen is oxidized because it undergoes a partial loss of electrons. Even though the loss is not complete enough to form ions, the hydrogen atoms in water have less electron density near them than they did in the H_2 molecule. The oxygen is reduced because it undergoes a partial gain of electrons. The oxygen atom in water has greater electron density near it than they did in the O_2 molecule.

Another approach to this type of problem is to go back to our earlier definitions of oxidation being gain of oxygen or loss of hydrogen and reduction being gain of hydrogen or loss of oxygen. This makes the decision about redox reactions much easier. The hydrogen is oxidized because it added oxygen to form water. Conversely, the oxygen is reduced because it added hydrogen to form water.

Summary

- Oxidation and reduction in molecular compounds are described.

Practice

In each of the following reactions, state whether C is oxidized or reduced:

1. $CH_3CH_2CH_2CH_3 \rightarrow CH_3CH{=}CHCH_3$
2. $CH_3CH{=}CH_2 \rightarrow CH_3CH_2CH_3$

In the following reaction, state whether O is oxidized or reduced:

3. $CH_3CH{=}O \rightarrow CH_3CH_2OH$

Review

1. Where are the electrons in the hydrogen and oxygen molecules covalent bonds?
2. How does oxygen gain electrons in the water molecule?
3. How does hydrogen lose electrons in the water molecule?

22.4 Corrosion

- Define corrosion.
- Give examples of corrosion processes.

Just rusting away

The tractor above was once a very useful piece of farm equipment. But it got old, probably broke down a lot, and you eventually couldn't get parts for it. You bought a new, more efficient tractor with all the latest gadgets. There is not much of a market for old tractors, so it sits parked out of the way, exposed to the weather, and quietly rusting away.

Corrosion

Rust is a combination of several different oxides of iron. The equations below show the steps involved in one of the many processes of rust formation.

$$2\text{Fe}(s)+\text{O}_2(g)+4\text{H}^+(aq)\rightarrow 2\text{Fe}^{2+}(aq)+2\text{H}_2\text{O}(l)$$
$$4\text{Fe}^{2+}(aq)+\text{O}_2(g)+6\text{H}_2\text{O}(l)\rightarrow 2\text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O}(s)+8\text{H}^+(aq)$$

Iron is first oxidized to iron(II) ions by oxygen. In the second step, the iron(II) ions are further oxidized and combine with water and oxygen gas to produce a hydrated form of iron(III) oxide known as rust. Rusting is one of many example of corrosion. **Corrosion** is the deterioration of metals by redox processes. Corrosion causes enormous amounts of damage to buildings, bridges, ships, cars, and other objects. It has been estimated that corrosion costs the U.S. economy over 100 billion dollars each year. A great amount of time and effort is spent to try to limit or prevent corrosion.

Corrosion Resistance

Some metals, such as gold and platinum, do not corrode easily because they are very resistant to oxidation by common substances. Some other metals begin to be oxidized, but are further protected from additional corrosion by a coating formed on the surface. Aluminum reacts with oxygen to form aluminum oxide, which remains tightly packed on the surface. The aluminum oxide prevents the interior of the aluminum from corroding. Not all corrosion is a result of reaction with oxygen. Copper corrodes by reaction with carbon dioxide to form copper(II) carbonate. This distinctive green compound is also called patina and prevents the copper underneath from further corrosion (see Statue of Liberty in the **Figure** 22.3).

FIGURE 22.3

Statue of Liberty.

Conversely, the iron oxides that form during the corrosion of iron form a surface that flakes off easily rather than remaining tight to the surface. This allows the iron to corrode completely through until the iron object is destroyed.

One way to prevent corrosion is to protect the surface of the metal. Covering the surface of the metal object with paint or oil will prevent corrosion by not allowing oxygen to contact it. Unfortunately, scratches in the paint or wearing off of the oil will allow the corrosion to begin. Corrosion-sensitive metals can also be coated with another metal that is resistant to corrosion. A "tin can" is actually made of iron coated with a thin layer of tin which protects the iron.

Corrosion can also be controlled by connecting the object to be protected to another object made of a metal that is corroded even more easily. When an iron nail is wrapped with a strip of zinc and exposed to water, the zinc (being a more active metal than iron) is oxidized while the iron remains intact. This technique, called cathodic protection, is commonly used to prevent the hulls of steel ships from rusting. Blocks of zinc are attached to the underside of the hull (see **Figure** 22.4). The zinc blocks preferentially corrode, keeping the hull intact. The zinc blocks must be periodically replaced to maintain the protection of the iron.

Summary

- The process of corrosion is described
- Examples of corrosion are given.

FIGURE 22.4

Small blocks of zinc are attached to the steel hull of this ship.

Practice

Read the material at the link below and define the following terms:

http://www.counteractrust.com/types%20of%20corrosion.htm

1. atmospheric.
2. galvanic.
3. high temperature.

Review

1. What is corrosion?
2. How does aluminum avoid complete corrosion?
3. What is the purpose of cathodic protection?

- **corrosion:** The deterioration of metals by redox processes.

22.5 Assigning Oxidation Numbers

- List the rules for determining oxidation numbers.
- Use these rules to determine oxidation number in materials.

Iron what?

Once we move from the element iron to iron compounds, we need to be able to designate clearly the form of the iron ion. In the example seen above, the iron has been oxidized to form iron oxide. Although Antoine Lavoisier first began the idea off oxidation as a concept, it was Wendell Latimer (1893-1955) who gave us the modern concept of oxidation numbers. His 1938 book *The Oxidation States of the Elements and Their Potentials in Aqueous Solution* laid out the concept in detail. Latimer was a well-known chemist who later became a member of the National Academy of Sciences. Not bad for a gentleman who started college planning on being a lawyer.

Assigning Oxidation Numbers

The **oxidation number** is a positive or negative number that is assigned to an atom to indicate its degree of oxidation or reduction. In oxidation-reduction processes, the driving force for chemical change is in the exchange of electrons between chemical species. A series of rules have been developed to help us:

1. For free elements (uncombined state), each atom has an oxidation number of zero. H_2, Br_2, Na, Be, K, O_2, P_4, all have oxidation number of 0.
2. Monatomic ions have oxidation number equal to charge. $Li^+ = +1$, $Ba^{2+} = +2$, $Fe^{3+} = +3$, $I^- = -1$, $O^{2-} = -2$, etc. Alkali metal oxidation numbers = +1. Alkaline earth oxidation numbers = +2. Aluminum

= +3 in all of its compounds. Oxygen's oxidation number is -2 *except* for hydrogen peroxide (H_2O_2), and peroxide ion (${O_2}^{2-}$) where it is -1.

3. Hydrogen's oxidation number is +1, except for when bonded to metals as the hydride ion forming binary compounds. In LiH, NaH, and CaH_2, the oxidation number is -1.
4. Fluorine has an oxidation number of -1 in all of its compounds.
5. Halogens (Cl, Br, I) have negative oxidation numbers when they form halide compounds. When combined with oxygen, they have positive numbers. In the chlorate ion (${ClO_3}^-$), the oxidation number of Cl +5, and the oxidation number of O is -2.
6. In a neutral atom or molecule, the sum of the oxidation numbers must be 0. In a polyatomic ion, the sum of the oxidation numbers of all the atoms in the ion must equal the charge on the ion.

Sample Problem: What is the oxidation number for Mn in the compound $KMnO_4$?

The oxidation number for K is +1 (rule 2)

The oxidation number for O is -2 (rule 2)

Since this is a compound (there is no charge indicated on the molecule), the net charge on the molecule is zero (rule 6)

So we have

$$\begin{aligned} +1+Mn+4(-2)&=0\\ Mn-7&=0\\ Mn&=+7 \end{aligned}$$

When dealing with oxidation numbers, we must always include the charge on the atom.

Another way to determine the oxidation number of Mn in this compound is to recall that the permanganate anion (MnO_4) has a charge of -1. In this case

$$\begin{aligned} Mn+4(-2)&=-1\\ Mn-8&=-1\\ Mn&=+7 \end{aligned}$$

Sample Problem: What is the oxidation number for iron in Fe_2O_3.

$$\begin{aligned} &O \text{ is} -2 \text{ (rule 2)}\\ &2Fe+3(-2)=0\\ &2Fe=6\\ &Fe=3. \end{aligned}$$

If we have the compound FeO, then $Fe+(-2)=0$ and $Fe=2$. Iron is one of those materials that can have more than one oxidation number.

The halogens (except for fluorine) can also have more than one number. In the compound NaCl, we know that Na is +1, so Cl must be -1. But what about $NaClO_3$?

$$\begin{aligned} Na &= 1 \\ O &= -2 \\ 1 + Cl + 3(-2) &= 0 \\ 1 + Cl - 6 &= 0. \\ Cl - 5 &= 0 \\ Cl &= +5. \end{aligned}$$

Not quite what we expected, but Cl, Br, and I will exhibit multiple oxidation numbers in compounds.

Summary

- Rules for determining oxidation numbers are listed.
- Examples of oxidation number determinations are provided.

Practice

Work the problems at the link below:

http://www.usca.edu/chemistry/genchem/oxnumb.htm

Review

1. What is the oxidation number for the element zinc?
2. Nitrogen can exist in several oxide forms. What is the oxidation number of N in NO? in N_2O? in NO_2?
3. What is the oxidation number of H in HCl? in NaH?

- **oxidation number:** A positive or negative number that is assigned to an atom to indicate its degree of oxidation or reduction.

22.6 References

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CHAPTER 23 Electrochemistry

Chapter Outline

23.1 Direct Redox Reactions

- Describe the use of the activity series of metals table.
- Predict reaction spontaneity based on the activity series table.

How much for that necklace?

Gold and silver are widely used metals for making jewelry. One of the reasons these metals are employed for this purpose is that they are very unreactive. They do not react in contact with most other metals, so they are more likely to stay intact under challenging conditions. Who wants their favorite piece of jewelry to fall apart on them?

Direct Redox Reactions

When a strip of zinc metal is placed into a blue solution of copper(II) sulfate (**Figure** 23.1), a reaction immediately begins as the zinc strip begins to darken. If left in the solution for a longer period of time, the zinc will gradually decay due to oxidation to zinc ions. At the same time, the copper(II) ions from the solution are reduced to copper metal (see **Figure** 23.2), which causes the blue copper(II) sulfate solution to become colorless.

The process that occurs in this redox reaction is shown below as two separate half-reactions, which can then be combined into the full redox reaction.

FIGURE 23.1
Copper sulfate solution.

FIGURE 23.2
Reaction of zinc metal in copper sulfate solution.

$$\begin{array}{ll}
\text{Oxidation :} & \mathrm{Zn}(s) \rightarrow \mathrm{Zn}^{2+}(aq) + 2e^- \\
\text{Reduction :} & \mathrm{Cu}^{2+}(aq) + 2e^- \rightarrow \mathrm{Cu}(s) \\
\hline
\text{Full Reaction :} & \mathrm{Zn}(s) + \mathrm{Cu}^{2+}(aq) \rightarrow \mathrm{Zn}^{2+}(aq) + \mathrm{Cu}(s)
\end{array}$$

Why does this reaction occur spontaneously? The activity series is a listing of elements in descending order of reactivity. An element that is higher in the activity series is capable of displacing an element that is lower on the series in a single-replacement reaction. This series is also listing of elements in order of ease of oxidation. The elements at the top are the easiest to oxidize, while those at the bottom are the most difficult to oxidize. The **Table** 23.1 shows the activity series together with each element's oxidation half-reaction.

TABLE 23.1: **Activity Series of Metals**

	Element	**Oxidation Half Reaction**
Most active or most easily oxidized	Lithium	$Li(s) \rightarrow Li^+(aq) + e^-$
	Potassium	$K(s) \rightarrow K^+(aq) + e^-$
	Barium	$Ba(s) \rightarrow Ba^{2+}(aq) + 2e^-$
	Calcium	$Ca(s) \rightarrow Ca^{2+}(aq) + 2e^-$
	Sodium	$Na(s) \rightarrow Na^+(aq) + e^-$
	Magnesium	$Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$
	Aluminum	$Al(s) \rightarrow Al^{3+}(aq) + 3e^-$
	Zinc	$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
	Iron	$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$
	Nickel	$Ni(s) \rightarrow Ni^{2+}(aq) + 2e^-$
	Tin	$Sn(s) \rightarrow Sn^{2+}(aq) + 2e^-$
	Lead	$Pb(s) \rightarrow Pb^{2+}(aq) + 2e^-$
	Hydrogen	$H_2(g) \rightarrow 2H^+(aq) + 2e^-$
	Copper	$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
	Mercury	$Hg(l) \rightarrow Hg^{2+}(aq) + 2e^-$
	Silver	$Ag(s) \rightarrow Ag^+(aq) + e^-$
	Platinum	$Pt(s) \rightarrow Pt^{2+}(aq) + 2e^-$
Least active or most difficult to oxidiz	Gold	$Au(s) \rightarrow Au^{3+}(aq) + 3e^-$

Notice that zinc is listed above copper on the activity series, which means that zinc is more easily oxidized than copper. That is why copper(II) ions can act as an oxidizing agent when put into contact with zinc metal. Ions of any metal that is below zinc, such as lead or silver, would oxidize the zinc in a similar reaction. These types of reactions are called **direct redox reactions** because the electrons flow directly from the atoms of the metal to the cations of the other metal. However, no reaction will occur if a strip of copper metal is placed into a solution of zinc ions, because the zinc ions are not able to oxidize the copper. In other words, such a reaction is nonspontaneous.

Summary

- The activity series of metal reactivities is given.
- Parameters for spontaneous reactions between metals are described.

Practice

Watch the video at the link below and answer the following questions:

MEDIA

Click image to the left for more content.

http://www.youtube.com/watch?v=2MawIDT5DFU

1. What happened when Mg and Zn were placed in the Pb^{2+} solution?

2. Did the Zn strip react in the Mg^{2+} solution?
3. How was Ag shown to be least reactive?

Review

1. What metals are high in the activity series?
2. What metals are low in the activity series?
3. Is tin easier to oxidize than magnesium?

- **direct redox reaction:** Electrons flow directly from the atoms of the metal to the cations of the other metal.

23.2 Electrochemical Reaction

- Define electrochemistry.
- Describe an electrochemical reaction.
- List the components of an electrochemical reaction.

What happened to that sculpture?

Metal exposed to the outside elements will usually corrode if not protected. The corrosion process is a series of redox reactions involving the metal of the sculpture. In some situations, the metals are deliberately left unprotected so that the surface will undergo changes that may enhance the esthetic value of the work.

Electrochemical Reactions

Chemical reactions either absorb or release energy and that energy can be in the form of electricity. **Electrochemistry** is a branch of chemistry that deals with the interconversion of chemical energy and electrical energy. Electrochemistry has many common applications in everyday life. Batteries of all sorts from those used to power a flashlight to a calculator to an automobile rely on chemical reactions to generate electricity. Electricity is used to plate objects with decorative metals like gold or chromium. Electrochemistry is important in the transmission of nerve impulses in biological systems. Redox chemistry, the transfer of electrons, is behind all electrochemical processes.

The reaction of zinc metal with copper(II) ions described above is called a direct redox process or reaction. The electrons that are transferred in the reaction go directly from the Zn atoms on the surface of the strip to the Cu^{2+} ions in the area of the solution right next to the zinc strip. Electricity on the other hand, requires the passage of electrons through a conducting medium, such as a wire, in order to do work. This work could be lighting a light bulb or powering a refrigerator or heating a house. When the redox reaction is direct, those electrons cannot be made to do work. Instead, we must separate the oxidation process from the reduction process and force the electrons to move from one place to another in between. That is the key to the structure of the electrochemical cell. An **electrochemical cell** is any device that converts chemical energy into electrical energy or electrical energy into chemical energy.

There are three components that make up an electrochemical reaction. There must be a solution where redox reactions can occur. These reactions generally take place in water to facilitate electron and ion movement. A conductor must exist for electrons to be transferred. This conductor is usually some kind of wire so that electrons can move from one site to another. Ions also must be able to move through some form of salt bridge that facilitates ion migration.

Summary

- Electrochemistry is defined.
- A description of an electrochemical cell is given.
- Components of an electrochemical reaction are listed.

Practice

Read the material at the link below and answer the following questions:

http://bouman.chem.georgetown.edu/S02/lect25/lect25.htm

1. Spontaneous reactions occur in what type of system?
2. Nonspontaneous reactions occur in what type of system?
3. What is potential?
4. How is potential measured?

Review

1. What is an electrochemical reaction?
2. What type of chemical reaction is involved?
3. What needs to be able to move in an electrochemical reaction?

- **electrochemical cell:** Any device that converts chemical energy into electrical energy or electrical energy into chemical energy.
- **electrochemistry:** A branch of chemistry that deals with the interconversion of chemical energy and electrical energy.

23.3 Voltaic Cells

- Describe the structure and function of a voltaic cell.

What made it twitch?

Luigi Galvani (1737-1798) was an Italian physician and scientist who did research on nerve conduction in animals. His accidental observation of twitching frog legs when they were in contact with an iron scalpel while they hung on copper hooks led to studies on electrical conductivity in muscles and nerves. He believed that animal tissues contained an "animal electricity" similar to the natural electricity that caused lightning to form.

Voltaic Cells

A **voltaic cell** is an electrochemical cell that uses a spontaneous redox reaction to produce electrical energy.

The voltaic cell (see **Figure** 23.3) consists of two separate compartments. A **half-cell** is one part of a voltaic cell in which either the oxidation or reduction half-reaction takes place. The left half-cell is a strip of zinc metal in a solution of zinc sulfate. The right half-cell is a strip of copper metal in a solution of copper(II) sulfate. The strips of metal are called electrodes. An **electrode** is a conductor in a circuit that is used to carry electrons to a nonmetallic part of the circuit. The nonmetallic part of the circuit is the electrolyte solutions in which the electrodes are placed.

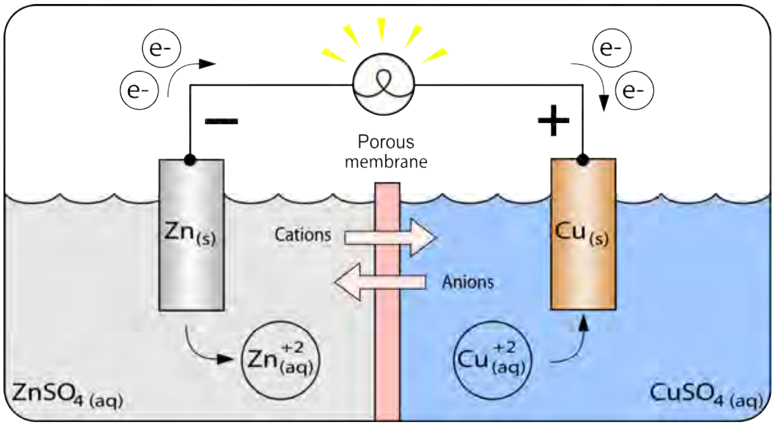


FIGURE 23.3
Voltaic cell.

A metal wire connects the two electrodes. A switch opens or closes the circuit. A porous membrane is between the two half-cells to complete the circuit.

The various electrochemical processes that occur in a voltaic cell occur simultaneously. It is easiest to describe them in the following steps, using the above zinc-copper cell as an example.

1. Zinc atoms from the zinc electrode are oxidized to zinc ions. This happens because zinc is higher than copper on the activity series and so is more easily oxidized.

$$\mathrm{Zn}(s) \rightarrow \mathrm{Zn}^{2+}(aq) + 2e^-$$

The electrode at which oxidation occurs is called the **anode**. The zinc anode gradually diminishes as the cell operates due to the loss of zinc metal. The zinc ion concentration in the half-cell increases. Because of the production of electrons at the anode, it is labeled as the negative electrode.

2. The electrons that are generated at the zinc anode travel through the external wire and register a reading on the voltmeter. They continue to the copper electrode.

3. Electrons enter the copper electrode where they combine with the copper(II) ions in the solution, reducing them to copper metal.

$$\mathrm{Cu}^{2+}(aq) + 2e^- \rightarrow \mathrm{Cu}(s)$$

The electrode at which reduction occurs is called the **cathode**. The cathode gradually increases in mass because of the production of copper metal. The concentration of copper(II) ions in the half-cell solution decreases. The cathode is the positive electrode.

4. Ions move through the membrane to maintain electrical neutrality in the cell. In the cell illustrated above, sulfate ions will move from the copper side to the zinc side to compensate for the decrease in Cu^{2+} and the increase in Zn^{2+}.

The two half-reactions can again be summed to provide the overall redox reaction occurring in the voltaic cell.

$$\mathrm{Zn}(s) + \mathrm{Cu}^{2+}(aq) \rightarrow \mathrm{Zn}^{2+}(aq) + \mathrm{Cu}(s)$$

Summary

- The structure of a voltaic cell is described.
- The reactions producing electron flow are given.

Practice

Read the material at the link below and answer the following questions:

http://chemed.chem.wisc.edu/chempaths/GenChem-Textbook/Galvanic-Cells/chemprime/CoreChem3AElectrochemical_Cells-699.html

1. What is the difference between an electrolytic cell and a voltaic cell?
2. Where does the oxidation reaction take place in a voltaic cell?
3. Where does the reduction reaction take place?
4. List some examples of voltaic cells that are of commercial importance.

Review

1. What does a voltaic cell do?
2. Why are the two electrodes physically separated?
3. What is the purpose of the porous membrane?

- **anode:** The electrode at which oxidation occurs.
- **cathode:** The electrode at which reduction occurs.
- **electrode:** A conductor in a circuit that is used to carry electrons to a nonmetallic part of the circuit.
- **half-cell:** One part of a voltaic cell in which either the oxidation or reduction half-reaction takes place.
- **voltaic cell:** An electrochemical cell that uses a spontaneous redox reaction to produce electrical energy.

23.4 Electrical Potential

- Define electrical potential.
- Define reduction potential.
- Define cell potential.

How many volts is that?

The voltmeter doesn't measure volts directly; it measures electric current flow. But don't worry – current flow and voltage can be directly related to one another. The first meters were called galvanometers and they used basic laws of electricity to determine voltage. They we heavy and hard to work with, but got the job done. The first multimeters were developed in the 1920s, but true portability had to wait until printed circuits and transistors replaced the cumbersome wires and vacuum tubes.

Electrical Potential

Electrical potential is a measurement of the ability of a voltaic cell to produce an electric current. Electrical potential is typically measured in volts (V). The voltage that is produced by a given voltaic cell is the electrical potential difference between the two half-cells. 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 and 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. In a zinc-copper voltaic cell, it is the copper(II) ions that will be reduced to copper metal. That is because the Cu^{2+} ions have a greater attraction for electrons than the Zn^{2+} ions in the other half-cell. Instead, the zinc metal is oxidized. The **reduction potential** is a measure of 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, oxidation will occur. The **cell potential (E_{cell})** is the difference in reduction potential between the two half-cells in an electrochemical cell.

Summary

- Definitions for type of electrical potential are given.

Practice

Read the material at the link below and answer the following questions:

http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1920/nernst-bio.html

1. Where was Nernst born?
2. What theory did he develop in 1889?
3. What musical instrument did he develop that musicians did not like?

Review

1. Why can’t we measure the electrical potential of an isolated half-cell?
2. What does the reduction potential tell us?
3. What is the cell potential?

- **cell potential (E_{cell}):** The difference in reduction potential between the two half-cells in an electrochemical cell.
- **electrical potential:** A measurement of the ability of a voltaic cell to produce an electric current.
- **reduction potential:** A measure of the tendency of a given half-reaction to occur as a reduction in an electrochemical cell.

23.5 Standard Hydrogen Electrode

- Describe the hydrogen electrode.
- Describe how this electrode is used in determining reduction potentials.

What is a standard?

We all compare ourselves to something. Can I run faster than you? Am I taller than my dad? These are relative comparisons that don't give a lot of useful data. When we use a standard for our comparisons, everybody can tell how one thing compares to another. The meter is the same everywhere in the world, so the 100 meter rack in one country is exactly the same distance as the 100 meter track on another country. We now have a universal basis for comparison.

Standard Hydrogen Electrode

The activity series allows us to predict the relative reactivities of different materials when used in oxidation-reduction processes. We also know we can create electric current by a combination of chemical processes. But how do we predict the expected amount of current that will flow through the system? We measure this flow as voltage (an electromotive force or potential difference).

In order to do this, we need some way of comparing the extent of electron flow in the various chemical systems. The best way to do this is to have a baseline that we use – a standard that everything can be measured against. For determination of half-reaction current flows and voltages, we use the **standard hydrogen electrode**. The **Figure** 23.4 illustrates this electrode. A platinum wire conducts the electricity through the circuit. The wire is immersed in a 1.0 M strong acid solution and H_2 gas is bubbled in at a pressure of one atmosphere and a temperature of 25°C. The half-reaction at this electrode is $H_2 \rightarrow 2H^+ + 2e^-$.

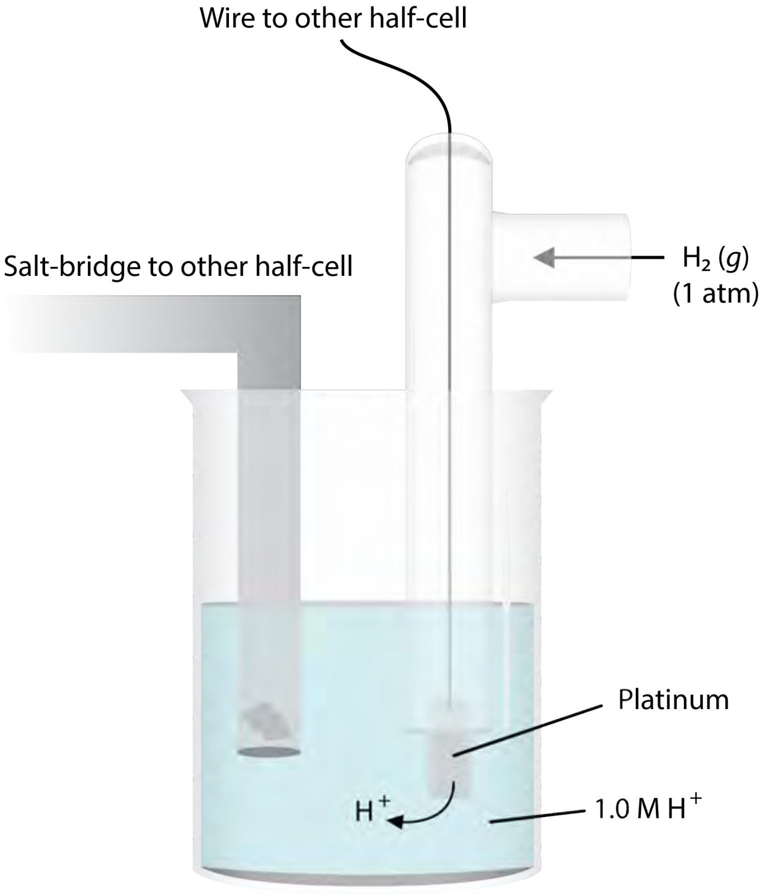


FIGURE 23.4

The standard hydrogen electrode.

Under these conditions, the potential for the hydrogen reduction is defined as exactly zero. We call this E^0, the standard reduction potential.

We can then use this system to measure the potentials of other electrodes in the half-cell. A metal and one of its salts (sulfate is often used) is in the second half-cell. We will use zinc as our example (see **Figure** 23.5).

As we observe the reaction, we notice that the mass of solid zinc decreases during the course of the reaction. This suggests that the reaction occurring in that half-cell is

$$\mathrm{Zn}(s) \rightarrow \mathrm{Zn}^{2+}(aq) + 2e^-$$

So, we have the following process occurring in the cell:

$$\begin{aligned}&\mathrm{Zn}(s) \rightarrow \mathrm{Zn}^{2+}(aq) + 2e^- \ (\text{anode} - \text{oxidation})\\&2\mathrm{H}^+ + 2e^- \rightarrow \mathrm{H}_2 \ (\text{cathode} - \text{reduction})\end{aligned}$$

and the measured cell voltage is 0.76 volts (abbreviated as v).

We define the standard emf (electromotive force) of the cell as:

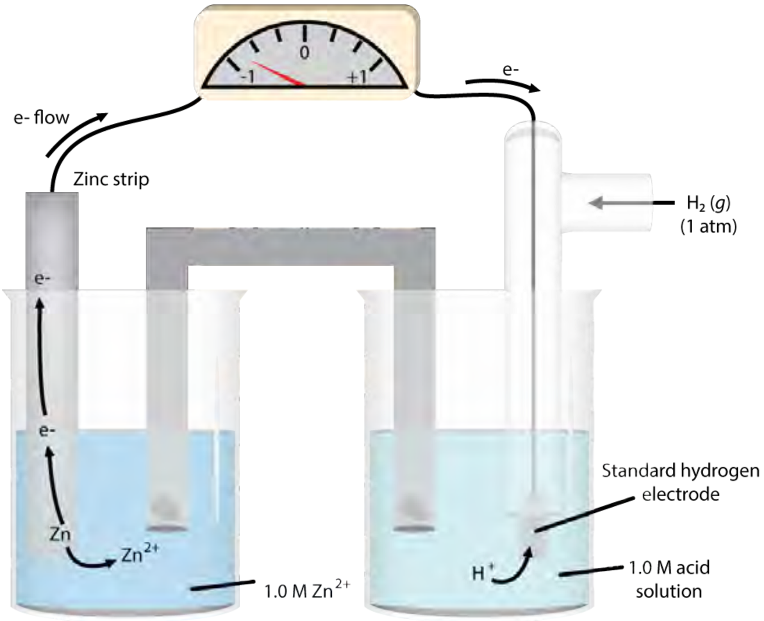


FIGURE 23.5

The standard hydrogen half-cell paired with a zinc half-cell.

$$
\begin{aligned}
E^0{}_{\text{cell}} &= E^0{}_{\text{cathode}} - E^0{}_{\text{anode}} \\
0.76\text{ V} &= 0 - E^0_{\text{Zn cell}} \\
E^0_{\text{Zn cell}} &= -0.76 \text{ volts}
\end{aligned}
$$

We can do the same determination with a copper cell (**Figure** 23.6).

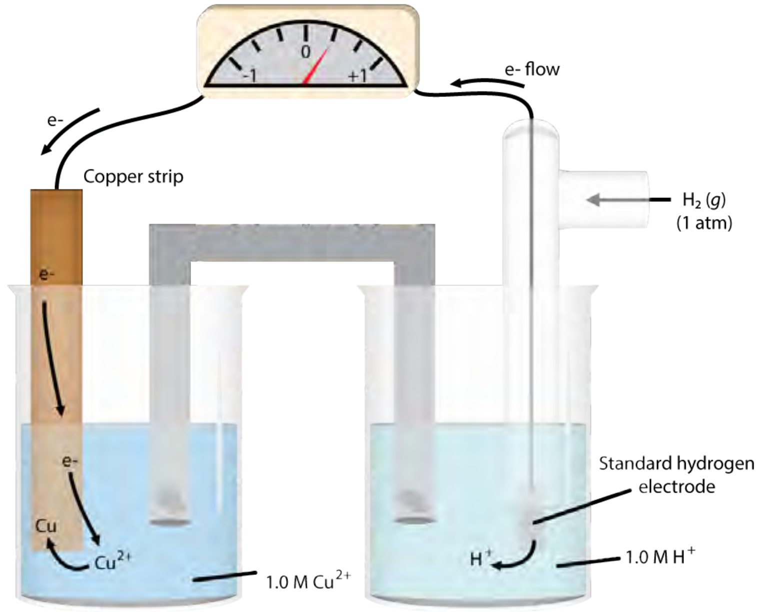


FIGURE 23.6

The standard hydrogen half-cell paired with a copper half-cell.

As we run the reaction, we see that the mass of the copper increases, so we write the half-reaction:

$$\mathrm{Cu}^{2+} + 2e^- \rightarrow \mathrm{Cu}$$

This makes the copper electrode the cathode. We now have the two half-reactions:

$$\begin{aligned} &\mathrm{H}_2 \rightarrow 2\mathrm{H}^+ + 2e^- \text{ (anode)} \\ &\mathrm{Cu}^{2+} + 2e^- \rightarrow \mathrm{Cu} \text{ (cathode)} \end{aligned}$$

and we determine the E^0 for the system to be 0.34 v.

Again, $E^0{}_{\text{cell}} = E^0{}_{\text{cathode}} - E^0{}_{\text{anode}}$

$0.34 \text{ V} = E^o_{\text{copper}} - 0$ so copper potential $= 0.34$ V

Now we want to build a system in which both zinc and copper are involved. We know from the activity series that zinc will be oxidized and cooper reduced, so we can use the values at hand:

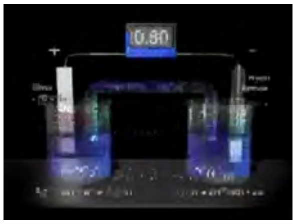
$E^0{}_{\text{cell}} = 0.34 \text{ V (copper)} - (-0.76 \text{ V zinc}) = 1.10$ volts for the cell

Summary

- The structure of the standard hydrogen electrode is described.
- Examples of using this electrode to determine reduction potentials are given.

Practice

Watch the video at the link below and answer the following questions:



MEDIA

Click image to the left for more content.

http://www.youtube.com/watch?v=mrOm6xZip6k

1. Why does a cation move through the salt bridge to the hydrogen side?
2. Why is the zinc half-cell the anode?
3. How is the standard potential defined?

Review

1. What is the defined potential of the hydrogen electrode?
2. What is the chemical composition of this electrode?
3. What are the standard conditions for the other half-cell?

- **standard hydrogen electrode:** The standard measurement of electrode potential for the thermodynamic scale of redox potentials.

23.6 Calculating Standard Cell Potentials

- Perform calculations of standard cell potential.
- Describe abilities of materials to participate in redox reactions based on standard cell potential data.

Keeping rust away

When exposed to moisture, steel will begin to rust fairly quickly. This creates a significant problem for items like nails that are exposed to the atmosphere. The nails can be protected by coated them with zinc metal, making a galvanized nail. The zinc is more likely to oxidize than the iron in the steel, so it prevents rust from developing on the nail.

Calculating Standard Cell Potentials

In order to function, any electrochemical cell must consist of two half-cells. The **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 highest reduction potential according to the table will undergo reduction within the cell. The half-cell with the lowest reduction potential will undergo oxidation within the cell. If those specifications are followed, the overall cell potential will be a positive value. The cell potential must be positive in order for redox reaction of the cell to be spontaneous. If a negative cell potential were to be calculated, that reaction would be spontaneous in the reverse direction.

TABLE 23.2: **Standard Reduction Potentials at 25°C**

Half-Reaction	E^0 **(V)**
$F_2 + 2e^- \rightarrow 2F^-$	+2.87

TABLE 23.2: (continued)

$PbO_2 + 4H^+ + SO_4{}^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	+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
$Al^{3+} + 3e^- \rightarrow Al$	-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

Sample Problem: Calculating Standard Cell Potentials

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.

Step 1: List the known values and plan the problem.

Known

- $E^0_{\text{Ag}} = +0.80 \text{ V}$
- $E^0_{\text{Sn}} = -0.14 \text{ V}$

Unknown

- $E^0_{cell} = ? \ V$

The silver half-cell will undergo reduction because its standard reduction potential is higher. The tin half-cell will undergo oxidation. The overall cell potential can be calculated by using the equation $E^0_{\text{cell}} = E^0_{\text{red}} - E^0_{\text{oxid}}$.

Step 2: Solve.

$$\begin{aligned}\text{oxidation (anode): } & \text{Sn}(s) \rightarrow \text{Sn}^{2+}(aq) + 2e^- \\ \text{reduction (cathode): } & \text{Ag}^+(aq) + e^- \rightarrow \text{Ag}(s)\end{aligned}$$

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. After doing that and adding to the tin half-cell reaction, the overall equation is obtained.

$$\text{overall equation} \qquad \text{Sn}(s) + 2\text{Ag}^+(aq) \rightarrow \text{Sn}^{2+}(aq) + 2\text{Ag}(s)$$

The cell potential is calculated.

$$E^0_{\text{cell}} = E^0_{\text{red}} - E^0_{\text{oxid}} = +0.80 \text{ V} - (-0.14 \text{ V}) = +0.94 \text{ V}$$

Step 3: Think about your result.

The standard cell potential is positive, so the reaction is spontaneous as written. Tin is oxidized at the anode, while silver ion 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.

Oxidizing and Reducing Agents

A substance which is capable of being reduced very easily is a strong oxidizing agent. Conversely, a substance which is capable of being oxidized very easily is a strong reducing agent. According to the standard cell potential table, fluorine (F_2) is the strongest oxidizing agent. It will oxidize any substance below on the table. For example, fluorine will oxidize gold metal according to the following reaction.

$$3\text{F}_2(g) + 2\text{Au}(s) \rightarrow 6\text{F}^-(aq) + 2\text{Au}^{3+}(aq)$$

Lithium metal (Li) is the strongest reducing agent. It is capable of reducing any substance above on the table. For example, lithium will reduce water according to this reaction.

$$2\text{Li}(s) + 2\text{H}_2\text{O}(l) \rightarrow 2\text{Li}^+(aq) + 2\text{OH}^-(aq) + \text{H}_2(g)$$

Using the table above will allow you to predict whether reactions will occur or not. For example, nickel metal is capable of reducing copper(II) ions, but is not capable of reducing zinc ions. Nickel (Ni) is below Cu^{2+}, but is above Zn^{2+} on the table. In order for two species to react spontaneously, they must be in an upper-left and lower-right diagonal orientation as shown below.

Summary

- Standard cell potential calculations are described.
- Guidelines for making predictions of reaction possibilities using standard cell potentials are given.

Practice

Read the material at the link below and answer the questions at the end:

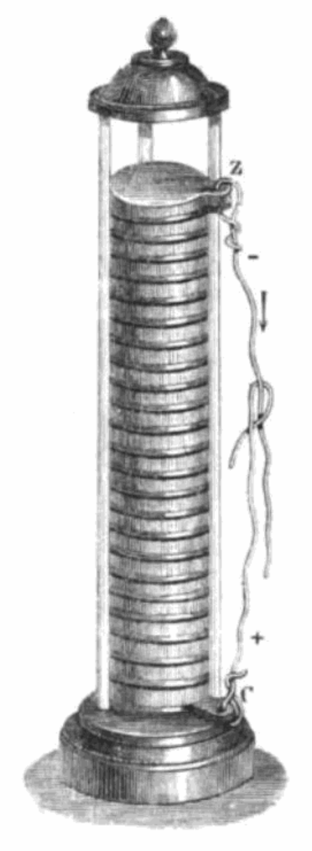
http://chemwiki.ucdavis.edu/Analytical_Chemistry/Electrochemistry/Voltaic_Cells/The_Cell_Potential#Problems

Review

1. What type of reaction will the half-cell with the highest reduction potential undergo?
2. What sign must the overall cell potential be in order for a reaction to be spontaneous?
3. Is Zn^{2+} a stronger or weaker reducing agent than Mg^{2+}?

23.7 Batteries

- Describe the construction of a dry cell.
- Write reactions for a regular dry cell and an alkaline dry cell.
- Describe the construction of a lead storage battery.
- Write reactions for the led storage battery.



Ouch, that hurts

Alessandro Volta developed the first "voltaic cell" in 1800 (pictured above). This battery consisted of alternating disks of zinc and silver with pieces of cardboard soaked in brine separating the disks. Since there were no voltmeters at the time (and no idea that the electric current was due to electron flow), Volta had to rely on another measure of battery strength: the amount of shock produced (it's never a good idea to test things on yourself). He found that the intensity of the shock increased with the number of metal plates in the system. Devices with twenty plates produced a shock that was quite painful. It's a good thing we have voltmeters today to measure electric current instead of "stick your finger on this and tell me what you feel".

Batteries

Two variations on the basic voltaic cell are the dry cell and the lead storage battery.

Dry Cells

Many common batteries, such as those used in a flashlight or remote control, are voltaic dry cells. These batteries are called dry cells because the electrolyte is a paste. They are relatively inexpensive, but do not last a long time and are not rechargeable.

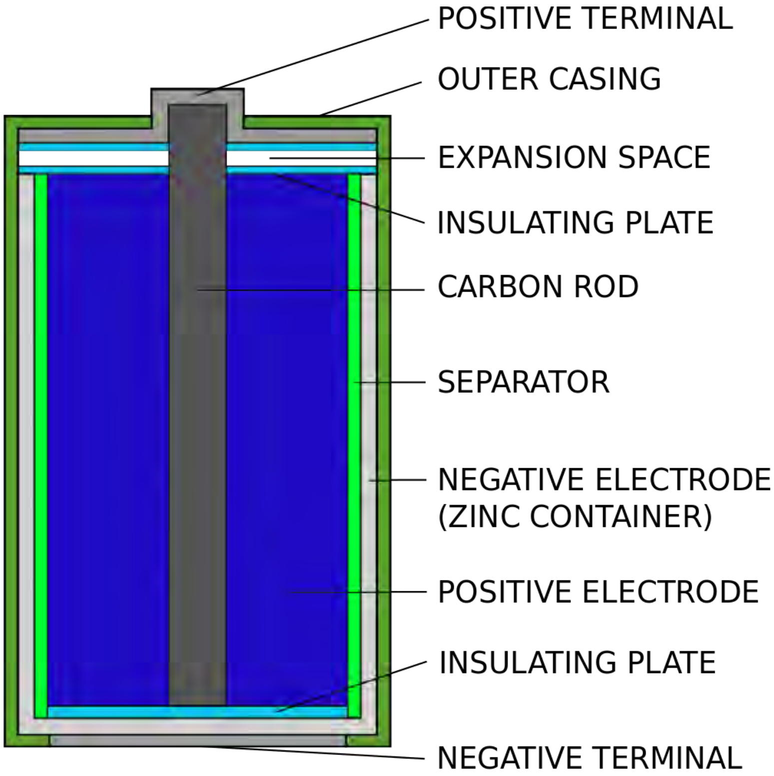


FIGURE 23.7

A zinc-carbon dry cell.

In the zinc-carbon dry cell, the anode is a zinc container, while the cathode is a carbon rod through the center of the cell. The paste is made of manganese(IV) oxide (MnO_2), ammonium chloride (NH_4Cl), and zinc chloride ($ZnCl_2$) in water. The half-reactions for this dry cell are:

Anode (oxidation): $\mathrm{Zn}(s) \rightarrow \mathrm{Zn}^{2+} + 2e^-$

Cathode (reduction): $2\mathrm{MnO}_2(s) + 2\mathrm{NH}_4{}^-(aq) + 2e^- \rightarrow \mathrm{Mn}_2\mathrm{O}_3(s) + 2\mathrm{NH}_3(aq) + \mathrm{H}_2\mathrm{O}(l)$

The paste prevents the contents of the dry cell from freely mixing, so a salt bridge is not needed. The carbon rod is a conductor only and does not undergo reduction. The voltage produced by a fresh dry cell is 1.5 V, but decreases during use.

An alkaline battery is a variation on the zinc-carbon dry cell. The alkaline battery has no carbon rod and uses a paste of zinc metal and potassium hydroxide instead of a solid metal anode. The cathode half-reaction is the same, but the anode half-reaction is different.

Anode (oxidation): $\mathrm{Zn}(s) + 2OH^-(aq) \rightarrow \mathrm{Zn(OH)}_2(s) + 2e^-$

Advantages to the alkaline battery are that it has a longer shelf life and the voltage does not decrease during use.

Lead Storage Batteries

A **battery** is a group of electrochemical cells combined together as a source of direct electric current at a constant voltage. Dry cells are not true batteries since they are only one cell. The lead storage battery is commonly used as the power source in cars and other vehicles. It consists of six identical cells joined together, each of which has a lead anode and a cathode made of lead(IV) oxide (PbO_2) packed on a metal plate.

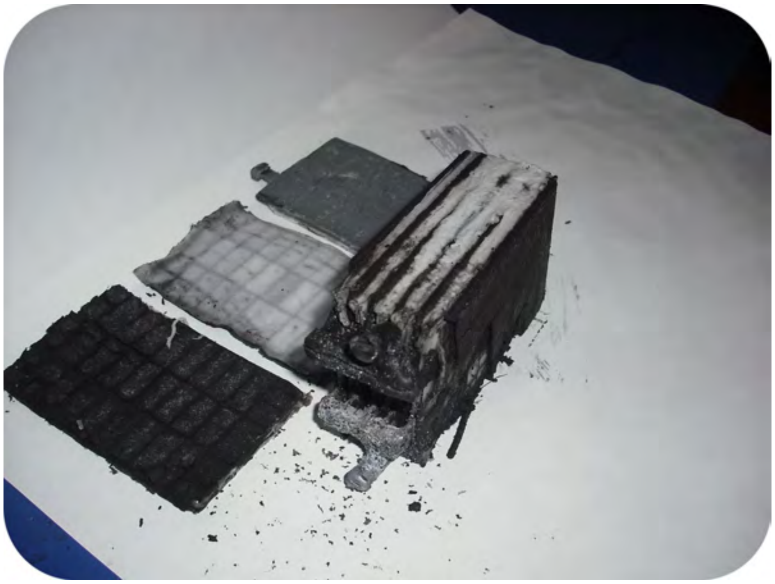


FIGURE 23.8

A lead storage battery, such as those used in cars, consists of six identical electrochemical cells and is rechargeable.

The cathode and anode are both immersed in an aqueous solution of sulfuric acid, which acts as the electrolyte. The cell reactions are:

$$\begin{array}{ll}
\text{Anode (oxidation):} & Pb(s) + {SO_4}^{2-}(aq) \rightarrow PbSO_4(s) + 2e^- \\
\text{Cathode (reduction):} & PbO_2(s) + 4H^+ + {SO_4}^{2-}(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l) \\
\hline
\text{Overall:} & Pb(s) + PbO_2(s) + 4H^+(aq) + 2{SO_4}^{2-}(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)
\end{array}$$

Each cell in a lead storage battery produces 2 V, so a total of 12 V is generated by the entire battery. This is used to start the car or power other electrical systems.

Unlike a dry cell, the lead storage battery is rechargeable. Note that the forward redox reaction generates solid lead(II) sulfate which slowly builds up on the plates. Additionally, the concentration of sulfuric acid decreases. When the car is running normally, its generator recharges the battery by forcing the above reactions to run in the opposite, or nonspontaneous direction.

$$2PbSO_4(s) + 2H_2O(l) \rightarrow Pb(s) + PbO_2(s) + 4H^+(aq) + 2{SO_4}^{2-}(aq)$$

This regenerates the lead, lead(IV) oxide, and sulfuric acid needed for the battery to function properly. Theoretically, a lead storage battery should last forever. In practice, the recharging is not 100% efficient because some of the lead(II) sulfate falls from the electrodes and collects on the bottom of the cells.

Summary

- Construction of a dry cell and a battery are given.

- Chemical reactions for both types are described.

Practice

Read the material at the link below and answer the following questions:

http://www.fueleconomy.gov/feg/fuelcell.shtml

also click on the fuel stack term highlighted on the page.

1. Where does hydrogen enter the fuel cell?
2. How are electrons produced?
3. Where do the electrons go?
4. What is the product of the fuel cell reaction?

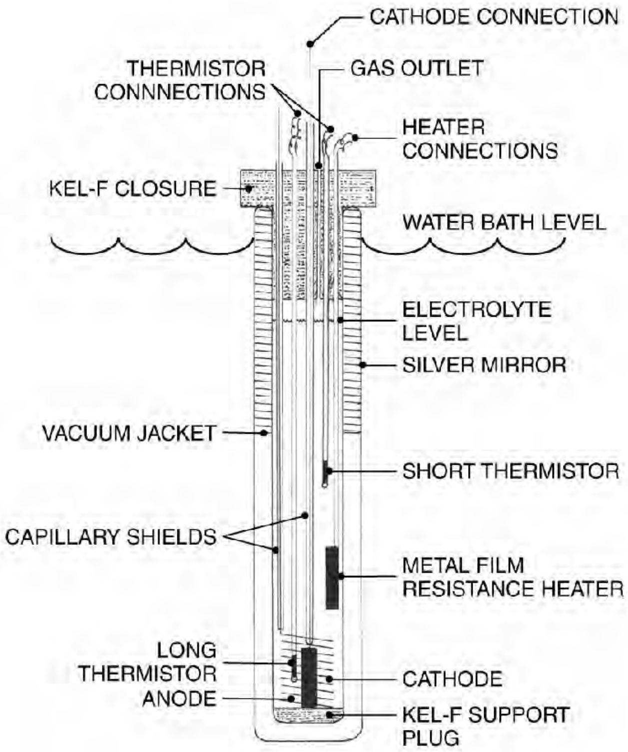
Review

1. What purpose does the carbon rod serve in a dry cell?
2. Where does an alkaline battery get its name?
3. Why is recharging a car battery not 100% efficient?

- **battery:** A group of electrochemical cells combined together as a source of direct electric current at a constant voltage.

23.8 Electrolytic Cells

- Define electrolysis.
- Describe the operation and function of an electrolytic cell.



Do we have heat yet?

In 1989, two scientists announced that they had achieved "cold fusion", the process of fusing together of elements at essentially room temperature to achieve energy production. The hypothesis was that the fusion would produce more energy than was required to cause the process to occur. Their process involved the electrolysis of heavy water (water molecules containing some deuterium instead of normal hydrogen) on a palladium electrode. The experiments could not be reproduced and their scientific reputations were pretty well shot. However, in more recent years, both industry and government researchers are taking another look at this process. The device illustrated above is part of a government project and NASA is also doing some studies. Cold fusion may not be so "cold" after all.

Electrolytic Cells

A voltaic cell uses a spontaneous redox reaction to generate an electric current. It is 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 made 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 appearance of 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. In an electrolytic cell, electric current is applied to provide a source of electrons for driving the reaction in a nonspontaneous direction. In a voltaic cell, the reaction goes in a direction that releases electrons spontaneously. In an electrolytic cell, the input of electrons from an external source forces the reaction to go in the opposite direction.

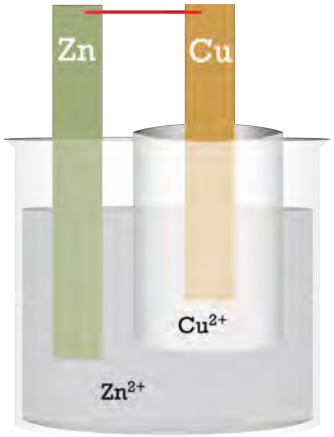


FIGURE 23.9

Zn/Cu cell.

The spontaneous direction for the reaction between Zn and Cu is for the Zn metal to be oxidized to Zn^{2+} ions, while the Cu^{2+} ions are reduced to Cu metal. That made the zinc electrode the anode and the copper electrode the cathode. When the same half-cells are connected to a battery via the 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.

oxidation (anode)	$\mathrm{Cu}(s) \rightarrow \mathrm{Cu}^{2+}(aq) + 2e^-$	$E^0 = -0.34$ V
reduction (cathode)	$\mathrm{Zn}^{2+}(aq) + 2e^- \rightarrow \mathrm{Zn}(s)$	$E^0 = -0.76$ V
overall reaction	$\mathrm{Cu}(s) + \mathrm{Zn}^{2+}(aq) \rightarrow \mathrm{Cu}^{2+}(aq) + \mathrm{Zn}(s)$	cellE^0

=-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. Another difference between a voltaic cell and an electrolytic cell is the signs of the electrodes. In a voltaic cell, the anode is negative and the cathode is positive. In an electrolytic cell, the anode is positive because it is connected to the positive terminal of the battery. The cathode is negative. Electrons still flow through the cell form the anode to the cathode.

Summary

- The function of an electrolytic cell is described.
- Reactions illustrating electrolysis are given.

Practice

Watch the video at the link below and answer the following questions:

MEDIA

Click image to the left for more content.

http://www.youtube.com/watch?v=y4yYF8gSHdA

1. What was the source of electricity?
2. What was the purpose of the steel attached to an electrode?
3. What is used to help carry the electric current?

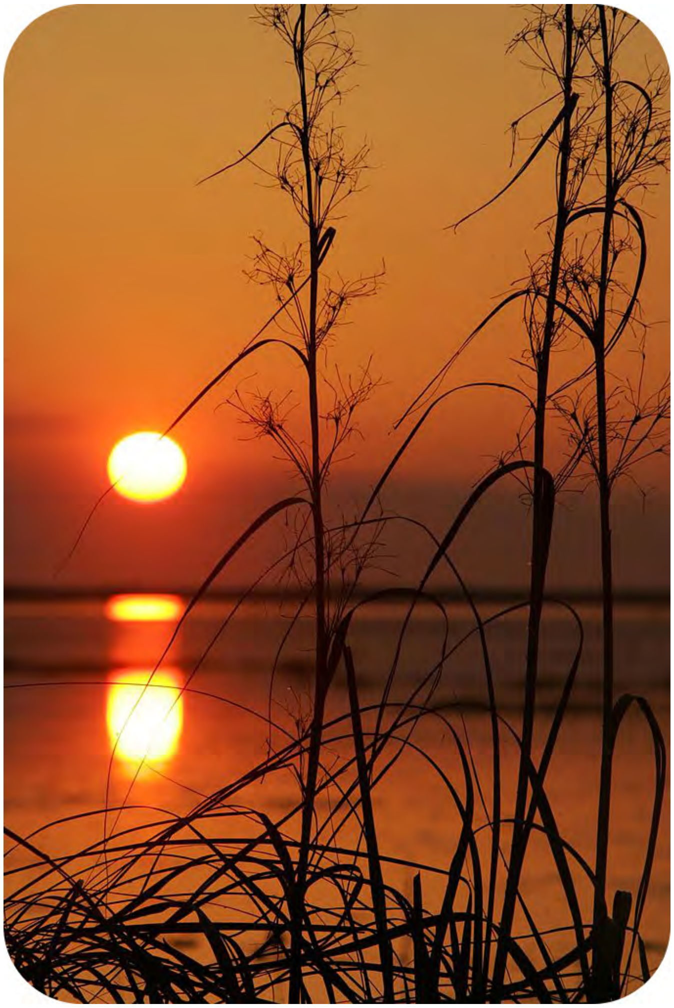
Review

1. What would be the products of a spontaneous reaction between Zn/Zn^{2+} and Cu/Cu^{2+}?
2. How do we know that the reaction forming Cu^{2+} is not spontaneous?
3. What would be the voltage for the reaction where Zn metal forms Zn^{2+}?

- **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.

23.9 Electrolysis of Water

- Describe the experimental set-up for the electrolysis of water.
- Write equations for the reactions involved in the process.



More energy from the sun?

With fossil fuels becoming more expensive and less available, scientists are looking for other energy sources. Hydrogen has long been considered an idea source, since it does not pollute when it burns. The problem has been finding ways to generate hydrogen economically. One new approach that is being studied is photoelectrolysis – the generation of electricity using photovoltaic cells to split water molecules. This technique is still in the research stage, but appears to be a very promising source of power in the future.

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 to which a small amount of an electrolyte such as H_2SO_4 has been added. The electrolyte is necessary because pure water will not carry enough charge due to the lack of ions. At the anode, water is oxidized to oxygen gas and hydrogen ions. At the cathode, water is reduced to hydrogen gas and hydroxide ions.

$$\begin{array}{lll}
\text{oxidation (anode):} & 2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^- & E^0 = -1.23\text{ V} \\
\text{reduction (cathode):} & 2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) & E^0 = -0.83\text{ V} \\
\hline
\text{overall reaction:} & 2H_2O(l) \rightarrow O_2(g) + 2H_2(g) & \text{cell}E^0
\end{array}$$

= -2.06 V

In order to obtain the overall reaction, the reduction half-reaction was multiplied by two to equalize the electrons. The hydrogen ion and hydroxide ions produced in each reaction combine to form water. The H_2SO_4 is not consumed in the reaction.

FIGURE 23.10

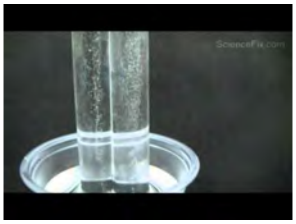
Apparatus for the production of hydrogen and oxygen gases by the electrolysis of water.

Summary

- The electrolysis of water is described.

Practice

Watch the video at the link below and answer the following questions:



MEDIA

Click image to the left for more content.

www.youtube.com/watch?v=HQ9Fhd7P_HA

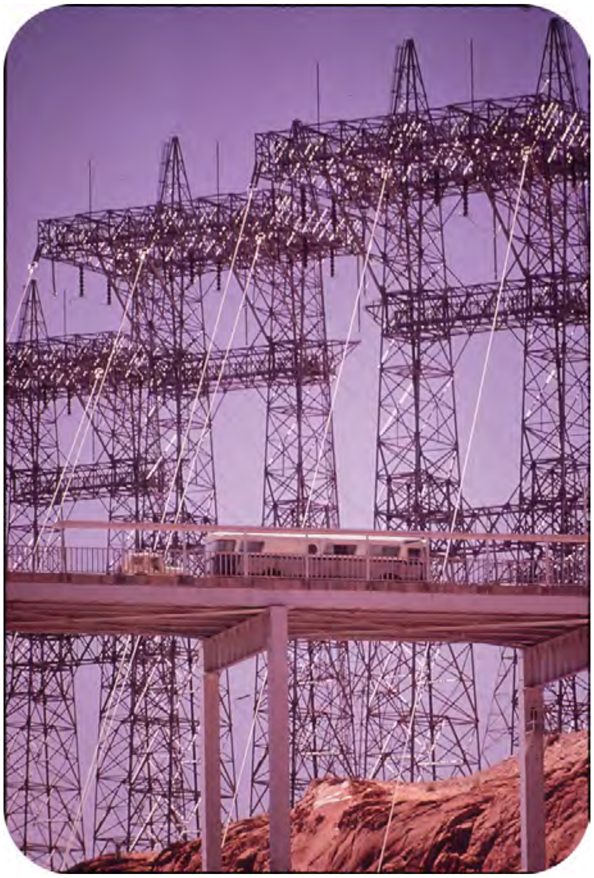
1. What are the electrodes?
2. What is the power source?
3. What is put in the water to facilitate flow of electricity?
4. Which test tube contains hydrogen gas?

Review

1. What are the electrodes used in the reaction?
2. Why is sulfuric acid used?
3. At which electrode does oxygen appear?

23.10 Electrolysis of Molten Salts and Electrolysis of Brine

- Write reactions for the electrolysis of molten NaCl in a Down's cell.
- Write reactions for the electrolysis of aqueous sodium chloride.



A big electric bill

Production of NaOH is an important industrial process. Three different methods are employed, all of which involve the use of electricity. When calculating the price of sodium hydroxide a company has to charge in order to make a profit, the cost of electricity has to be factored in. To make a metric ton of NaOH requires between 3300-5000 kWh (kilowatt hours). Compare that with the power needed to run an average house. You could power a home for 6-10 months with the same amount of electricity.

Electrolysis of Molten Sodium Chloride

Molten (liquid) sodium chloride can be electrolyzed to produce sodium metal and chlorine gas. The electrolytic cell used in the process is called a **Down's cell** (see **Figure** 23.11).

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.

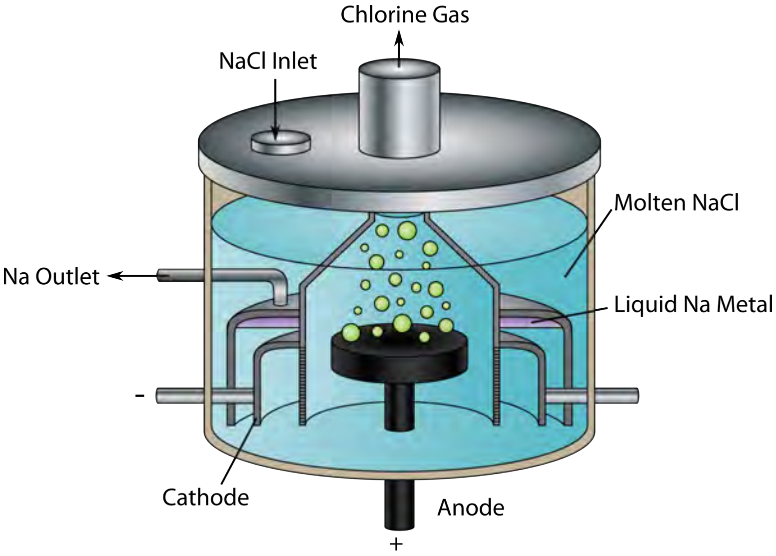


FIGURE 23.11

A Down's cell is used for the electrolysis of molten sodium chloride.

oxidation (anode): $2\text{Cl}^-(l) \rightarrow \text{Cl}_2(g) + 2e^-$ $E^0 = -1.36\ \text{V}$

reduction (cathode): $\text{Na}^+(l) + e^- \rightarrow \text{Na}(l)$ $E^0 = -2.71\ \text{V}$

overall reaction: $2\text{Na}^+(l) + 2\text{Cl}^-(l) \rightarrow 2\text{Na}(l) + \text{Cl}_2(g)$ cellE^0

= -4.07 V

The battery must supply over 4 volts to carry out this electrolysis. This reaction is a major source of production of chlorine gas and is the only way to obtain pure sodium metal. Chlorine gas is widely used in cleaning, disinfecting, and in swimming pools.

Electrolysis of Aqueous 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 as the process in molten NaCl. 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.

oxidation (anode): $2\text{Cl}^-(aq) \rightarrow \text{Cl}_2(g) + 2e^-$ $E^0 = -1.36\ \text{V}$

reduction (cathode): $2\text{H}_2\text{O}(l) + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^-$ $E^0 = -0.83\ \text{V}$

overall reaction: $2\text{Cl}^-(aq) + 2\text{H}_2\text{O}(l) \rightarrow \text{Cl}_2(g) + \text{H}_2(g) + 2\text{OH}^-(aq)$ cellE^0

= -2.19 V

Since hydroxide ion is also a product of the net reaction, the important chemical sodium hydroxide (NaOH) is obtained from evaporation of the aqueous solution at the end of the hydrolysis.

Summary

- The reactions involving the electrolysis of molten NaCl are described.
- The reactions involving the electrolysis of brine are described.

Practice

Read the material at the link below and answer the following questions:

http://www.citycollegiate.com/sblock1.htm

1. How is sodium removed from the cell?
2. Why is $CaCl_2$ added to the system?
3. Why doesn't metallic calcium contaminate the sodium production?

Review

1. What are the products of the electrolysis of molten NaCl?
2. What are the products of the electrolysis of aqueous NaCl?
3. What spectator ion is not shown in the overall equation for the electrolysis of aqueous NaCl?

- **brine:** An aqueous solution of sodium chloride.
- **Down's cell:** An apparatus used for the industrial manufacture of sodium metal and chlorine gas.

23.11 Electroplating

- Define electroplating.
- Write a typical electroplating reaction.

Does anybody know where we are?

The astrolabe (pictured above disassembled) was a device used to study the motions of planets and to do surveying. Most astrolabes were made of brass, but this one has been overlaid with gold which is wearing off. Persian mystics also used astrolabes for following the stars and making astrological predictions.

Electroplating

Many decorative objects like jewelry are manufactured with the aid of an electrolytic process. **Electroplating** is a process in which a metal ion is reduced in an electrolytic cell and the solid metal is deposited onto a surface. The **Figure** 23.12 shows a cell in which copper metal is to be plated onto a second metal.

The cell consists of a solution of copper sulfate and a strip of copper which acts as the anode. The metal (Me) is the cathode. The anode is connected to the positive electrode of a battery, while the metal is connected to the negative electrode.

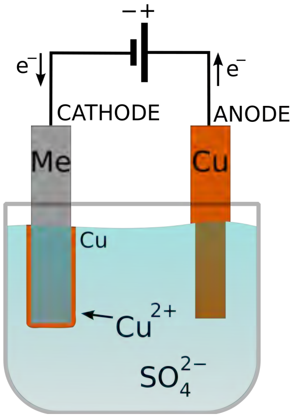


FIGURE 23.12

Electroplating of second metal by copper.

When the circuit is closed, copper metal from the anode is oxidized, allowing copper ions to enter the solution.

$$\text{anode}: \ \mathrm{Cu}^0(s) \rightarrow \mathrm{Cu}^{2+}(aq) + 2e^-$$

Meanwhile copper ions from the solution are reduced to copper metal on the surface of the cathode (the second metal):

$$\text{cathode}: \ \mathrm{Cu}^{2+}(aq) + 2e^- \rightarrow \mathrm{Cu}^0(s)$$

The concentration of copper ions in the solution is effectively constant. The electroplating process transfers metal from the anode to the cathode of the cell. Other metals commonly plated onto objects include chromium, gold, silver, and platinum.

Summary

- The process of electroplating is described.

Practice

Watch the video at the link below and answer the following questions:

MEDIA

Click image to the left for more content.

http://www.youtube.com/watch?v=Q8Xo43sfLgY

1. What is the solution used?
2. How did he test the system?
3. Why are batteries better than wall current for the electrical current?
4. What was the anode?

Review

1. In the electroplating with copper, what is the anode?
2. What supplies the electric current?
3. What other metals can be coated onto objects?

- **electroplating:** A process in which a metal ion is reduced in an electrolytic cell and the solid metal is deposited onto a surface.

23.12 References

1. Courtesy of Mass Communication Specialist Seaman John Wagner, US Navy. http://commons.wikimedia.org/wiki/File:US_Navy_070420-N-3038W-077_Sailors_look_at_silver_and_gold_jewelry_from_vendors_on_the_aft_mess_decks_aboard_the_Nimitz-class_aircraft_carrier_USS_John_C._Stennis_%28CVN_74%29.jpg. Public Domain
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CHAPTER 24

Nuclear Chemistry

Chapter Outline

24.1 Discovery of Radioactivity

- Define radioactivity.
- List key scientists involved in the development of information about radioactivity.

What's that sign mean?

If you visit the nuclear medicine department of a large hospital, you are very likely to see the symbol shown above. The sign means that radioactive materials are present and special safety precautions need to be taken. These materials are used for diagnosis and treatment of many diseases. The people using these materials are specially trained to handle them safely. Radioactive materials should be respected, but not feared.

Discovery of Radioactivity

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 Francis Aston (1877-1925) to the conclusion in 1919 that some elements with different atomic weights were actually the same element. Aston used a mass spectrograph to separate isotopes of different elements. He won the Nobel Prize in Chemistry for this work in 1922.

Natural Radioactivity

The discovery of X-rays in 1895 by Wilhelm Röntgen produced great interest in what caused this phenomenon. One researcher was Henri Becquerel, who studied the fluorescent properties of uranium salts, thinking they had something to do with X-rays. He soon learned that uranium could expose a photographic plate without an external input of energy (thought to be needed to produce uranium fluorescence). Becquerel also showed that these emissions could be affected by a magnetic field, which was not true for X-rays.

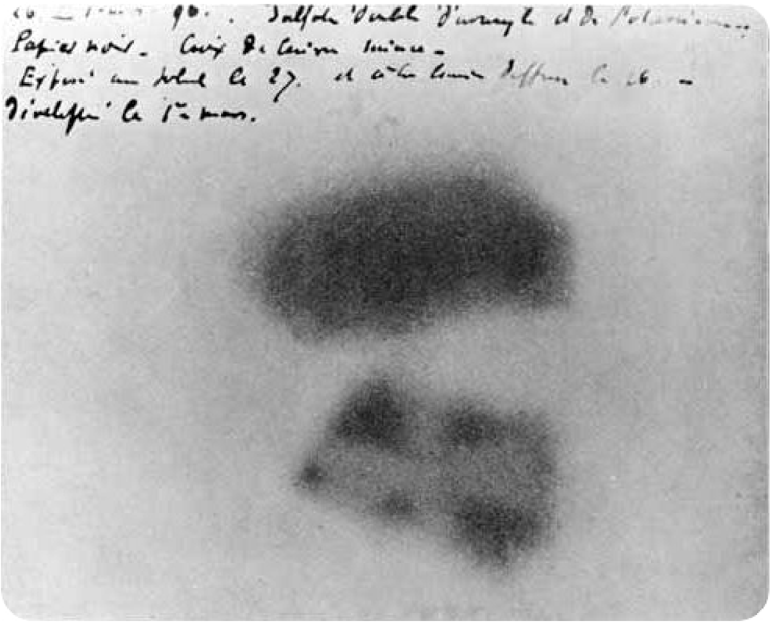


FIGURE 24.1

Becquerel's experiment - uranium exposure to photographic plate.

Pierre and Marie Curie studied the properties of uranium salts with the express purpose of identifying the details of these emissions. They were the first to coin the term "**radioactivity**", meaning the spontaneous emission of radiation in the form of particles or high energy photons resulting from a nuclear reaction. The major contributions to the work came from Marie who showed that the amount of radioactivity present was due to the amount of a specific element and not due to some 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 and Henri Becquerel. She won the Nobel Prize in Chemistry in 1911.

A later researcher (Ernest Rutherford) as able to show there were three different types of radioactive emissions. These emissions differed in terms of mass, charge, and the ability to penetrate materials. He designated them simply as alpha (α) emissions, beta (β) emissions, and gamma (γ) emissions.

Radioactivity involves the spontaneous emission of material 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. Some typical radioactive elements are technetium (atomic number 43), promethium (atomic number 61), and all elements atomic number 84 (polonium) and higher. There are four primary types of emission, either involving release of a particle from the nucleus or energy. In many instances, both energy and a particle are produced in the radioactive event.

It should be noted that some elements considered to be stable do have radioactive isotopes. Carbon-14 is radioactive, but is only a small fraction of the total amount of carbon in existence (about one part per trillion carbon atoms). Hydrogen also has a radioactive isotope known as hydrogen-3 or tritium, again a very small fraction of the total hydrogen present.

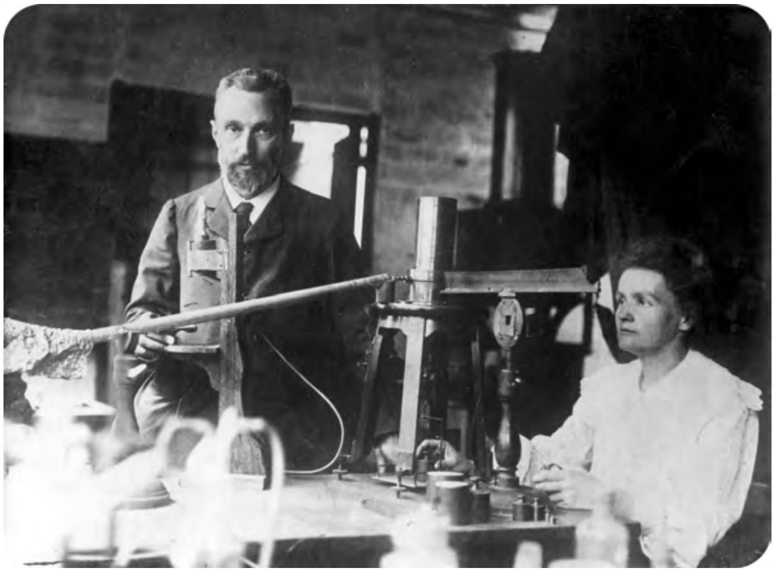


FIGURE 24.2

Pierre and Marie Curie in their lab.

Summary

- The early history of the discovery of radioactivity is described.

Practice

Read the material at the link below and answer the following questions:

http://www.chemteam.info/Radioactivity/Disc-of-Alpha&Beta.html

1. What did Rutherford use to detect radioactivity?
2. What did he use to block the radioactive emissions?
3. How did he know there were two types of emissions?

Review

1. Who first discovered the phenomenon of radioactivity?
2. Who first used the term "radioactivity"?
3. What did Ernest Rutherford find?

- **radioactivity:** Spontaneous emission of particles and/or energy from an unstable atomic nucleus.

24.2 Nuclear Decay Processes

- List the decay processes.
- Describe the alpha decay process.
- Describe the beta decay process.
- Describe gamma emission.
- Describe positron emission.

You did what to my hamburger?

Food irradiation is a sensitive subject to many people. The practice involves exposure of the food to ionizing radiation in order to kill harmful bacteria such as Salmonella that cause sickness. The food is essentially unchanged and has not lost any nutritive value. Parasites and insect pests are easily destroyed by this process, while bacteria take longer to kill. Viruses are not affected by the radiation treatment. Don't worry – the food is not radioactive and you will not glow in the dark if you eat it.

Nuclear Decay Processes

Radioactive decay involves the emission of a particle and/or energy as one atom changes into another. In most instances, the atom changes identity and becomes a new element. There are four different kinds of emissions than can occur.

Alpha emission

Alpha (α) decay involves the release of helium ions from the nucleus of an atom. This ion consists of two protons and two neutrons and has a 2+ charge. Release of an α-particle produces a new atom that has an atomic number two less than the original atom and an atomic weight that is four less. A typical alpha decay reaction is the conversion of uranium-238 to thorium:

$$^{238}_{92}\mathrm{U} \rightarrow {}^{234}_{90}\mathrm{Th} + {}^{4}_{2}\alpha^{+}$$

We see a decrease of two in the atomic number (uranium to thorium) and a decrease of four in the atomic weight (238 to 234). Usually the emission is not written with atomic number and weight indicated since it is a common particle whose properties should be memorized. Quite often the alpha emission is accompanied by gamma (γ) radiation, a form of energy release. Many of the largest elements in the periodic table are alpha-emitters.

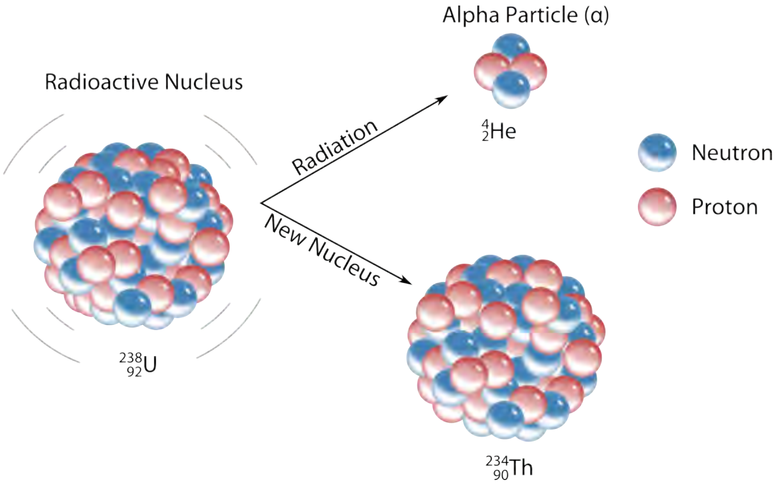


FIGURE 24.3

Emission of alpha particle from nucleus.

Beta emission

Beta (β) decay is a more complicated process. Unlike the α-emission, which simply expels a particle, the β-emission involves the transformation of a neutron in the nucleus to a proton and an electron. The electron is then ejected from the nucleus. In the process, the atomic number increases by one while the atomic weight stays the same. As is the case with α-emissions, the β-emissions are also often accompanied by γ-radiation.

A typical beta decay process involves carbon-14, often used in radioactive dating techniques. The reaction forms nitrogen-14 and an electron:

$$^{14}_{6}\mathrm{C} \rightarrow {}^{14}_{7}\mathrm{N} + {}^{0}_{-1}e$$

Again, the beta emission is usually simply indicated by the Greek letter β; memorization of the process is necessary in order to follow nuclear calculations.

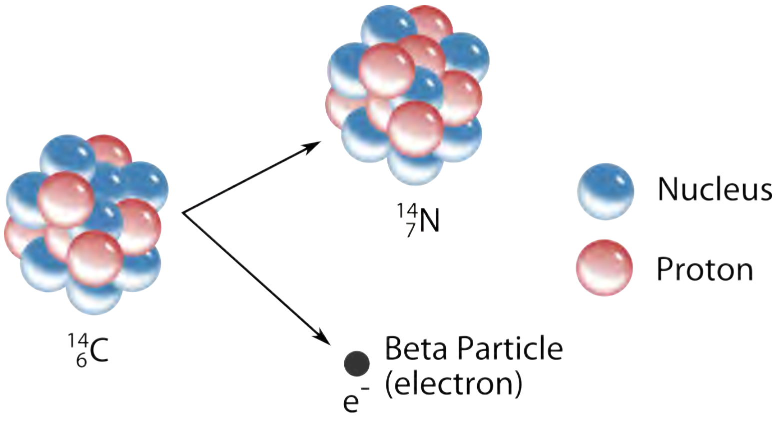


FIGURE 24.4

Beta emission.

Gamma emission

The **gamma (γ) radiation** is simply energy. It may be released by itself or more commonly in association with other radiation events. There is no change of atomic number or atomic weight in a simple γ-emission. Often, an isotope may produce γ-radiation as a result of a transition in a metastable isotope. This type of isotope may just "settle", with a shifting of particles in the nucleus. The composition of the atom is not altered, but the nucleus could be considered more "comfortable" after the shift. This shift increases the stability of the isotope from the energetically unstable (or "metastable") isotope to a more stable form of the nucleus.

Positron emission

A **positron** is a positive electron (a form of antimatter). This rare type of emission occurs when a proton is converted to a neutron and a positron in the nucleus, with ejection of the positron. The atomic number will decrease by one while the atomic weight does not change. A positron is often designated by β^+.

Carbon-11 emits a positron to become boron-11:

$$^{11}_{6}C \rightarrow {}^{11}_{5}B + {}^{0}_{+1}\beta$$

Summary

- Radioactive decay processes are described.

Practice

Read the material at the link below and answer the questions at Practice Problem 3.

Review

1. What is gamma emission?
2. What isotope is formed when U-238 emits an alpha particle?
3. What isotope produces boron-11 when it emits a positron?

- **alpha decay:** Emission of two protons plus two neutrons.

- **beta decay:** Emission of an electron.
- **gamma emission:** Emission of energy.
- **positron emission:** Emission of a positive electron.

24.3 Detection of Radioactivity

- List and define terms used to discuss the amount of radioactivity present.
- Describe devices used to measure radioactivity.

Your own uranium mine?

Uranium is coming to be worth more on the open market after a steep decline in prices several years ago. So people are out there looking for more uranium. But they are not waving Geiger counters around to find this material. All the surface uranium has been found. So they have to study geology, such as the rocks in the picture above. Deep holes are drilled to explore the underground geology of a site and the rocks obtained are chemically analyzed. No more clicking – just modern-day geology and chemistry.

Detection of Radioactivity

Radioactivity is determined by measuring the number of decay processes per unit time. Perhaps the easiest way is simply to determine the number of counts/minute, with each count measuring a single decay process, such as the emission of an α-particle. A particular isotope may have an activity of 5,000 counts/minute (cpm) while another isotope might only have 250 cpm. The amount of activity gives a rough indication of the amount of the radioisotope present – the higher the activity, the more radioactive isotope in the sample.

Units of measurement

The **curie (Ci)** is one measure of the rate of decay (named after Pierre and Marie Curie). One curie is equivalent to 3.7×10^{10} disintegrations per second. Since this is obviously a large and unwieldy number, radiation is often expressed in millicuries or microcuries (still very large numbers). Another measure is the **becquerel (Bq)**, named after Henri Becquerel. The becquerel is defined as an activity of one disintegration/second. Both of these units are concerned with the disintegration rate of the radioactive isotope and give no indication of dosage to the target material.

Exposure gives an indication of the amount of radiation that travels through the air. Two factors influence the amount of exposure a person may receive – time and intensity. Acute exposure indicates a large amount of radiation received over a short period of time. Chronic exposure deals with lower levels and a longer period of time. Dose equivalence combines the amount of radiation received and the medical effect of that radiation. Calculations of exposure and dose equivalence are complicated and will not be pursued at this time.

Personal dosimeters

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** – a film badge that will fog up when exposed to radiation. The amount of fogging is proportional to the amount of radiation present. These devices are not very sensitive to low levels of radiation. More sensitive systems use crystals that respond in some way to radioactivity by registering the number of emissions in a given time. These systems tend to be more sensitive and more reliable than film badges.

FIGURE 24.5
Dosimeter

Geiger counters

A **Geiger counter** provides a sensitive means of detecting radioactivity. A tube is filled with an inert gas, which will conduct electricity when radiation enters it. When a charged particle comes into the tube, it changes the electrical potential between the anode and the cathode. This change in potential in the tube produces a change in voltage in the electrical circuit and registers as a count. 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 in sophisticated experiments.

FIGURE 24.6

Geiger counter.

Summary

- Units for the measurement of radioactivity are described.
- Instruments for the detection of radioactivity are described.

Practice

Read the material at the link below and answer the following questions:

http://www.explainthatstuff.com/how-geiger-counters-work.html

1. Who invented the Geiger counter?
2. What happens when a radioactive particle collides with gas molecules inside the tube?
3. What causes current to flow and register a count?

Review

1. What is the most common unit of radioactivity?
2. How does a dosimeter detect radioactivity?
3. What detects the presence of a radioactive emission in a Geiger counter?

- **becquerel (Bq):** An activity of one disintegration/second.
- **curie (Ci):** 3.7×10^{10} disintegrations per second.
- **dosimeter:** A film badge that will fog up when exposed to radiation.
- **Geiger counter:** A device for detecting radioactive emissions.

24.4 Half-Life

- Define half-life.
- Calculate half-life when given decay data.

We're putting it where?

Uranium isotopes produce plutonium-239 as a decay product. The plutonium can be used in nuclear weapons and is a power source for nuclear reactors, which generate electricity. This isotope has a half-life of 24,100 years, causing concern in regions where radioactive plutonium has accumulated and is stored. At some storage sites, the waste is slowly leaking into the groundwater and contaminating nearby rivers. The 24,100 year half-life means that it will be with us for a very long time.

Half-Life

Radioactive materials lose some of their activity each time a decay event occurs. This loss of activity can be estimated by determining the **half-life** of an isotope. The half-life is defined as that period of time needed for one-half of a given quantity of a substance to undergo change. For a radioisotope, every time a decay event occurs, a count is detected on the Geiger counter or other measuring device. A specific isotope might have a total count of 30,000 cpm. In one hour, the count could be 15,000 cpm (half the original count). So the half-life of that isotope is one hour. Some isotopes have long half-lives – the half-life of U-234 is 245,000 years. Other isotopes have shorter half-lives. I-131, used in thyroid scans, has a half-life of 8.02 days.

Half-life Calculations

Information on the half-life of an isotope can be used to calculate how much radioactivity of that isotope will be present after a certain period of time. There is a formula that allows calculation at any time after the initial count, but we are going to just look at loss of activity after different half-lives. The isotope I-125 is used in certain laboratory procedures and has a half-life of 59.4 days. If the initial activity of a sample of I-125 is 32,000 cpm, how much activity will be present in 178.2 days? We begin by determining how many half-lives are represented by 178.2 days:

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

Then we simply count activity:

$$\begin{aligned} \text{initial activity } (t_0) &= 32,000 \text{ cpm} \\ \text{after one half-life} &= 16,000 \text{ cpm} \\ \text{after two half-lives} &= 8,000 \text{ cpm} \\ \text{after three half-lives} &= 4,000 \text{ cpm} \end{aligned}$$

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

For the more mathematically inclined, the following formula can be used to calculate the amount of radioactivity remaining after a given time:

$$N_t = N_0 \times (0.5)^{\text{number of half-lives}}$$

where $N_t =$ activity at time t

$N_0 =$ initial activity at time $= 0$

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

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

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

Half-lives of different elements vary considerably:

TABLE 24.1: Isotope Half-Lives

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

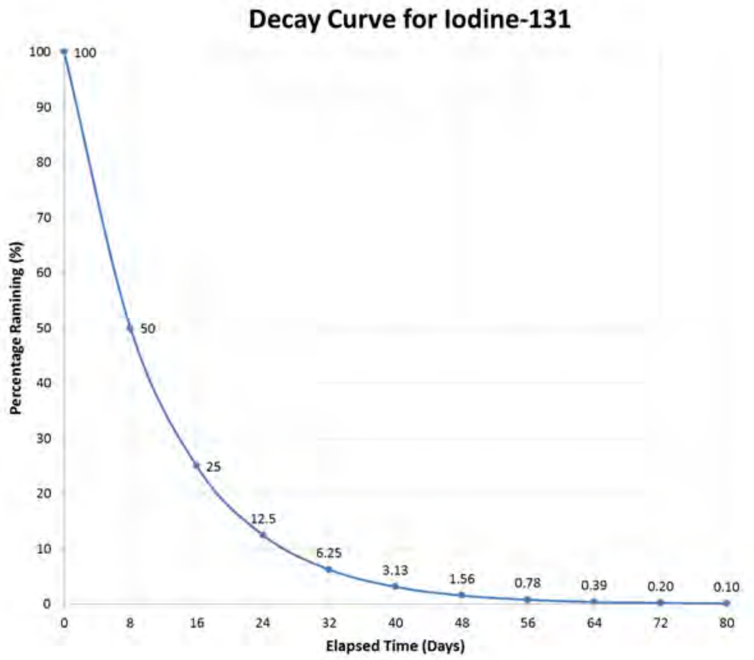


FIGURE 24.7

Typical radioactive decay curve.

We have talked about the activity and decay of individual isotopes. In the real world, there is a decay chain that takes place until a stable end-product is produced. For U-238, the chain is a long one, with a mix of isotopes having very different half-lives. The end of the chain resides in lead, a stable element that does not decay further.

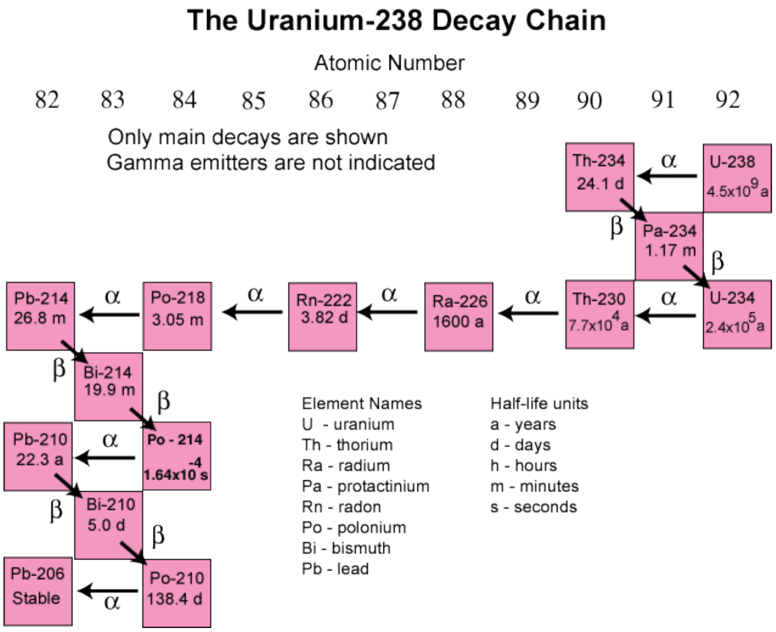


FIGURE 24.8

Decay of uranium to stable end-product.

Summary

- Half-life is defined.
- Calculations involving half-life are described.

Practice

Read the material at the link below and work problems 2, 4, 6, 7, and 9.

http://www.chemteam.info/Radioactivity/WS-Radioactivity2.html

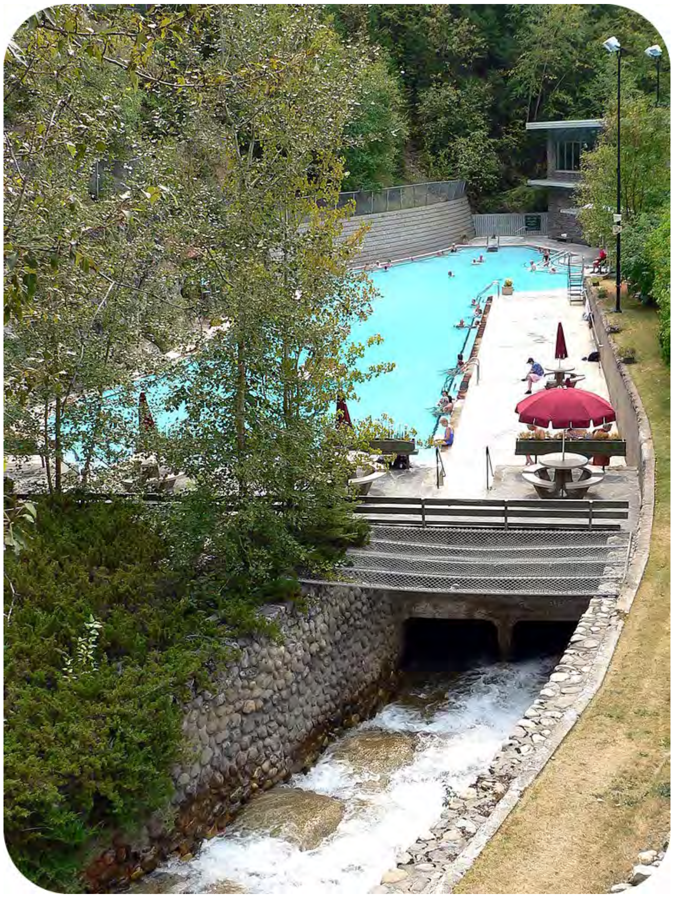
Review

1. Define half-life.
2. What is the half-life of uranium-234?
3. What is the half-life of polonium-214?
4. What is the end-product of the decay of uranium-238?

- **half-life:** That period of time needed for one-half of a given quantity of a substance to undergo change.

24.5 Background Radiation

- Define background radiation.
- List sources of background radiation.



Ease those aches and pains

Sitting in a hot bath or spa has always been a great prescription for dealing with sore muscles. For some reason, people thought it was even more beneficial to immerse themselves in radioactive hot springs and drink water containing radioactive materials (some still do). In the early 1900s, people spent millions of dollars on treatments and "radioactive water" in the belief that all their ills would be taken care of. Radioactivity in the water was usually due to radon gas that leaked up from deep underground, formed by decay of other radioisotopes. The hot springs above is used because of the hot springs, not the radioactivity. There is some residual radon in the water and air, but not enough to represent a health hazard (or any healing properties). So, sit in one of the pools and enjoy a relaxing time.

Background Radiation

We are all exposed to a small amount of radiation in our daily lives. This **background radiation** comes from naturally occurring sources and from human- produced radiation. Exposure to X-rays and nuclear medicine isotopes, sources in the ground, and cosmic radiation account for almost half the background exposure of the average

American. Radon gas, formed from the decay of uranium and thorium isotopes, is responsible for a little over half the total amount of background radiation. See the **Table** 24.2 for background sources.

TABLE 24.2: **Sources of Background Radiation**

radon	54%
consumer products	3%
nuclear medicine	4%
cosmic radiation	8%
terrestrial	8%
internal	11%
X-rays	11%
other	1%

The problem of radon

Small amounts of uranium and thorium are found in the soil of a large number of areas in the U.S. When radioactive isotopes of these elements decay, radon is one of the products formed. Radon is a colorless, odorless gas and is chemically inert, being one of the noble gases.

Radon is also radioactive and can easily be inhaled into the lungs. Over time, this internal radon exposure can lead to the development of lung cancer. The incidence of lung cancer for smokers is much higher than that for non-smokers since smoking has already begun to produce lung damage, and the radon simply makes it worse. Radon exposure is highest in homes due to the lack of good air circulation to move the gas out of the residence. There are a number of inexpensive approaches to decreasing your exposure to radon.

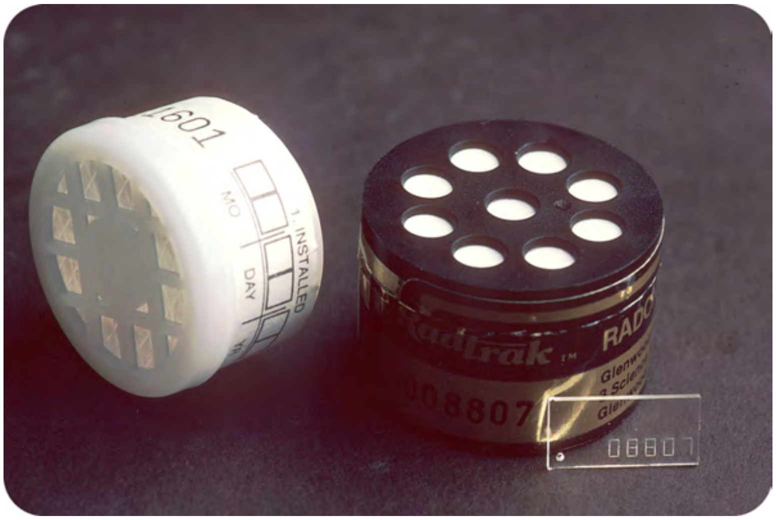


FIGURE 24.9
Radon test kit.

Summary

- Background radiation is defined.
- Sources of background radiation are listed.

Practice

Read the material at the link below and answer the following questions:

http://www.lung.org/healthy-air/home/resources/radon.html

1. Where does radon come from?
2. What are the health hazards of radon?
3. How can your home lower radon indoors?

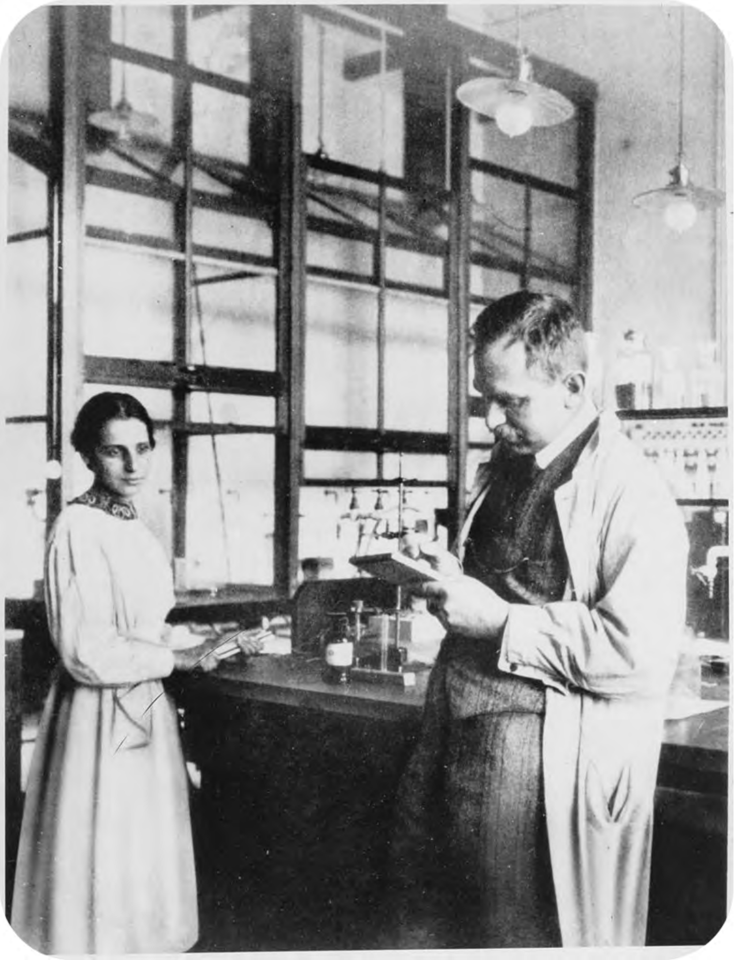
Review

1. What is background radiation?
2. What are some naturally-occurring sources of background radiation?
3. What is the major source of background radiation?

- **background radiation:** Radiation from naturally occurring sources and from human-produced radiation.

24.6 Nuclear Fission Processes

- Define nuclear fission.
- Give examples of nuclear fission processes.



An unexpected result

Nuclear fission was first discovered by two German scientists Fritz Strassman and Otto Hahn in the 1930s. They began their work by bombarding uranium with neutrons, hoping to create other large elements. Instead, they were very surprised to find Ba-141, a much smaller element. They immediately contacted Lise Meitner who carried out calculations to demonstrate that fission had taken place.

Nuclear Fission

Radioactive decay with the release of alpha or beta particles is not the only way new isotopes are formed. There are nuclei, which will split when a neutron collides with them. The products are two isotopes, each of which is roughly half the mass of the original atom. A small amount of mass is "left over" and becomes energy, as predicted by Einstein's famous equation $E = mc^2$, that relates mass and energy. The neutron must be a "slow" neutron, traveling

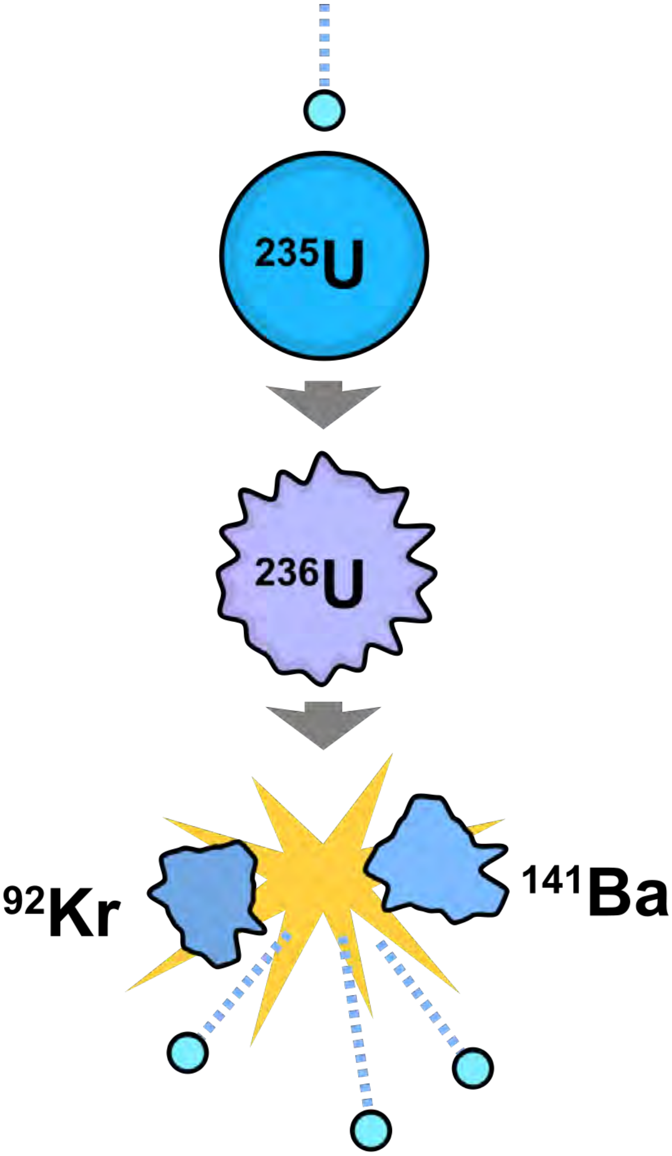


FIGURE 24.10

Fission of uranium nucleus produced by collision with a neutron.

at a speed that is approximately that of the molecules of gas at the same temperature in the system producing the neutrons. High-speed ("fast") neutrons will not produce **nuclear fission**.

The example above illustrates the basic nuclear fission process. A neutron (generally produced by some controlled process, not usually a natural event) collides with an atom of U-235. Momentarily, a U-236 atom forms which then fissions into two smaller atoms (Kr-93 and Ba-141) in the diagram. This process results in the release of three new neutrons, which can then initiate fission reactions with more atoms. We will see later how this propagation of neutrons can be employed in a reactor for the generation of electricity.

An extended version of this process can be seen in the figure below. Not every collision of a neutron with U-235 results in a fission reaction. A neutron from the initial fission process may strike an atom of U-238, which does not continue the process. Another neutron may not collide with a nucleus and is lost in the environment. However, a third neutron produced from the initial collision can collide with more U-235 and continue the cascade reaction to produce more neutrons.

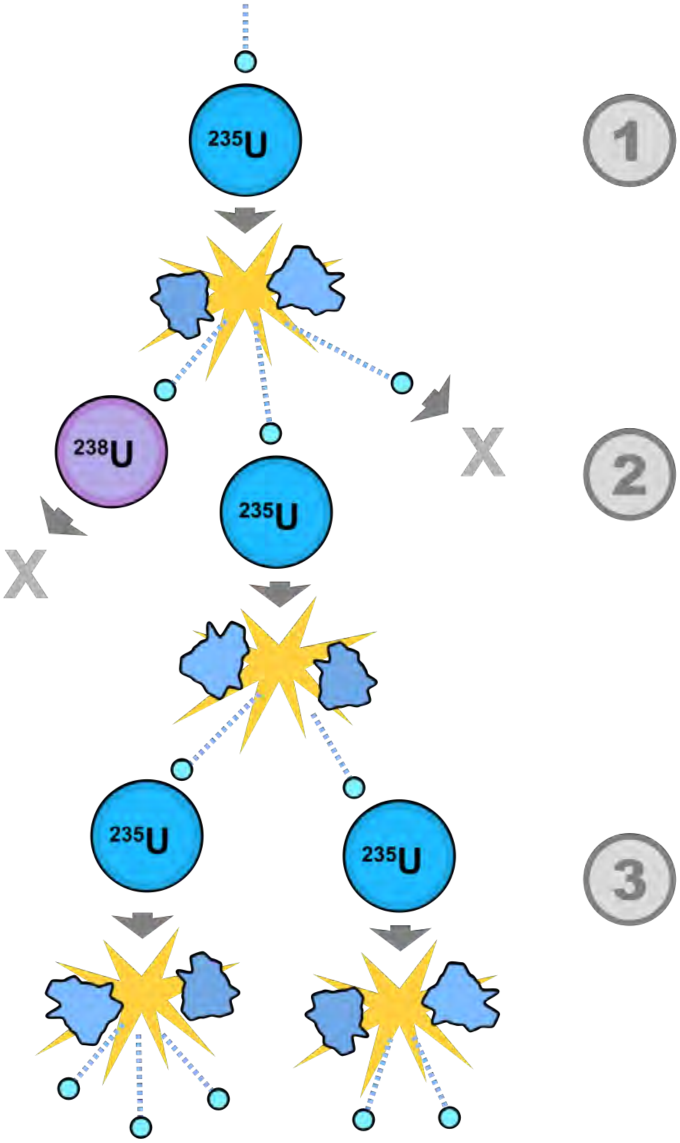


FIGURE 24.11
Fission reaction with U-235.

Typical nuclear fission reactions balance in terms of mass. The total mass of the reactants is equal to the total mass of the products:

$$^{235}_{92}\text{U} + ^{1}_{0}n \rightarrow ^{92}_{36}\text{Kr} + ^{142}_{56}\text{Ba} + 2^{1}_{0}n + \text{energy}$$

There are a total of 236 mass units on the left of the equation and 236 mass units on the right. In the same manner, we see 92 protons on the left and 92 on the right. The energy that is released is the binding energy that holds the nucleus together.

Another set of fission products from U-235 can be seen in this reaction:

$$^{235}_{92}\text{U} + ^{1}_{0}n \rightarrow ^{95}_{42}\text{Mo} + ^{139}_{57}\text{La} + 2^{1}_{0}n + \text{energy}$$

Again we see that the total number of mass units and of protons is equal on both sides of the equation.

Summary

- The process of nuclear fission is described.
- Examples of nuclear fission processes are illustrated.

Practice

Read the material at the link below about the energy involved in nuclear fission and answer the following questions:

http://www.euronuclear.org/info/encyclopedia/n/nuclear-fission.htm

1. How much kinetic energy is released in the fission products?
2. How much kinetic energy is released in the fission neutrons?
3. Is gamma emission a part of the fission process?

Review

1. What is nuclear fission?
2. What kind of neutron is needed?
3. What else is released besides smaller nuclei?

- **nuclear fission:** The process by which a heavy atomic nucleus is split into two or more smaller nuclei by a slow-moving neutron with the release of energy.

24.7 Nuclear Power Generation

- List sources for electrical power in the United States.
- Describe how a nuclear power plant generates electricity.

Things don't always work the way they should

On Wednesday, March 28, 1979, the residents of Middleton, PA woke up to a very scary situation. The nuclear power plant near the town had experienced a series of malfunctions that led to release of some radioactive gases into the atmosphere, along with a partial meltdown of the reactor core. Fortunately, follow-up studies have shown that there were no health effects on workers or the general public. A thorough investigation was conducted that led to significant improvements in safety and operations of these power plants. One of the two reactors was shut down completely, but the other one is still in operation and will be permanently deactivated in 2014.

Nuclear Power Generation

The generation of electricity is critical for operation of businesses, health care delivery, schools, homes, and other users of electrical power. According 2011 statistics, coal is used for 42% of the power generated, with natural gas being employed for another 25% of this important commodity. Nuclear power plants are employed in about 19% of the cases, with renewable energy sources supplying the last 13%. All of these fuels are used to heat water to generate steam. The steam then turns a turbine to generate electricity for use.

The diagram below shows the layout of a typical nuclear power plant. The radioactive rods are in the red container along with water, which is heated to steam. The energy for this heat comes from fission reactions of uranium. 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 play an important role in the modulation of the nuclear chain reaction (usually a collision of a neutron with uranium). Each collision produces more neutrons than were present initially. If left uncontrolled, the reaction would soon get out of control. Rods are commonly made of boron or a number of metals or metal alloys. The purpose of the control rods is to absorb neutrons to regulate the rate of the chain reaction so that the water does not overheat and destroy the reactor.

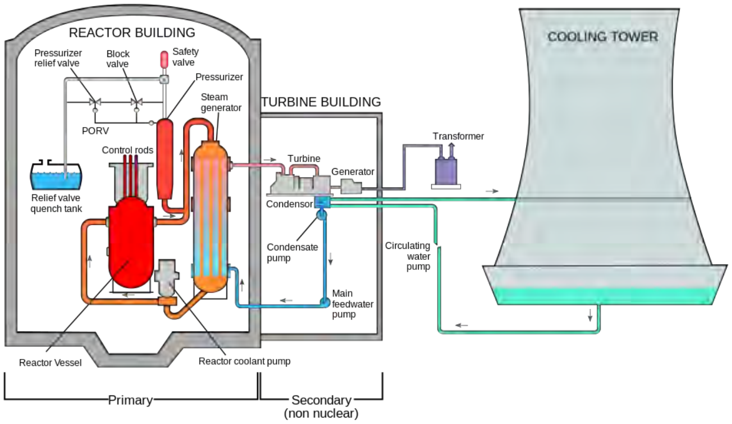


FIGURE 24.12

Schematic for a nuclear power plant.

Nuclear power is also used to propel ships. The turbine can be connected to a propeller system. The rotating turbine shaft will turn the propeller to move the ship.

FIGURE 24.13

Nuclear submarine.

Summary

- The operation of a nuclear power plant is described.

Practice

Read the material at the link below and answer the following questions:

http://www.epa.gov/radtown/nuclear-plant.html

1. How hazardous is enriched uranium?
2. How is spent nuclear waste stored?
3. Why are people who live near nuclear power plants issued potassium iodide tablets?

Review

1. How much of our nation's electricity is provided by nuclear power?
2. What heats the water to generate steam in a nuclear power plant?
3. What do the control rods do?

24.8 Nuclear Fusion

- Define nuclear fusion.
- Describe nuclear fusion reactions.

Elements being born

A number of reactions take place in the sun that cannot be duplicated on earth. Some of these reactions involve the formation of large elements from smaller ones. So far, we have only been able to observe formation of very small elements. The reaction sequence observed appears to be the following: Hydrogen-1 atoms collide to form the larger hydrogen isotopes hydrogen-2 (deuterium) and hydrogen-3 (tritium). In the process, positrons and gamma rays are formed. The positrons will collide with any available electrons and annihilate, producing more gamma rays. In the process, tremendous amounts of energy are produced to keep us warm and the sun still reacting.

Nuclear Fusion

In contrast to nuclear fission, which results in smaller isotopes being formed from larger ones, the goal of **nuclear fusion** is to produce larger materials from the collision of smaller atoms. The forcing of the smaller atoms together results in tighter packing and the release of energy. As seen in the **Figure** 24.14, energy is released both in the formation of the larger atom. He from the fusion of hydrogen-2 and hydrogen-3 as well as energy release from the expulsion of a neutron.

This release of energy is what drives research on fusion reactors today. If such a reaction could be accomplished, it could provide a clean source of nuclear energy. Unlike fission reactions, nuclear fusion does not produce radioactive products that represent hazards to living systems.

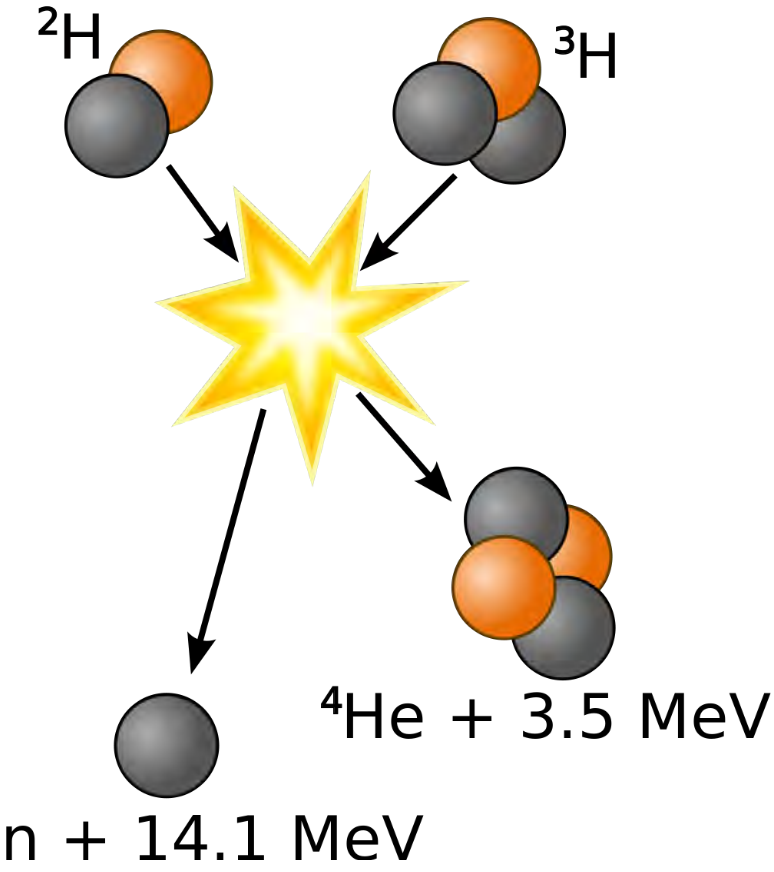


FIGURE 24.14
Nuclear fusion reaction between deuterium and tritium.

Nuclear fusion reactions in the laboratory have been extraordinarily difficult to achieve. Extremely high temperatures (in the millions of degrees) are required. Ways need to be developed to force the atoms together and hold them there long enough to react. The neutrons released during the fusion reactions can interact with atoms in the reactor and convert them to radioactive materials. Some success has been achieved, but the journey to feasible fusion power is still a long and uncertain one.

Summary

- The process of nuclear fusion is described.
- Examples of nuclear fusion reactions are given.

Practice

Read the material at the ling below and answer the following questions:

http://science.howstuffworks.com/fusion-reactor.htm

1. What temperatures are needed for fusion to occur?
2. Why is high pressure needed?
3. What does a magnetic confinement reactor do?
4. How does an inertial confinement method work?

Review

1. What is nuclear fusion?
2. Why is nuclear fusion of interest today?
3. What is one problem with studying nuclear fusion in the laboratory?

- **nuclear fusion:** A process in which atomic nuclei are fused together to form heavier nuclei.

24.9 Penetrating Ability of Emissions

- Define penetrating ability.
- Describe the penetrating ability of different radioactive emissions.

What kind of pig?

The container pictured above stores a radioisotope that will be administered to a patient as part of a medical treatment. The isotope is stored in a lead container that blocks the radiation from escaping and causing exposure to people. This lead container is called a “pig”, a term long used for referring to castings of lead or other metals. The origin of the term is not clear, but was probable first applied to these containers by the people who made them.

Penetrating Ability of Emissions

The various emissions will differ considerably in their ability to go through matter, known as their **penetrating ability**. The α-particle has the least penetrating power since it is the largest and slowest emission. It can be blocked by a sheet of paper or a human hand. Beta particles are more penetrating than alpha, but can be stopped by a thin sheet of aluminum. Of the three basic types of emissions, gamma particle are the most penetrating. A thick lead shielding is required to stop gamma emissions. Positrons represent a special case in that they annihilate when they come in contact with electrons. The collision of a positron and an electron results in the formation of two gamma emissions that go 180 degrees away from each other.

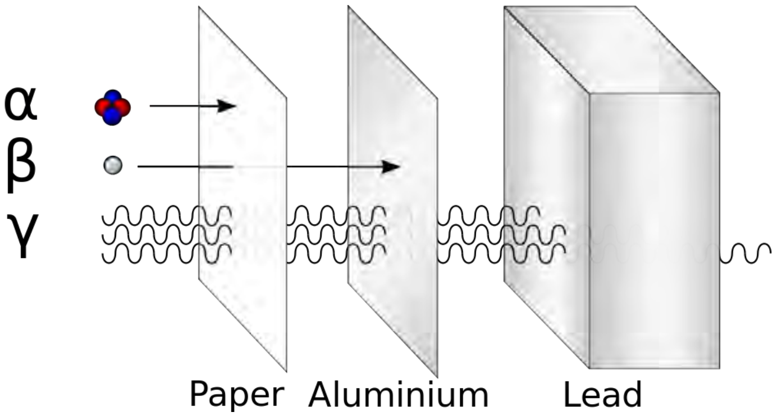


FIGURE 24.15

Penetrating ability of radioactive emissions.

Alpha and beta particles are charged – their need for shielding is different from gamma rays. Blocking of alpha particles can easily be accomplished by as little as 10 mm plastic or paper. Beta emissions represent a somewhat different situation. The negative charge has the potential for activating the element being used to block the radiation. Lead and tungsten are large atoms with many protons and neutrons in their nuclei. While the beta electron may be blocked, the target material could become irradiated in the process.

High-density materials are much more effective protection against gamma emissions than low-density ones. Gamma rays are usually blocked effectively by lead shielding. The thickness of the shielding will determine the effectiveness of the protection offered by the lead.

Summary

- The relative penetrating abilities of radioactive emissions are described.

Practice

Read the material at the link below and answer the following questions:

http://www.epa.gov/radiation/understand/protection_basics.html

1. How does time impact radiation exposure?
2. How does distance impact exposure?
3. What is shielding?

Review

1. What is penetrating ability?
2. Which radioactive emission has the greatest penetrating ability?
3. How can alpha particles be blocked?
4. What is a problem with blocking beta emissions?

- **penetrating ability:** Ability of a radioactive emission to pass through matter.

24.10 Effects of Radiation

- Describe the process of protein synthesis.
- Describe the effect of ionizing radiation on the protein synthesis process.
- Describe the effects of ionizing radiation on humans.

That's in our food?

Bacterial contamination in our food often makes the news. There are many bacteria present on raw food, especially raw meat. Campylobacter (pictured above), salmonella, and other microorganisms can be found, even after cooking if the meat has not been sufficiently exposed to the heat. Ionizing radiation can be used to disrupt the DNA-RNA-protein synthesis cycle that allows the bacteria to reproduce. Cobalt-60 is a common radiation source, as is cesium-137. The Army is also experimenting with spent fuel cells from nuclear reactors. But, just to be safe, order that burger well-done.

Effects of Radiation

In order to understand better how cellular radiation damage occurs, we need to take a quick review of how the cell functions. **DNA** in the nucleus is responsible for protein synthesis and for 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 produce damage to the cell.

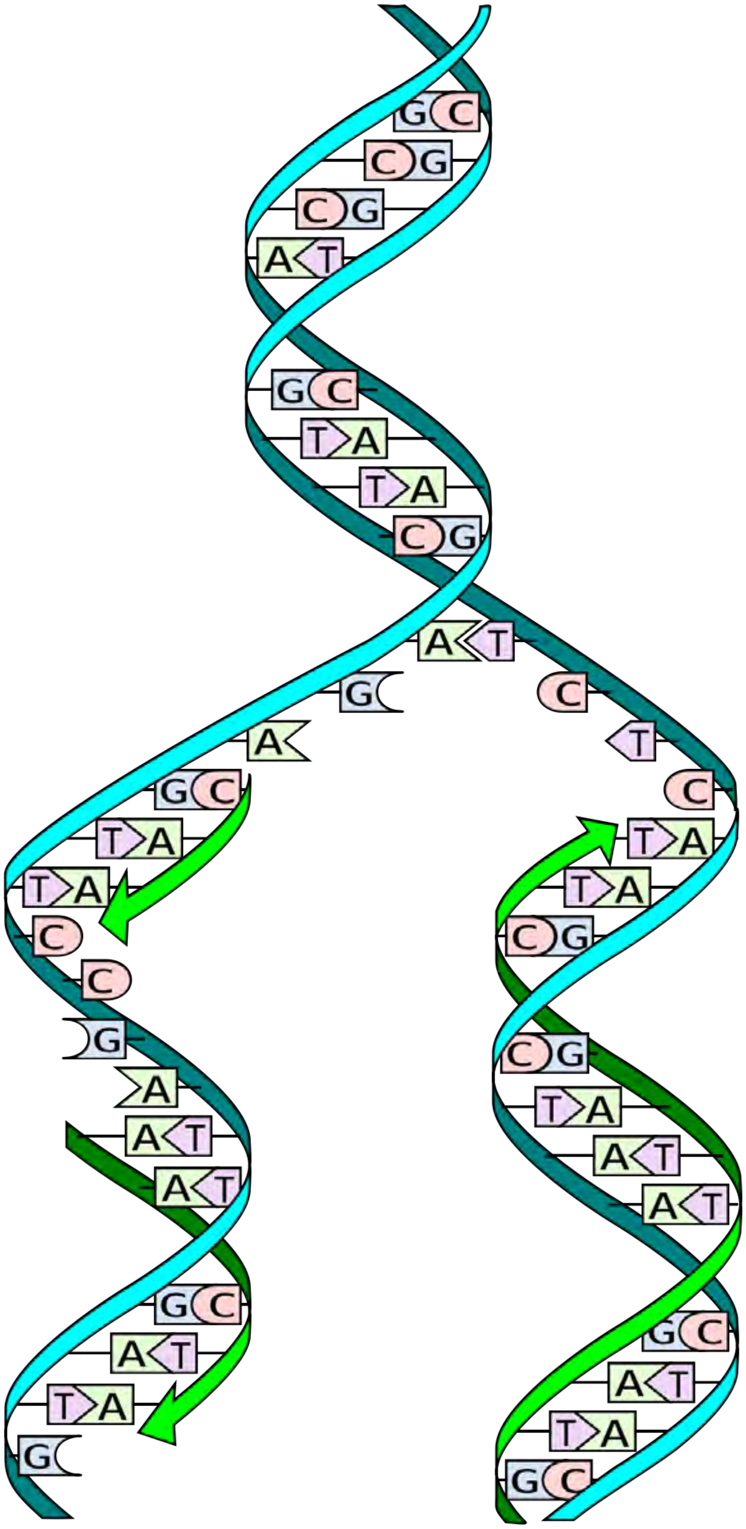


FIGURE 24.16

DNA replication.

The major effect of ionizing radiation on the cell is the disruption of the DNA strand. With the DNA structure damaged, the cell cannot reproduce in its normal fashion. Protein synthesis is affected, as are a number of processes necessary for proper cell function. One common effect is the generation of cancer cells. 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. Tissue damage is also common in people with severe exposure to radiation.

Effects of Radiation on Humans

We can see two general types of effects when humans are exposed to radiation. Low-level exposure can lead to development of cancer. The regulatory processes regulating cell growth are disrupted, leading to uncontrolled growth of abnormal cells. Acute exposure can produce nausea, weakness, skin burns, and internal tissue damage. Cancer patients receiving radiation therapy experience these symptoms, but the radiation is targeted to a specific site in the body so that the damage is primarily to the cancer cells and the patient recovers from the exposure.

Summary

- Basic cellular processes leading to protein synthesis are described.
- Effects of ionizing radiation on protein synthesis are listed.
- The impact of ionizing radiation on human health is shown.

Practice

View the presentation at the link below and answer the following questions:

http://www.wisc-online.com/Objects/ViewObject.aspx?ID=AP1302

1. How does the DNA prepare for the process of protein synthesis?
2. Where does the messenger RNA go after it is made?
3. What does the messenger RNA attach to in order to start protein synthesis?
4. What is a protein composed of?

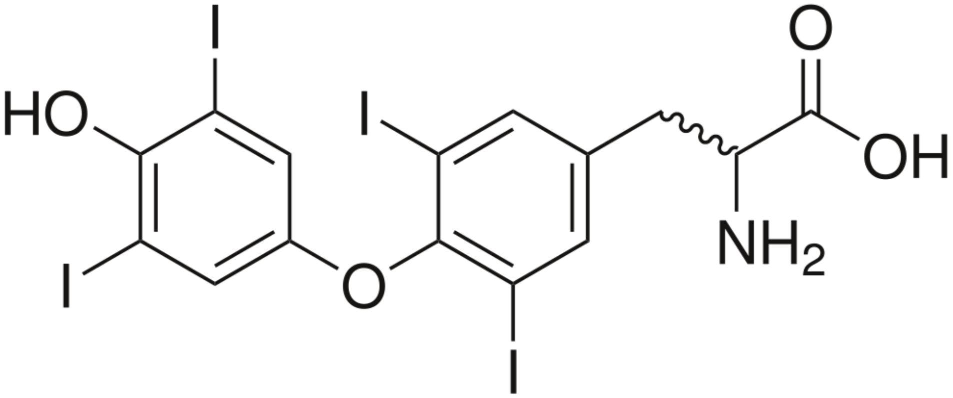
Review

1. What is the major effect of ionizing radiation on the cell?
2. What are acute effects of radiation damage?
3. What are long term-effects of radiation damage?

- **DNA:** A large molecule in the cell nucleus responsible for protein synthesis.
- **messenger RNA (mRNA):** Sets the pattern for protein synthesis outside the nucleus.

24.11 Radioisotopes in Medical Diagnosis and Treatment

- List radioisotopes that are used in medical diagnosis and/or treatment.



Why am I moving so slowly?

The molecule pictured above is thyroxine, a compound produced by the thyroid gland. This molecule regulates how the body uses energy. In a condition known as hypothyroidism, the thyroid makes less thyroxine than normal. The person with this disease feels tired all the time and often puts on weight. Treatment with thyroid hormone supplements takes care of the problem. So, another excuse is needed when you want to sleep in late.

Radioisotopes in Medical Diagnosis and Treatment

Radioisotopes are widely used to diagnose disease and to effect treatment. For diagnosis, the isotope is administered and then located in the body using a scanner of some sort. The decay product (often gamma emission) can be located and the intensity measured. The amount of isotope taken up by the body can then give information as to the extent of the medical problem.

An isotope of iodine (I-131) is used in both the diagnosis and treatment of thyroid cancer. The thyroid will normally absorb iodine to produce the iodine-containing thyroid hormones. An overactive thyroid gland will absorb the radioactive material which can then destroy excess thyroid tissue or any cancer of the thyroid. The material is sometimes used to image cancers in other parts of the body.

Technetium-99m is perhaps the most widely used radioisotope in diagnosis and treatment (the “m” stands for metastable). This isotope decays to Tc-99 and a gamma emission of low intensity, making the radiation damage fairly negligible. The half-life is about six hours, so it will remain in the body for some time. Tc-99m can be used to look at cardiac damage. As the isotope flows in the blood stream, if there is less blood flow in the heart, there will be less isotope concentrated in the heart muscle. Similar information can be obtained for blood flow in the brain.

Isotopes can be very useful in scans to locate cancer cells. This patient has multiple tumors that have spread (metastasized) from the main tumor. A radioisotope has been attached to **antibodies** that bind to specific cancer cells. The very dark spots in the armpits, neck, and groin represent areas where tumor cells exist.

Many other examples could be presented. There are presently over 25 different isotopes in use for diagnosis and treatment. A very partial list can be seen in the **Table** 24.3:

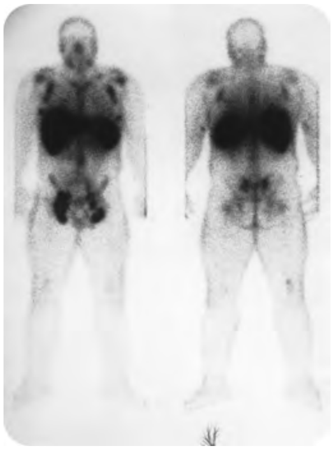


FIGURE 24.17

Radioisotope scan to detect tumors.

TABLE 24.3: **Radioisotopes Employed in Diagnosis and/or 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

Summary

- Radioisotopes used in medical diagnosis and treatment are described.

Practice

Read the material at the link below and answer the following questions:

http://www.rsc.org/images/essay5_tcm18-17767.pdf

1. What was the first application of radioisotopes in medicine?
2. Where does Tc-99m come from?
3. How does Tc99m allow us to study blood flow in the heart?

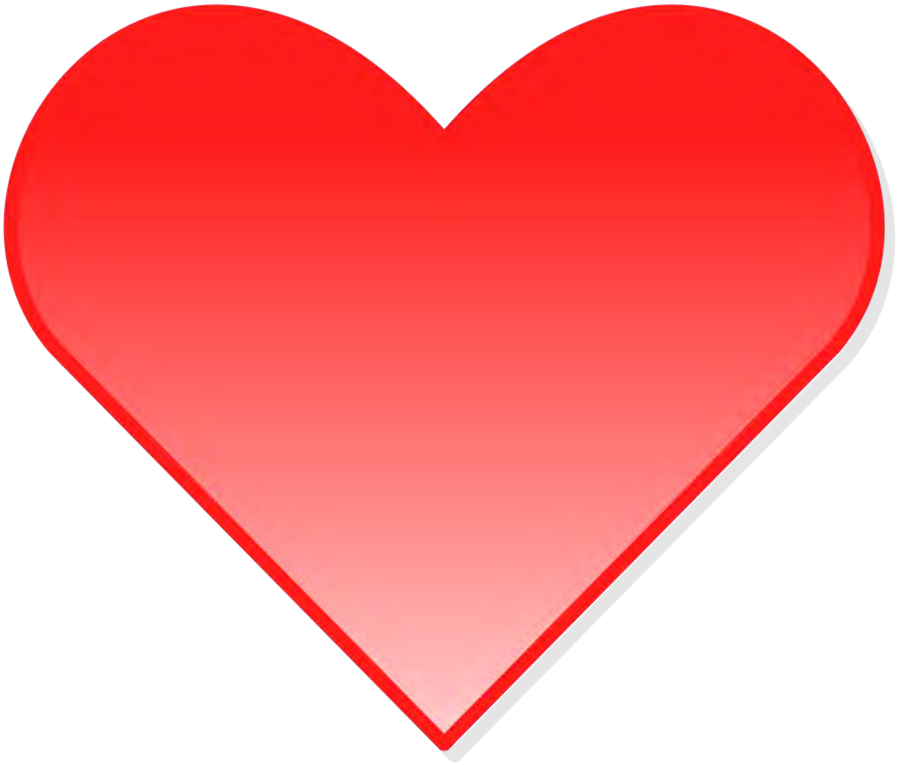
Review

1. How does I-131 treat thyroid cancer?
2. How does Tc-99m show cardiac damage?
3. What isotope would you use to study red blood cells?

- **antibody:** A protein that attaches to a specific molecule.

24.12 PET Scans

- Describe the basic approach used in PET scans.
- Describe applications for PET scans.



Can you really feel emotions in your heart?

Does your heart beat faster when you are scared? Do you have a tender feeling in your heart for that "special person"? Sorry to disappoint you, but that is actually simply a response generated by the brain. Scientists tell us that the seat of emotions is in the brain. Using PET scans and other techniques, they are looking at specific areas of the brain that process and store information dealing with strong emotions. They haven't localized the love site, but they're working on it.

PET Scans

One of the more interesting and useful approaches to radioisotope use in medicine is **positron emission tomography (PET)**, often referred to as a PET scan. This technique is especially useful in studying the processes in the brain. Many compounds do not enter the brain because of what is called the "**blood-brain barrier**," a filtering system to block material from being transported into brain tissue. This mechanism serves to protect the brain from a wide variety of harmful substances.

In order to get a good picture of what is happening in the brain, radiolabels are attached to different compounds that will enter the brain. Since the brain uses about 25% of the glucose found in the body, 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 labels 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. 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 emissions that are 180° apart from one another. The 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 24.18
Scanner used to detect positron emissions.

One useful application of PET scanning is in the diagnosis of Alzheimer's disease. This debilitating condition primarily occurs in elderly individuals. A protein known as beta-amyloid gradually forms deposits in the brain called plaque. Memory loss and impaired movement are the result of the plaque growth.

The compound known as Pittsburgh compound B is often used to identify areas of plaque in the brain. The radiolabel is C-11 (half-life is 20.38 minutes).

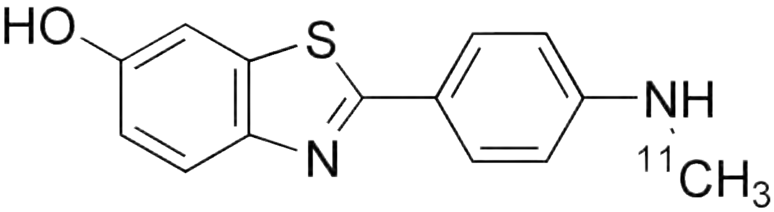


FIGURE 24.19
Pittsburgh compound B used in diagnosis of Alzheimer's disease.

The label attaches to plaque and can be observed using PET scans.

The computer translates the amount of 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. The individual with Alzheimer's demonstrates high concentrations of the beta-amyloid in numerous areas of the brain.

Other studies have been done looking at brain function in drug addicts. One of the theories about drug addiction involves the amount of dopamine (a chemical that is a part of the system to transport nerve impulses). Studies of

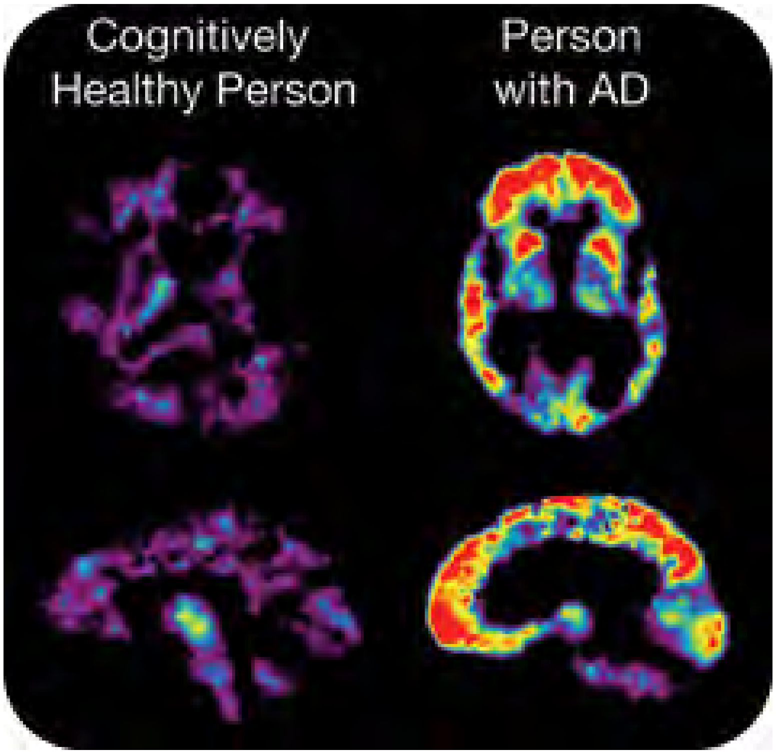


FIGURE 24.20
Brain scans using Pittsburgh compound B to locate plaque.

dopamine action in the brain have been helpful in understanding addictive processes.

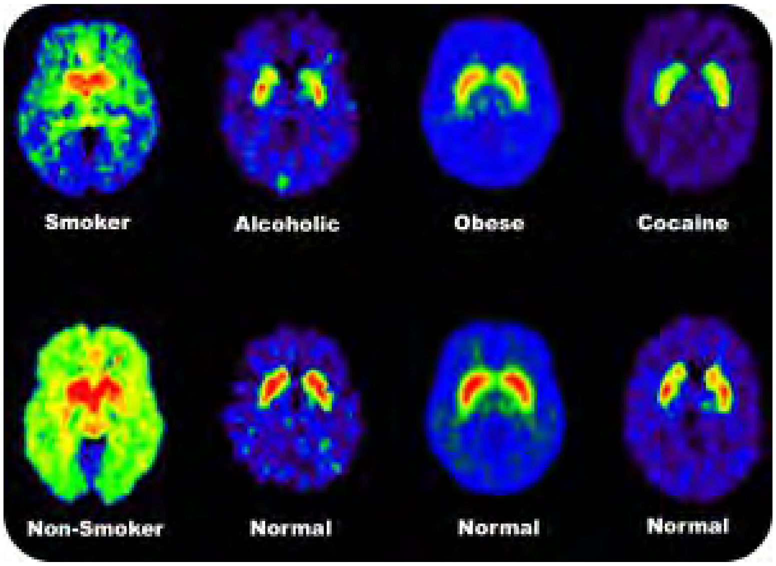


FIGURE 24.21
PET scan of dopamine binding in brains of normal and addicted individuals.

The images above show binding of chemicals that attach 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. Since dopamine is somehow linked with the sense of pleasure, these data may help to bring a better understanding to the biochemical processes in drug addiction.

Summary

- PET scan techniques and results are described.

Practice

Read the material at the link below and answer the following questions:

http://brainblogger.com/2011/03/04/imaging-the-musical-brain/

1. What compound did the researchers label?
2. Why was dopamine used?
3. What was the not-so-surprising finding?

Review

1. What happens when a positron collides with an electron?
2. Why is glucose used for many brain studies?
3. Why is F-18 often used as a radiolabel?

- **blood-brain barrier:** A filtering system to block material from being transported into brain tissue.
- **PET:** Positron emission tomography.

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CHAPTER 25 Organic Chemistry

Chapter Outline

25.1 Organic Chemistry

- Define organic chemistry.
- List characteristics of organic molecules.

How many molecules are there?

How many carbon-containing molecules are there? The current estimate is around 20 million different organic compounds that we know about. Why the uncertainty? Every day, scientists are coming up with new compounds. Some of these materials are of interest for a research project, while others are destined to be developed for a commercial market. As soon as we get a number, it's out of date.

Organic Chemistry

At one time in history, it was thought that only living things were capable of synthesizing the carbon-containing compounds present in cells. For that reason, the term organic was applied to those compounds. Eventually it was proved that carbon-containing compounds could be synthesized from inorganic substances, but the term organic has remained. Currently, **organic compounds** are covalently bonded compounds containing carbon, excluding carbonates and oxides. By this definition, compounds such as carbon dioxide (CO_2) and sodium carbonate (Na_2CO_3) are considered to be inorganic. **Organic chemistry** is the study of organic compounds.

Organic chemistry is a very vast and complex subject. There are millions of known organic compounds, which is far more than the number of inorganic compounds. The reason lies with the uniqueness of carbon's structure and bonding. Carbon has four valence electrons and so makes four separate covalent bonds in compounds. Carbon has the ability to bond to itself repeatedly, making long chains of carbon atoms as well as ringed structures. These bonds can be single, double, or triple covalent bonds. Carbon readily makes covalent bonds with other elements, primarily hydrogen, oxygen, nitrogen, halogens, and several other nonmetals. The figure below shows ball-and-stick models of two of the many organic compounds.

FIGURE 25.1

Stearic acid is composed of many carbon (black) and hydrogen (white) atoms, along with two oxygen (red) atoms

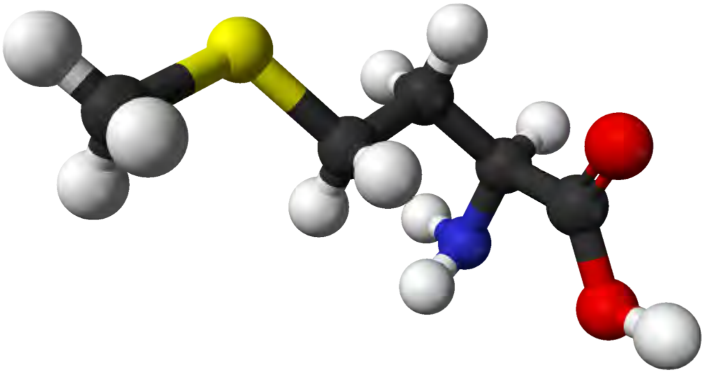


FIGURE 25.2

Methionine is composed of carbon, hydrogen, oxygen, nitrogen (blue), and sulfur (yellow) atoms

The related field of biochemistry overlaps to some extent with organic chemistry. **Biochemistry** is the study of the chemistry of living systems. Many biochemical compounds are considered to be organic chemicals. Both the molecules shown above are biochemical materials in terms of their use in the body, but organic chemical in terms of their structure and chemical reactivity.

Summary

- Organic chemistry is defined.
- Examples of organic chemicals are described.

Practice

Read the material at the site below and answer the following questions:

http://www.dummies.com/how-to/content/the-basics-of-organic-chemistry.html

1. What is the focus in organic chemistry?
2. What are functional groups?
3. What is the relationship between melting point and reactivity?

Review

1. What is organic chemistry?

2. What is an organic compound?
3. How do biochemistry and organic chemistry overlap?

- **biochemistry:** The study of the chemistry of living systems.
- **organic chemistry:** The study of organic compounds.
- **organic compounds:** Covalently bonded compounds containing carbon, excluding carbonates and oxides.

25.2 Straight-Chain Alkanes

- Define hydrocarbon and list classes of hydrocarbons.
- Define alkane.
- List the first ten alkanes and draw their structures.

More efficient transportation

As our country looks at oil shortages in the future, we are searching for alternative transportation fuel sources. One very viable possibility is propane gas. Power and acceleration are comparable to gasoline-powered vehicles and fuel efficiency is greater. Propane has a higher octane rating than regular gasoline, leading to much longer engine life. When properly set up, propane engines can produce lower amounts of air pollution. We are seeing growing use in buses, trucks, and police cars. Pictured above is a prototype of a minibus that will run on propane fuel. Maybe your next car will burn propane.

Straight-Chain Alkanes

Hydrocarbons

A **hydrocarbon** is an organic compound that is made up of only carbon and hydrogen. A hydrocarbon is the simplest kind of organic molecule and is the basis for all other more complex organic compounds. Hydrocarbons can be divided into two broad categories. **Aliphatic hydrocarbons** are hydrocarbons that do not contain the benzene group or a benzene ring. **Aromatic hydrocarbons** contain one or more benzene rings. We will discuss aliphatic hydrocarbons first.

Alkanes

An **alkane** is a hydrocarbon in which there are only single covalent bonds. The simplest alkane is methane, with the molecular formula CH_4. The carbon is the central atom and makes four single covalent bonds to hydrogen atoms.

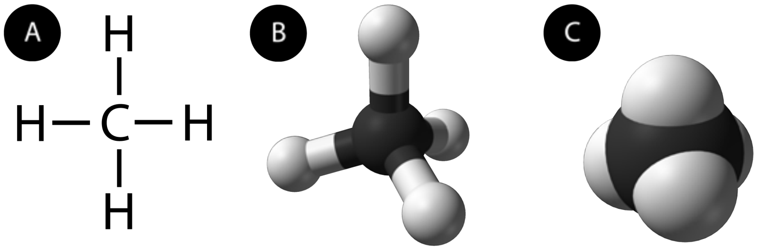
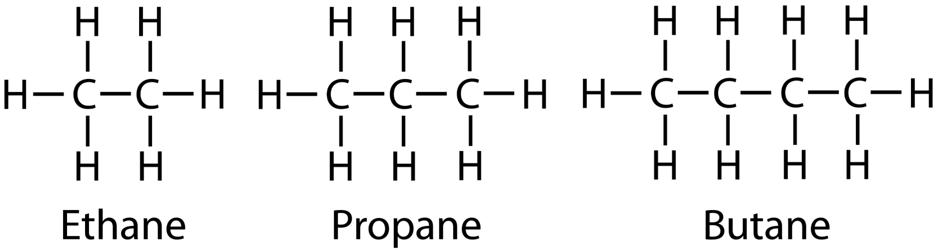


FIGURE 25.3

Methane is the simplest hydrocarbon and is shown with a structural formula, a ball-and-stick model, and a space-filling model.

The next simplest alkane is called ethane (C_2H_6) and consists of two carbon atoms with a single covalent bond between them. Each carbon is then able to bond to three hydrogen atoms. The alkane series progresses from there, increasing the length of the carbon chain by one carbon at a time. Structural formulas for ethane, propane (C_3H_8), and butane (C_4H_{10}) are shown below.



These alkanes are called straight-chain alkanes because there the carbon atoms are connected in one continuous chain with no branches. Naming and writing structural and molecular formulas for the straight-chain alkanes is straightforward. The name of each alkane consists of a prefix that specifies the number of carbon atoms and the ending –ane. The molecular formula follows the pattern of C_nH_{2n+2} where n is the number of carbons in the chain. The **Table** 25.1 lists the first ten members of the alkane series.

TABLE 25.1: **First Ten Members of the Alkane Series**

Name	Molecular Formula	Condensed Structural Formula	Boiling Point (°C)
Methane	CH_4	CH_4	-161.0

TABLE 25.1: (continued)

Ethane	C_2H_6	CH_3CH_3	-88.5
Propane	C_3H_8	$CH_3CH_2CH_3$	-42.0
Butane	C_4H_{10}	$CH_3CH_2CH_2CH_3$	0.5
Pentane	C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$	36.0
Hexane	C_6H_{14}	$CH_3CH_2CH_2CH_2CH_2CH_3$	68.7
Heptane	C_7H_{16}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	98.5
Octane	C_8H_{18}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	125.6
Nonane	C_9H_{20}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	150.7
Decane	$C_{10}H_{22}$	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	174.1

Note that the table shows a variation of a structural formula called a condensed structural formula. In this formula, the covalent bonds are understood to exist between each carbon and the hydrogens associated with it as well as between carbons. This table also shows that the boiling points of the alkanes steadily increase as the length of the carbon chain increases. This is due to an increase in the strength of the intermolecular attractive forces and is a general feature of other organic molecules as well.

Summary

- Hydrocarbon definition and classifications are given.
- Alkanes are defined and listed.

Practice

Read the material at the web site below and answer the following questions:

1. What is the composition of natural gas?
2. How is crude oil separated into fractions?
3. What is “cracking”?

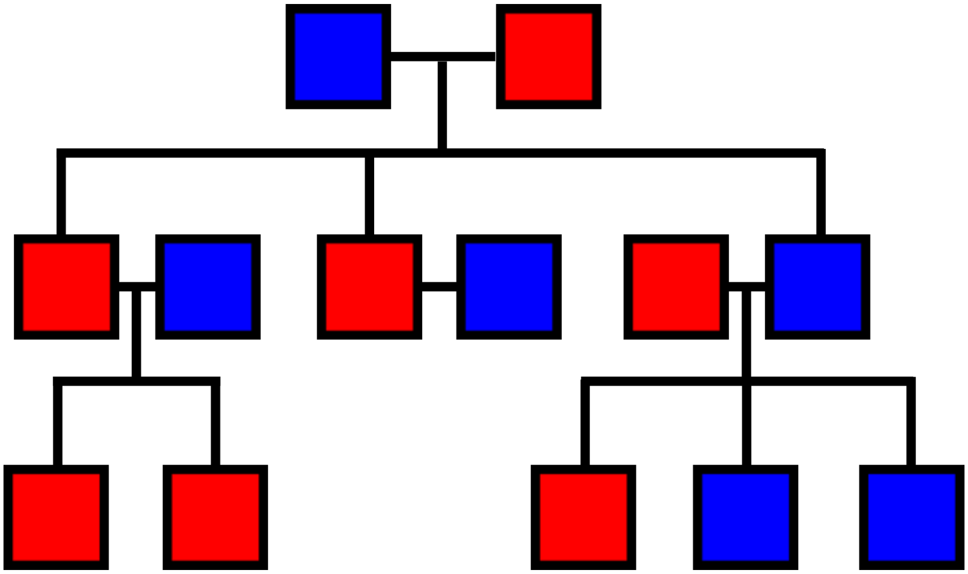
Review

1. What is a hydrocarbon?
2. What is an alkane?
3. Name the alkane that has five carbons in its chain.

- **aliphatic hydrocarbons:** Hydrocarbons that do not contain the benzene group or a benzene ring.
- **alkane:** A hydrocarbon in which there are only single covalent bonds.
- **aromatic hydrocarbons:** Contain one or more benzene rings.
- **hydrocarbon:** An organic compound that is made up of only carbon and hydrogen.

25.3 Branched Alkanes

- List the rules for naming branched alkanes.
- Use the rules to name branched alkane structures.

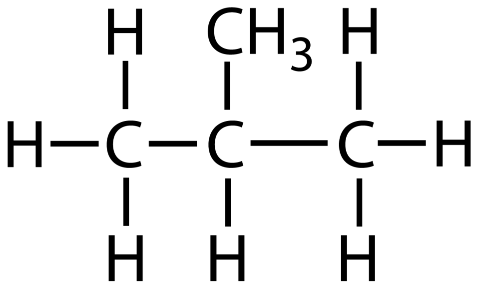


Who is my great-aunt?

Tracing your family tree can be both fun and exciting. But you need to know exact names in order to do this right. A name that is close or "maybe it's ..." is not enough. A good family tree is one where all the relatives are carefully and precisely identified. After all, you would prefer that great-great-great-uncle to be royalty and not a horse thief.

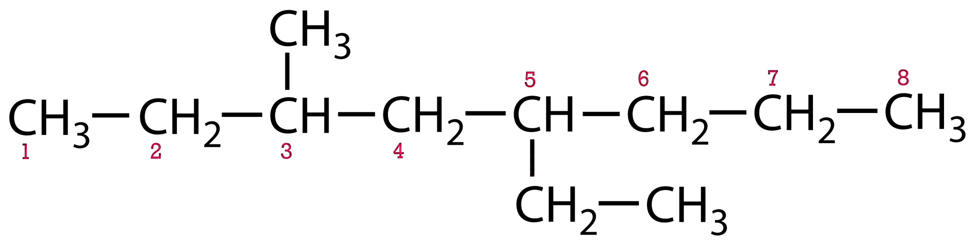
Branched Alkanes

Beginning with butane, there is an alternate structure possible that is not a straight chain. The structural formulas below show a structure with a three-carbon chain that has a $–CH_3$ group attached to the middle carbon.



The name of this molecule is 2-methylpropane. The molecular formula is still C_4H_{10}, which is the same formula as butane. A **structural isomer** is one of multiple molecules that have the same molecular formula, but different structural formulas. Butane and 2-methylpropane are structural isomers.

2-methylpropane is an example of a type of alkane called a branched alkane. The IUPAC system of nomenclature for branched alkanes follows a set of steps which will be applied to the example molecule below.



1. Find the longest continuous chain of carbon atoms in the molecule. This is called the parent chain. In the example, the longest chain is eight carbon atoms and so the parent hydrocarbon is octane.
2. Number the carbon atoms in the parent chain. To do this, start at the end that will give the smallest numbers possible to the carbon atoms where the branches originate. In the example above, the branches are on carbons 3 and 5 when the chain is numbered left-to-right. If it were to be numbered right-to-left, the branches would be on carbons 4 and 6, so the left-to-right order is preferable.
3. The atoms attached to the parent chain are called substituents. A substituent that is a hydrocarbon is called an **alkyl group**. The names of alkyl groups use the same prefixes as the alkanes, but with a –yl suffix. So a 1-carbon alkyl group is a methyl group, a 2-carbon alkyl group is an ethyl group, and so on. The substituents are named by placing the number from the parent carbon chain in front of the name of the substituent. In the current example, we have 3-methyl and 4-ethyl substituents.
4. Use a prefix to indicate the appearance of more than one of the same substituent in the structural formula. Two of the same group is tri-, three is tri-, four is tetra-, etc. For example, if methyl groups were attached to both carbons 2 and 3, that part of the name would be 2, 3-dimethyl-. This rule does not apply to the current structure above.
5. Multiple different substituents are listed in alphabetical order. Ignore any of the prefixes from rule 4. In the current example, the 5-ethyl- comes before the 3-methyl.
6. Commas are used to separate multiple numbers. Hyphens come between the number and the name of a substituent. The parent name comes immediately after the last substituent. There are no blank spaces in the name.

The correct name for the above structure according to the IUPAC system is 5-ethyl-3-methyloctane.

Summary

- Nomenclature rules for branched hydrocarbons are given.

Practice

Work the problems at the link below:

http://chemware.co.nz/orgquiz.htm

Review

1. What is an alkyl group?
2. How are alkyl substituents listed?
3. If there are three methyl groups on the same carbon, what is the prefix used?

- **alkyl group:** A substituent that is a hydrocarbon.
- **structural isomer:** One of multiple molecules that have the same molecular formula, but different structural formulas.

25.4 Alkenes and Alkynes

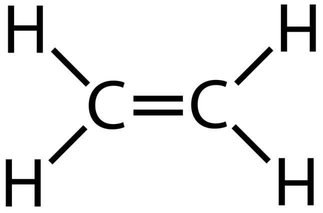
- Define alkene and alkyne.
- Draw structures of common alkenes and alkynes.

Better than a hacksaw

One of the most effective ways to cut metal is with an oxy-acetylene torch. Very high temperatures can be created when acetylene burns in oxygen. Mixed 1:1 with oxygen, a temperature of over 3000°C can be achieved. Energy release is high – the net heat of combustion is 1300 kJ/mole. Safety precautions need to be observed since the gas is very explosive. For welding and cutting, the oxy-acetylene torch is one of the best ways to go.

Alkenes and Alkynes

An **alkene** is a hydrocarbon with one or more carbon-carbon double covalent bonds. The simplest alkene is composed of two carbon atoms and is called ethene (shown below). Each carbon is bonded to two hydrogen atoms in addition to the double bond between them.



The hybridization of each carbon atom is sp^2 with trigonal planar geometry. All the atoms of the molecule lay in one plane. Like the alkane series, the names of alkenes are based on the number of atoms in the parent chain. Naming follows the same rules as for alkanes with the addition of using a number to indicate the location of the double bond. Propene (C_3H_6) has three carbons total, while butene (C_4H_8) has four. The general formula for alkenes with one double bond is C_nH_{2n}. Alkenes are called unsaturated hydrocarbons. An **unsaturated hydrocarbon** is a hydrocarbon that contains less than the maximum number of hydrogen atoms that can possibly bond with the number of carbon atoms present.

The location of the carbon-carbon double bond can vary. The 4-carbon alkene generic name is butene. Since the double bond can be located in more than one place, we have 1-butene and 2-butene:

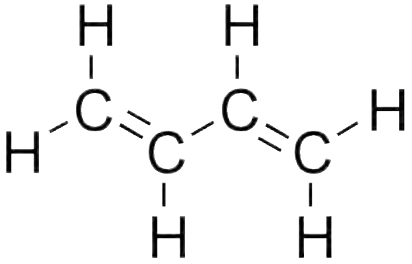
$$CH_2{=}CH-CH_2-CH_3$$

1-butene

$$CH_3-CH{=}CH-CH_3$$

2-butene

Molecules with multiple double bonds are also quite common. The formula below shows a four-carbon chain with double bonds between carbons 1 and 2 and between carbons 3 and 4. This molecule is called 1,3-butadiene.

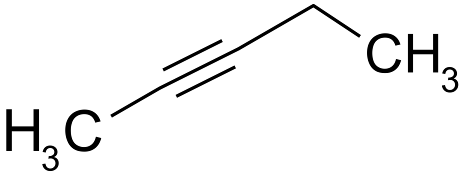


Alkynes

An **alkyne** is a hydrocarbon with one or more carbon-carbon triple covalent bonds. The simplest alkyne consists of two carbon atoms and is called ethyne (common name: acetylene).

$$H-C\equiv C-H$$

The ethyne molecule is linear, with sp hybridization for each carbon atom. The general formula of alkynes with one triple bond is C_nH_{2n-2}. Alkynes are also unsaturated hydrocarbons. Other alkynes exist, such as 2-pentyne:



Summary

- Structures of alkene and alkyne are given.
- Structures of typical alkenes and alkynes are shown.

Practice

Answer the questions at the site below:

http://www.docbrown.info/page06/PRalkenes/alkeneQmc.htm

Review

1. What is an alkene?
2. What is an alkyne?
3. Can a compound have more than one carbon-carbon double bond in it?

- **alkene:** A hydrocarbon with one or more carbon-carbon double covalent bonds.
- **alkyne:** A hydrocarbon with one or more carbon-carbon triple covalent bonds.
- **unsaturated hydrocarbon:** A hydrocarbon that contains less than the maximum number of hydrogen atoms that can possibly bond with the number of carbon atoms present.

25.5 Isomers

- Define isomer.
- Define structural isomer and give examples.
- Define geometric isomer and give examples.

What difference does the isomer make?

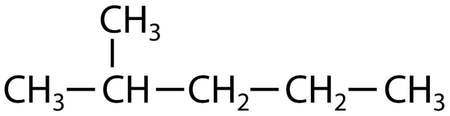
As we get more into the complexities of organic chemistry, we will see how shape affects reactions. One common reaction for alkenes is the addition of hydrogen across the double bond to form the corresponding alkane. Because of the geometry of the reaction, different 2-butene shapes have different heats of reaction. These differences are important both from a theoretical standpoint as well as from the point of view of industrial applications. More energy needed means a higher cost and a more expensive product.

Isomers

One of the interesting aspects of organic chemistry is that it is three-dimensional. A molecule can have a shape in space that may contribute to its properties. Molecules can differ in the way the atoms are arranged – the same combination of atoms can be assembled in more than one way. These compounds are known as **isomers,** molecules with the same molecular formulas, but different arrangements of atoms. We will look at some isomer possibilities for alkane and alkenes.

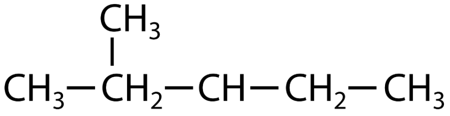
Structural Isomers

A **structural isomer** is one in which two or more or organic compounds have the same molecular formulas but different structures. The two pentane molecules below differ only in the location of the methyl group.



$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2-CH_2-CH_3$$

2-methylpentane



$$CH_3-CH_2-\overset{\displaystyle CH_3}{\overset{|}{CH_2}}-CH-CH_2-CH_3$$

3-methylpentane

Alkenes can also demonstrate structural isomerism. In alkenes, there are multiple structural isomers based on where in the chain the double bond occurs. The condensed structural formulas of 1-butene and 2-butene show this.

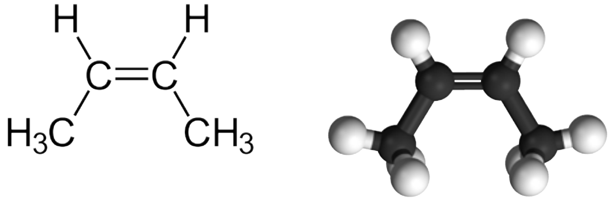
$CH_2{=}CH-CH_2-CH_3$ $CH_3-CH{=}CH-CH_3$

1-butene 2-butene

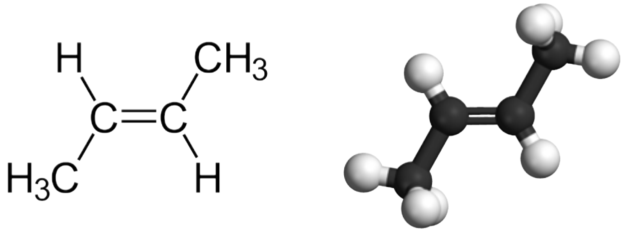
The number in the name of the alkene refers to the lowest numbered carbon in the chain that is part of the double bond.

With 2-butene there is also a different type of isomerism called geometric isomerism. **Geometric isomers** are isomers in which the order of atom bonding is the same but the arrangement of atoms in space is different. The double bond in an alkene is not free to rotate because of the nature of the pi bond. Therefore, there are two different ways to construct the 2-butene molecule. **Figure** below shows the two geometric isomers, called *cis*-2-butene and *trans*-2-butene.

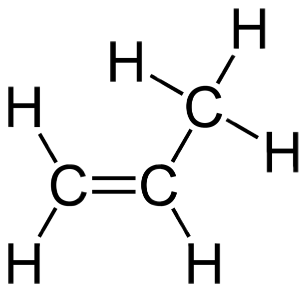
cis-2-butene



trans-2-butene



The *cis* isomer has the two single hydrogen atoms on the same side of the molecule, while the *trans* isomer has them on opposite sides of the molecule. In both molecules, the bonding order of the atoms is the same. In order for geometric isomers to exist, there must be a rigid structure in the molecule to prevent free rotation around a bond. If the double bond in an alkene was capable of rotating, the two geometric isomers above would not exist. In addition, the two carbon atoms must each have two different groups attached for there to be geometric isomers. Propene has no geometric isomers because one of the carbon atoms has two single hydrogens bonded to it.



Physical and chemical properties of geometric isomers are generally different. While *cis*-2-butene is a polar molecule, *trans*-2-butene is nonpolar. Heat or irradiation with light can be used to bring about the conversion of one geometric isomer to another. The input of energy must be large enough to break the pi bond between the two carbon atoms, which is weaker than the sigma bond. At that point, the now single bond is free to rotate and the isomers can interconvert.

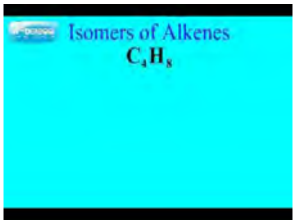
As with alkenes, alkynes display structural isomerism beginning with 1-butyne and 2-butyne. However, there are no geometric isomers with alkynes because there is only one other group bonded to the carbon atoms that are involved in the triple bond.

Summary

- Structural and geometric isomers are defined.
- Examples of alkane and alkene isomers are given.

Practice

Watch the video at the link below and answer the following questions:



MEDIA

Click image to the left for more content.

http://www.youtube.com/watch?v=CGPyTUrSF2E

1. What does the molecular formula tell us?
2. What does the structural formula tell us?
3. What do you add to the name is two double bonds are present in the molecule?

Review

1. What is a structural isomer?
2. What is a geometric isomer?
3. Could 1-butene have geometric isomers?

- **geometric isomers:** Isomers in which the order of atom bonding is the same but the arrangement of atoms in space is different.
- **isomers:** Molecules with the same molecular formulas, but different arrangements of atoms.
- **structural isomer:** One in which two or more or organic compounds have the same molecular formulas but different structures.

25.6 Cyclic Hydrocarbons

- Define cyclic hydrocarbon.
- Define cycloalkane.
- Draw structures and name typical cyclic hydrocarbons.

From benzene to balloons

Although cyclcohexane can be isolated from petroleum products, a major source for this chemical is from the hydrogenation of benzene. Much of the cyclohexane produced is used to manufacture intermediates for the production of nylon. The nylon balloons pictured above no doubt had their start in a chemical plant where hydrogen gas and benzene were reacted at high temperatures to form cyclohexane. This cycloalkane then undergoes nitration to begin the process of forming the long strands of nylon that can be made into balloons, ropes, clothing, and many other useful products.

Cyclic Hydrocarbons

A **cyclic hydrocarbon** is a hydrocarbon in which the carbon chain joins to itself in a ring. A **cycloalkane** is a cyclic hydrocarbon in which all of the carbon-carbon bonds are single bonds. Like other alkanes, cycloalkanes are saturated compounds. Cycloalkanes have the general formula of C_nH_{2n}. The simplest cycloalkane is cyclopropane, a three-carbon ring.

The structural formulas of cyclic hydrocarbons can be represented in multiple ways, two of which are shown above. Each atom can be shown as in the structure on the left. A convenient shorthand is to omit the element symbols and

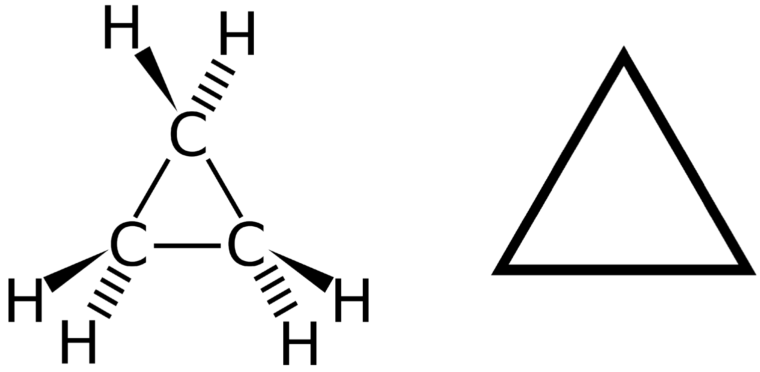
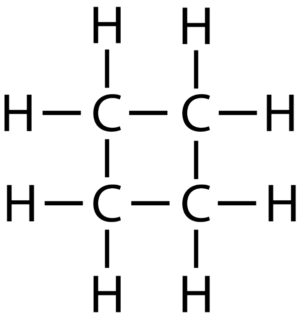


FIGURE 25.4

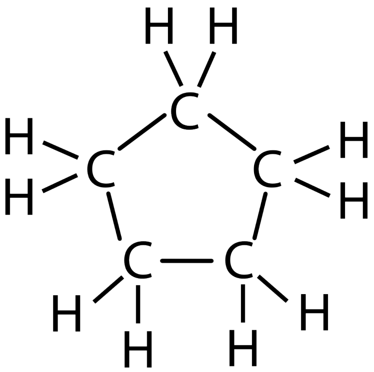
Cyclopropane is the simplest cycloalkane. Its highly strained geometry makes it rather unstable and highly reactive.

only show the shape, as in the triangle on the right. Carbon atoms are understood to be the vertices of the triangle.

The carbon atoms in cycloalkanes are still sp^3 hybridized, with an ideal bond angle of 109.5°. However, an examination of the cyclopropane structure shows that the triangular structure results in a C-C-C bond angle of 60°. This deviation from the ideal angle is called ring strain and makes cyclopropane a fairly unstable and reactive molecule. Ring strain is decreased for cyclobutane, with a bond angle of 90°, but is still significant. Cyclopentane has a bond angle of about 108°C. This minimal ring strain for cyclopentane makes it a more stable compound.

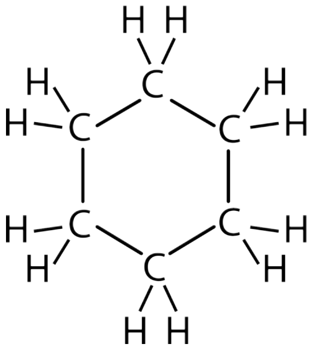


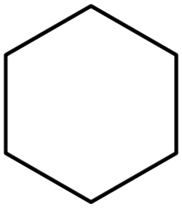
cyclobutane

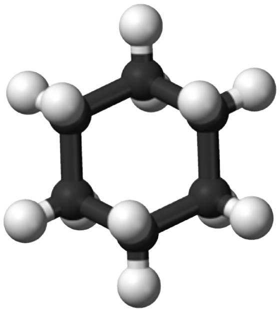


cyclopentane

Cyclohexane is a six-carbon cycloalkane shown below.







All three of the depictions of cyclohexane are somewhat misleading because the molecule is not planar. In order to reduce the ring strain and attain a bond angle of approximately 109.5°, the molecule is puckered. The puckering of the ring means that every other carbon atom is above and below the plane. The **Figure** 25.5 shows two possibilities for the puckered cyclohexane molecule. Each of the structures is called a conformation. The conformation on the right is called the boat conformation, while the one on the left is called the chair conformation.

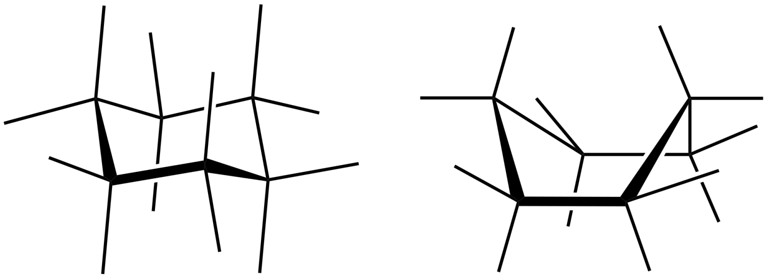
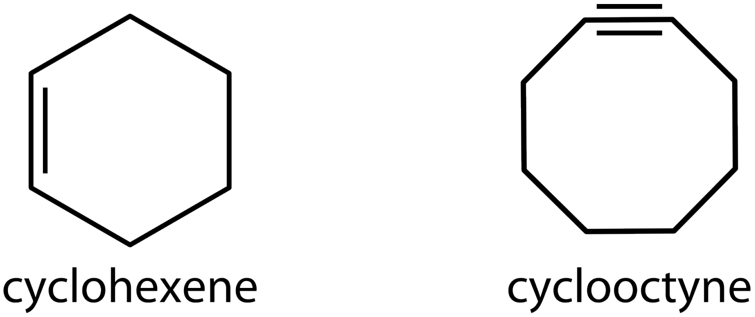


FIGURE 25.5
Chair (left) and boat (right) conformations for cyclohexane.

Larger cycloalkanes also exist, but are less common. Cyclic hydrocarbons may also be unsaturated. A **cycloalkene** is a cyclic hydrocarbon with at least one carbon-carbon double bond. A **cycloalkyne** is a cyclic hydrocarbon with at least one carbon-carbon triple bond. Shown below are the simplified structural formulas for cyclohexene and cyclooctyne.



Summary

- Definition of cyclic hydrocarbon and cyclic alkane are given.
- Names and structures of typical cyclic hydrocarbons are given.

Practice

Name the compounds at the link below:

http://www.physicsforums.com/showthread.php?t=302801

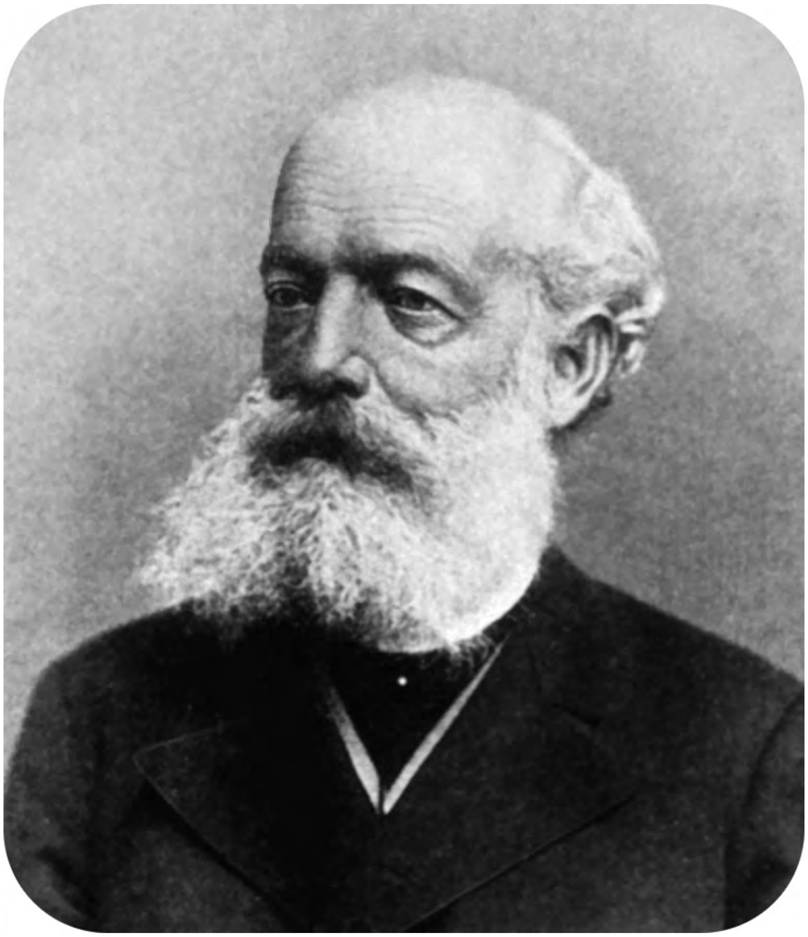
Review

1. Why is cyclopropane so reactive?
2. Why is cyclopentane stable?
3. Name the two forms of cyclohexane.

- **cyclic hydrocarbon:** A hydrocarbon in which the carbon chain joins to itself in a ring.
- **cycloalkane:** A cyclic hydrocarbon in which all of the carbon-carbon bonds are single bonds.
- **cycloalkene:** A cyclic hydrocarbon with at least one carbon-carbon double bond.
- **cycloalkyne:** A cyclic hydrocarbon with at least one carbon-carbon triple bond.

25.7 Aromatic Hydrocarbons

- Describe the structure of the benzene ring.
- List the nomenclature rules for aromatic compounds.
- Use the rules to name aromatic compounds.

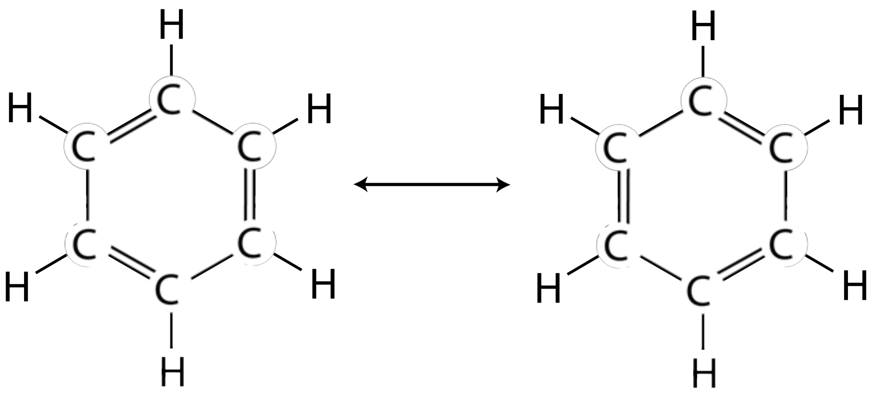


A really bad dream

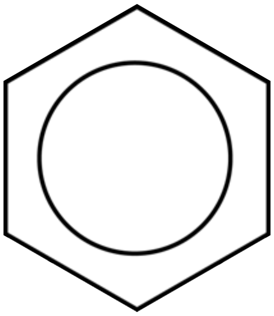
Friedrich Kekulé was a German chemist in the 1800s. He supposedly was thinking about the structure of the benzene ring when he fell asleep. While asleep, he dreamed of a snake eating its tail. He used this idea to propose the cyclic structure for benzene. Whether or not he actually had the dream has been debated ever since. Whatever happened (subconscious thinking or bad food?), the tale has persisted until today.

Aromatic Hydrocarbons

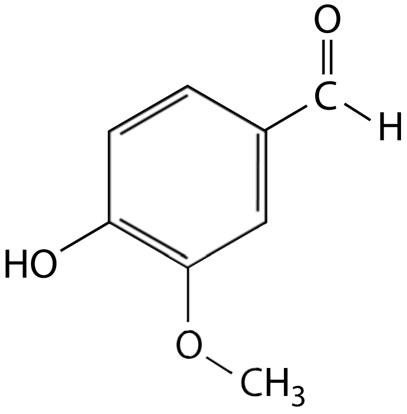
Benzene is the parent compound of the large family of organic compounds known as aromatic compounds. Unlike cyclohexane, benzene only contains six hydrogen atoms, giving the impression that the ring is unsaturated and each carbon atom participates in one double bond. Two different structures with alternating single and double bonds around the ring can be written for benzene.



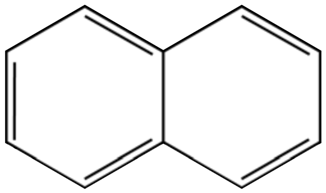
In benzene, the true bonding between carbon atoms is neither a single nor a double bond. Rather, all of the bonds are a hybrid of a single and double bond. In benzene, the pi bonding electrons are free to move completely around the ring. **Delocalized electrons** are electrons that are not confined to the bond between two atoms, but are instead allowed to move between three or more. The delocalization of the electrons in benzene can best be shown by showing benzene with a ring inside the hexagon, with the hydrogen atoms understood.



Delocalization of the electrons makes for a more stable molecule than a similar molecule that does not have delocalized electrons. Benzene is a more stable and less reactive compound than straight-chain hexenes. The sp^2 hybridization of the carbon atoms results in a planar molecule as opposed to the puckered structure of cyclohexane. Benzene rings are common in a great many natural substances and biomolecules. The figure below shows the structural formulas for vanilla and naphthalene, which is commonly used in mothballs.



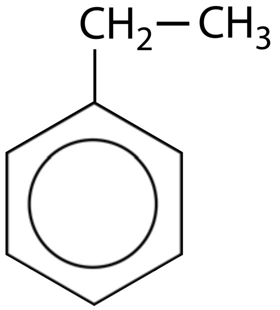
Vanilla



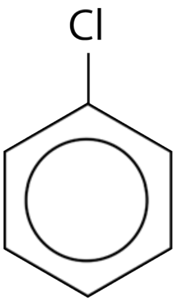
Naphthalene

Nomenclature of Aromatic Compounds

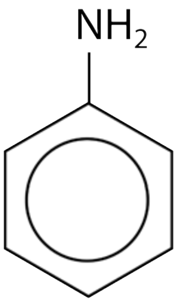
The simplest aromatic compounds are benzene rings with one substituent replacing one of the hydrogen atoms. If this substituent is an alkyl group, it is named first, followed in one word with “benzene”. The molecule shown below is therefore called ethylbenzene.



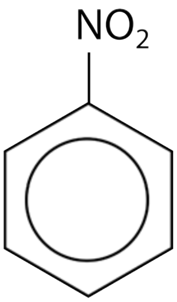
Substituents can be groups other than alky groups. If a chlorine atom were substituted for a hydrogen, the name becomes chlorobenzene. An –NH_2 group is called an amino group, so the corresponding molecule is called aminobenzene, often referred to as aniline. An –NO_2 group is called a nitro group and so the third example below is nitrobenzene.



chlorobenzene

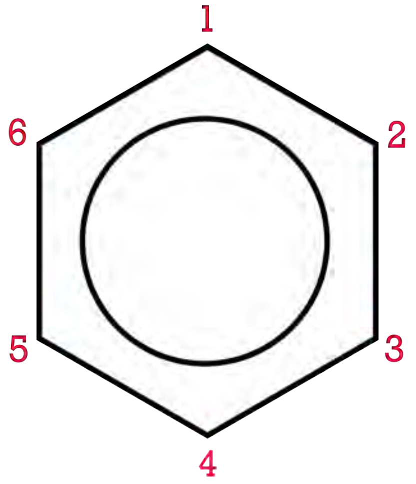


aminobenzene

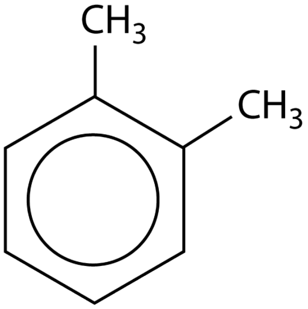


nitrobenzene

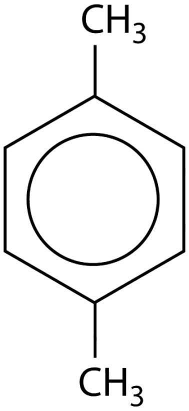
If more than one substituent is present, their location relative to each other can be indicated by numbering the positions on the benzene ring.



The number of the carbon then precedes the name of the substituent in the name, with the numbers separated by a comma. As with branched alkanes, the system requires that the numbers be the lowest possible and that prefixes be used for more than one of the same substituent. If there are different substituents, the first in alphabetical order is given the lower number and listed first. The structures below are called 1,2-dimethylbenzene and 1-ethyl-4-methylbenzene.

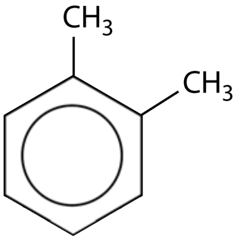


1,2-dimethylbenzene

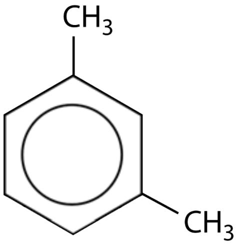


1,4-dimethylbenzene

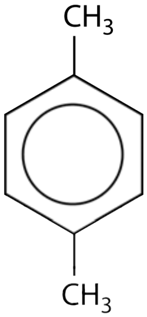
An alternate system for naming di-substituted benzene rings uses three different prefixes: *ortho*, *meta*, and *para*. If two groups are in the ortho position, they are on adjacent carbon atoms. The meta positioning refers to being in a 1, 3 arrangement. The para positioning refers to being in a 1, 4 arrangement. Shown below are the three possibilities for dimethylbenzene, also called xylene.



1,2-dimethylbenzene
or
ortho-dimethylbenzene

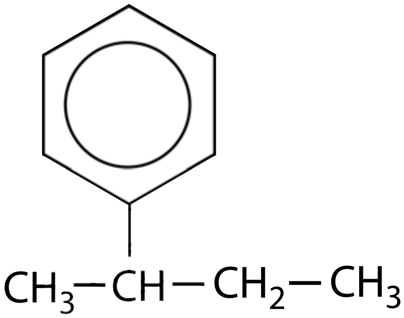


1,3-dimethylbenzene
or
meta-dimethylbenzene



1,4-dimethylbenzene
or
para-dimethylbenzene

Lastly, a benzene ring missing one hydrogen atom ($-C_6H_5$) can itself be considered the substituent on a longer chain of carbon atoms. That group is called a *phenyl* group and so the molecule below is called 2-phenylbutane.



Summary

- The structure and nomenclature of aromatic compounds are described.

Practice

Read the material at the link below:

http://www.chemguide.co.uk/basicorg/conventions/names3.html

At the bottom of the page, click on "Questions on naming aromatic compounds" in the green box and do as many of the problems (both naming and structure drawing) as you can.

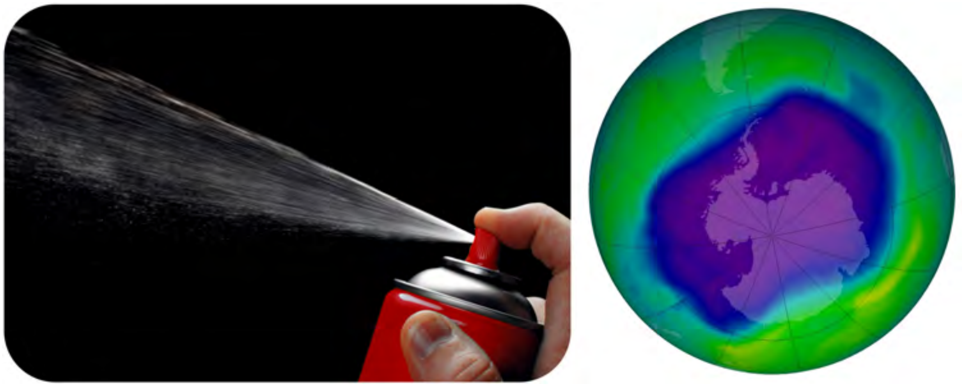
Review

1. What is characteristic of aromatic compounds?
2. What is the rule for numbering substituents on the ring?
3. How is numbering affected if there is more than one type of substituent group?

- **delocalized electrons:** Electrons that are not confined to the bond between two atoms, but are instead allowed to move between three or more.

25.8 Alkyl Halides

- Define alkyl halide.
- Give the nomenclature rules for naming alkyl halides.
- Use the nomenclature rules to name alkyl halides when give the structural formula.



Is the hold in the ozone getting bigger?

A class of simple alkyl halides called chlorofluorocarbons (CFCs) was once very widely used in aerosol sprays and as refrigerants. Once such example is CCl_3F, called trichlorofluoromethane. Unfortunately, CFCs are harmful to the ozone layer of our upper atmosphere. Ozone is critical in limiting the amount of damaging ultraviolet radiation that reaches the Earth. The CFC would react with the ozone and destroy it, leaving the earth less protected.

Beginning in the late 1970's, ozone depletion was recognized as a significant phenomenon. The most dramatic decrease in ozone occurs seasonally over the continent of Antarctica. The size and duration of the ozone hole steadily increased, with the largest hole recorded in 2006 (see figure above). Fortunately, most countries have recognized the danger of CFCs and dramatically curtailed their use in recent years. It is hoped that ozone depletion will slow and that the ozone layer may eventually come back to its earlier levels.

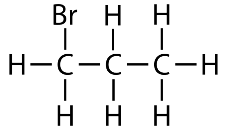
Alkyl Halides

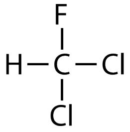
An **alkyl halide** is an organic compound in which one or more halogen atoms are substituted for one or more hydrogen atoms in a hydrocarbon. The general formulas for organic molecules with functional groups use the letter R to stand for the rest of the molecule outside of the functional group. Because there are four possible halogen atoms (fluorine, chlorine, bromine, or iodine) that can act as the functional group, we can use the general formula $R-X$ to represent an alkyl halide. The rules for naming simple alkyl halides are listed below.

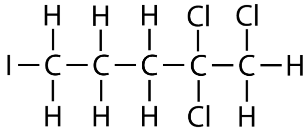
1. Name the parent compound by finding the longest continuous carbon atom chain that also contains the halogen. Add a prefix for the particular halogen atom. The prefixes for each of the four halogens are *fluoro-*, *chloro-*, *bromo-*, and *iodo-*. If more than one kind of halogen atom is present, put them in alphabetical order. If there is more than one of the same halogen on a given carbon atom, use the prefixes *di-*, *tri-*, or *tetra-* before the prefix for the halogen.
2. As with hydrocarbons, number the carbon chain in a way that makes the sum of halogen numbers as low as possible. If different halogens are in equivalent positions, give the lower number to the one that comes first in alphabetical order.
3. Add the numerical prefix into the name before the halogen prefix.

4. Separate numbers with commas and separate numbers from names or prefixes with a hyphen. There are no spaces in the name.

Listed below are some examples of names and structural formulas of a few alkyl halides.


1-bromopropane


dichlorofluoromethane


1,2,2-trichloro-5-iodopentane

Note that for the structure based on methane, no number needs to be used since there is only one carbon atom. In the third example, the chloro is listed first alphabetically and the chain is numbered so that the sum of the numbers is as low as possible.

Uses of Alkyl Halides

Alkyl halides are often used as synthetic intermediates in the laboratory. Although these compounds were one widely used as dry cleaning solvents, coolants in refrigerators and air conditioners, and propellants in hairsprays and deodorants, increasing awareness of their toxicity has led to a wide-spread decrease in applications for these materials. Some specific compounds are still used. Halothane (2-bromo-2-chloro-1,1,1-trifluoroethane) is still used in some situations as an inhalation anesthetic. The compound DDT is a very effective pesticide, but is only used when nothing else works because of its harmful effects on the environment.

Summary

- The structure and naming of alkyl halides is described.
- Uses for alkyl halides are listed.

Practice

Do the problems at the link below:

http://dl.clackamas.edu/ch106-01/practice.htm

Review

1. What is an alkyl halide?
2. Why are alkyl halides not used much commercially these days?
3. How are halogens listed in naming?

- **alkyl halide:** An organic compound in which one or more halogen atoms are substituted for one or more hydrogen atoms in a hydrocarbon.

25.9 Alcohols

- Assign IUPAC names to alcohols when given the structure.
- Indicate whether an alcohol is primary, secondary, or tertiary.
- Describe physical properties of alcohols.

How cold can it get?

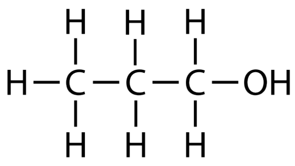
Water freezes at 0°C which creates problems for cars in the winter. The water in the engine would freeze and crack the engine block. To prevent this, antifreeze is added to lower the freezing point of the liquid. The most common antifreeze is an alcohol known as propylene glycol. It has largely replaced the much more toxic ethylene glycol. Methanol can also be used as an antifreeze, mainly in windshield wiper fluid.

Alcohols

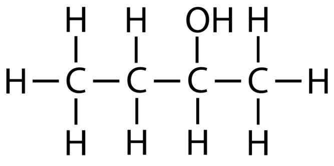
An **alcohol** is an organic compound that contains one or more hydroxyl ($-$OH) groups. The general formula for alcohols is R$-$OH. Do not confuse alcohols with inorganic bases that contain the hydroxide ion (OH^-). The –OH group in an alcohol is covalently bonded to a carbon atom and does not ionize in solution. The steps for naming alcohols are listed below.

1. Name the parent compound by finding the longest continuous carbon atom chain that also contains the hydroxyl group. If there is one hydroxyl group in the molecule, change the final *–e* in the name of the alkane to *–ol*. If there is more than one hydroxyl group, use the full name of the alkane and add a suffix to indicate the number of hydroxyl groups. For example, two hydroxyl groups is *–diol*, three is *–triol*, etc.
2. Number the carbon chain in a way that makes the sum of hydroxyl numbers as low as possible.
3. Add the numerical prefix into the name before the name of the alcohol.
4. Separate numbers with commas and separate numbers from names or prefixes with a hyphen. There are no spaces in the name.

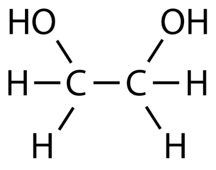
Following are three examples of alcohols and their IUPAC names.



1-propanol

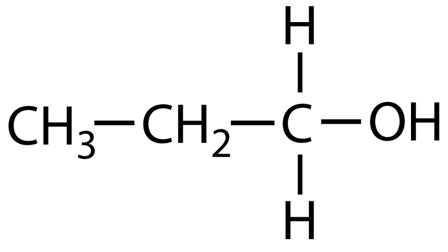


2-butanol

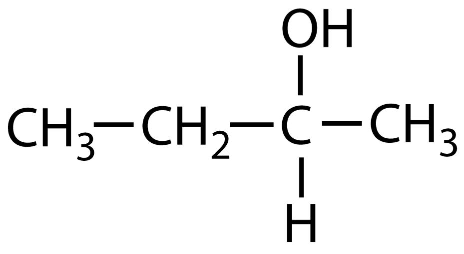


1,2-ethanediol

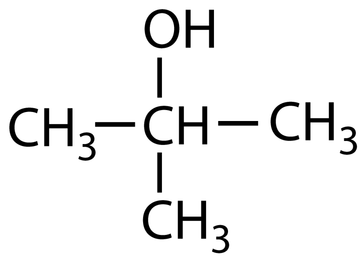
Aliphatic alcohols can be classified according to the number of R groups attached to the carbon with the hydroxyl group. If one R group is attached to that carbon, the alcohol is a primary alcohol. If two R groups are attached, the alcohol is a secondary alcohol. If three R groups are attached, the alcohol is a tertiary alcohol. Shown below is an example of each. The primary alcohol is 1-propanol, the secondary alcohol is 2-butanol, and the tertiary alcohol is 2-methy-2-propanol.



Primary Alcohol



Secondary Alcohol



Tertiary Alcohol

Properties of Alcohols

The smallest and lightest alcohols (methanol, ethanol, propanol) are completely soluble in water in all proportions. In a solution, the hydroxyl groups of alcohol molecules and the water molecules form hydrogen bonds with each other, resulting in complete miscibility. However, as the length of the carbon chain increases, the solubility decreases. The solubility of 1-butanol is 7.4 g per 100 g of water, that of 1-pentanol is 2.7 g per 100 g water and 1-octanol is 0.06 g per 100 g water. The carbon chain portion of the larger alcohol molecule is nonpolar and leads to the decreased solubility of the overall compound.

Hydrogen bonding also explains the relatively high boiling points of alcohols compared to alkanes of similar molar mass (see **Table** 25.2).

TABLE 25.2: **Boiling Point Comparison of Alkanes and Alcohols**

Compound	Formula	Molar Mass (g/mol)	Boiling Point (°C)
ethane	CH_3CH_3	32	-88
methanol	CH_3OH	30	64.7
propane	$CH_3CH_2CH_3$	44	-42.1
ethanol	CH_3CH_2OH	46	78.3

Only weak London dispersion forces hold molecules of nonpolar alkanes together in the liquid phase. Consequently, less energy is required to break these molecules away from the surface of the liquid and turn them into a vapor. The stronger hydrogen bonding between alcohol molecules means that more energy is required to convert the liquid to vapor and boiling points are high.

Summary

- The structure and nomenclature rules for alcohols are given.
- Properties of alcohols are described.

Practice

Do the problems at the link below:

http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/Questions/Alcohols/alcohol1.htm

Review

1. What is the general formula for an alcohol?
2. Why are alcohols soluble in water?
3. What is the boiling point of ethanol?

- **alcohol:** An organic compound that contains one or more hydroxyl ($-$OH) groups.

25.10 Ethers

- Describe the naming of ethers.
- Describe uses for ethers.

Start your engines

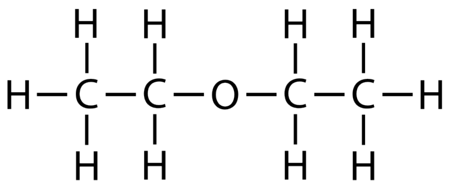
Race car drivers are always looking for that "edge" that will make them go faster (legally) than their competitors. One way to get more speed is to burn the gasoline in the car engine more efficiently. Methyl-t-butyl ether (MTBE) has been sued for this purpose, but is being discontinued due to concerns about contamination of drinking water by leaking fuel tanks containing this compound.

Ethers

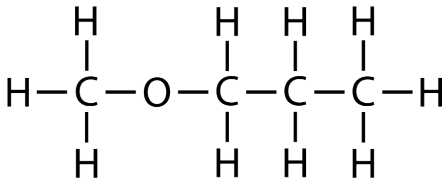
An **ether** is an organic compound in which two hydrocarbon groups are bonded to the same atom of oxygen. An ether is represented by the general formula R−O−R'. The R' in the formula means that the hydrocarbon group can be the same as R or it can be different. The steps for naming ethers are listed below.

1. The parent compound is given by the word *ether*, which appears at the end of the name.
2. The names of each alkyl group come before the word ether. If the two alkyl groups are the same, the prefix *–di* is used. If the two alkyl groups are different, they are listed in alphabetical order.
3. Spaces are left between the names of the alkyl groups (if different) and before the word *ether*.

Shown below are two examples of ethers with their IUPAC names.



diethyl ether



methyl propyl ether

Properties of Ethers

Like alcohols, ethers are also quite soluble in water. The lone-pair electrons on the oxygen atom of the ether can hydrogen bond with the hydrogen atoms of water molecules. Similar to alcohols, the solubility is greater for ethers that have shorter length R groups. The boiling points of ethers are much lower than the boiling points of alcohols. Ether molecules do not have hydrogen atoms that are covalently bonded to a highly electronegative atom, and so ether molecules cannot hydrogen bond with each other. The weaker intermolecular force acting between ether molecules results in boiling points which are much closer to alkanes of similar molar mass than to alcohols.

The anesthetic effects of ether were first discovered in the 1840s. Diethyl ether was used as a general anesthetic for patients undergoing surgery for many years. However, ethers are very flammable and have undesirable side effects such as nausea and vomiting. Safer alternatives to ether are now used in anesthesia and the primary use of ethers today is as a solvent for other organic compounds.

Summary

- The structure and nomenclature of ethers is given.
- Uses for ethers are described.

Practice

Read the material at the link below and answer the following questions:

http://www.slideshare.net/Tvaden/anesthesia-history-of-ether

1. What was used for anesthesia before 1846?
2. Who did the first successful public surgery using ether?
3. What did Morton try to patent ether as?

Review

1. What is the generic formula for an ether?
2. Do ethers boil at higher or lower temperatures than the alcohol with a similar structure?
3. Why are ethers water-soluble?

- **ether:** An organic compound in which two hydrocarbon groups are bonded to the same atom of oxygen.

25.11 Aldehydes and Ketones

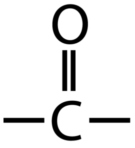
- Describe the basic structure of aldehydes and ketones.
- Use the IUPAC system to name aldehydes and ketones.
- Describe the physical properties of aldehydes and ketones.

That tastes good.

There's nothing like the smell of a fresh cinnamon roll. The taste is even better. But what causes that delicious taste? This flavoring comes from the bark of a tree (actually, several different kinds of trees). One of the major compounds responsible for the taste and odor of cinnamon is cinnamaldehyde. Cinnamon has been widely used throughout the centuries to treat a number of different disorders. In ancient times, doctors believed it could cure snakebite, freckles, and the common cold. Today there are several research studies being carried out on the health benefits of cinnamon. So, enjoy that cinnamon roll – it just might be good for you.

Aldehydes and Ketones

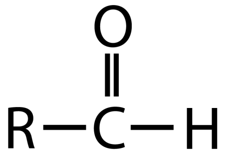
Aldehydes and ketones are two related categories of organic compounds that both contain the **carbonyl group**, shown below.



$$-\overset{\overset{\displaystyle O}{\|}}{C}-$$

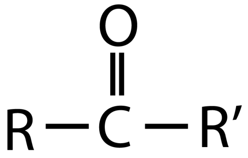
(Carbonyl Group)

The difference between aldehydes and ketones is the placement of the carbonyl group within the molecule. An **aldehyde** is an organic compound in which the carbonyl group is attached to a carbon atom at the end of a carbon chain. A **ketone** is an organic compound in which the carbonyl group is attached to a carbon atom within the carbon chain. The general formulas for each are shown below.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-H$$

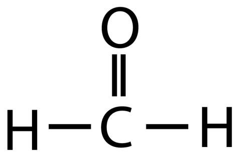
aldehyde



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-R'$$

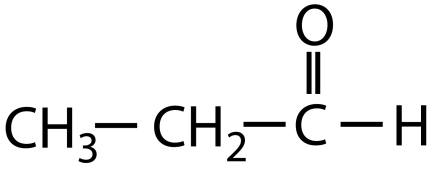
ketone

For aldehydes, the R group may be a hydrogen atom or any length carbon chain. Aldehydes are named by finding the longest continuous chain that contains the carbonyl group. Change the *–e* at the end of the name of the alkane to *–al*.



$$H-\overset{\overset{\displaystyle O}{\|}}{C}-H$$

methanal

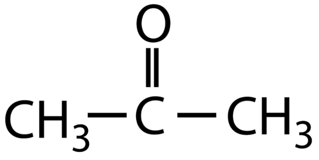


$$CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-H$$

propanal

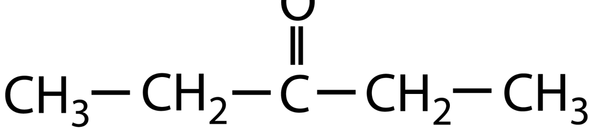
For ketones, R and R' must be carbon chains, of either the same or different lengths. The steps for naming ketones, followed by two examples, are shown below.

1. Name the parent compound by finding the longest continuous chain that contains the carbonyl group. Change the *–e* at the end of the name of the alkane to *–one*.
2. Number the carbon atoms in the chain in a way that the carbonyl group has the lowest possible number.
3. Add the numerical prefix into the name before the name of the ketone.
4. Use a hyphen between the number and the name of the ketone.



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

propanone



$$CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_3$$

3-pentanone

Properties of Aldehydes and Ketones

Aldehydes and ketones can work weak hydrogen bonds with water through the carbonyl oxygen atom. The lower members of both series (3 carbons or fewer) are soluble in water in all proportions. As the length of the carbon chain increases, water solubility decreases. Similar to ethers, neither aldehydes nor ketones can hydrogen bond with themselves. As a result, their boiling points are generally lower than those of alcohols. Unlike alkanes however, aldehydes and ketones are polar molecules due to the more electronegative oxygen atom. The dipole-dipole interactions are stronger than the dispersion forces present in alkanes. The boiling points of aldehydes and ketones are intermediate between those of alkanes and alcohols. For example, the boiling point of ethane is -89°C, ethanal is 20°C, and ethanol is 78°C.

Methanal, commonly known as formaldehyde, was once commonly used as a biological preservative for dead animals. In recent years formaldehyde has been shown to be a carcinogen and so has been replaced for this purpose by safer alternatives. Aldehydes are currently used in the production of resins and plastics. The simplest ketone, propanone, is commonly called acetone. Acetone is a common organic solvent that was once used in most nail polish removers, but has largely been replaced by other solvents.

Summary

- The structures of aldehydes and ketones are described.
- Rules for naming aldehydes and ketones are listed.
- Physical properties of aldehydes and ketones are given.

Practice

Answer the questions at the link below:

http://www.docbrown.info/page06/WMtestsNotes/aldketQmc.htm

Review

1. What is an aldehyde?
2. What is a ketone?
3. Can aldehydes or ketones hydrogen bond to themselves?

- **aldehyde:** An organic compound in which the carbonyl group is attached to a carbon atom at the end of a carbon chain.
- **carbonyl group:** Organic functional group composed of a carbon double-bonded to an oxygen.
- **ketone:** An organic compound in which the carbonyl group is attached to a carbon atom within the carbon chain.

25.12 Carboxylic Acids

- Describe the structure and naming of carboxylic acids.
- Describe the physical properties of carboxylic acids.
- List the uses of carboxylic acids.

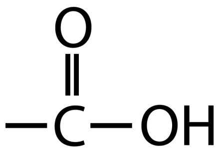
FIGURE 25.6
1737 table centerpiece with containers for sugar and oil or vinegar.

What can you do with vinegar?

Vinegar (dilute acetic acid) is available in every grocery store in the country. The large one-gallon jugs can be found in households everywhere. One magazine published an article listing 150 ways to use vinegar, from cleaning dirt off your computer to cleaning window blinds. A mixture of vinegar and baking soda is an excellent way to clean sink drains. You can also clean your carpets and your piano keys. Not bad for something that you thought of only for putting on food.

Carboxylic Acids

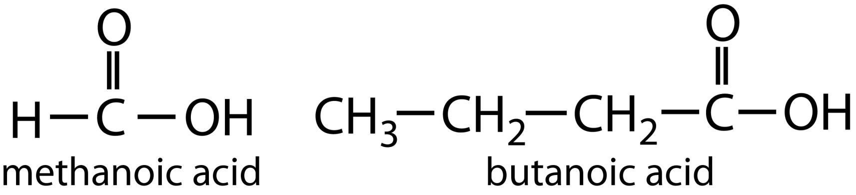
Organic acids such as acetic acid all contain a functional group called a **carboxyl group**.



$$-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

(Carboxyl Group)

The carboxyl group contains the C=O of the carbonyl group, with the carbon atom also being bonded to a hydroxyl (−OH) group. A **carboxylic acid** is an organic compound that contains the carboxyl functional group. The general formula for a carboxylic acid can be abbreviated as –COOH. The carbon atom of the carboxyl group may be attached to a hydrogen atom or to a carbon chain. The naming of a carboxylic acid is as follows: Name the parent compound by finding the longest continuous chain that contains the carboxyl group. Change the *–e* at the end of the name of the alkane to *–oic acid*.



Properties of Carboxylic Acids

Carboxylic acids are all weak acids. In aqueous solution, the O−H bond of the hydroxyl group can break, yielding a negative carboxylate ion and the hydrogen ion.

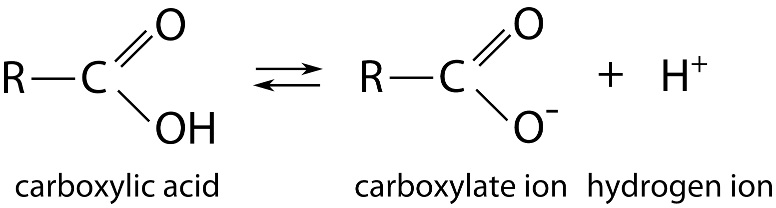


FIGURE 25.7

Equilibrium between carboxyl group and carboxylate anion.

The smaller members of the aliphatic carboxylic acid series are colorless, volatile liquids with strong odors. Ethanoic acid is commonly known as acetic acid and common household vinegar is a 5% solution of acetic acid. Larger carboxylic acids are solids with low melting points. There are a great many aromatic carboxylic acids, which are all crystalline solids. Carboxylic acids can form intermolecular hydrogen bonds and thus have relatively high melting and boiling points compared to other organic compounds that cannot hydrogen bond. Carboxylic acids with shorter carbon chains are very soluble in water, while those with longer carbon chains are less soluble.

Many carboxylic acids occur naturally in plants and animals. Citrus fruits such as oranges and lemons contain citric acid.

Ethanoic and citric acids are frequently added to foods to give them a tart flavor. Benzoic, propanoic, and sorbic acids are used as food preservatives because of their ability to kill microorganisms that can lead to spoilage. Methanoic and ethanoic acids are widely used in industry as starting points for the manufacture of paints, adhesives, and coatings.

Summary

- The structure and nomenclature of carboxylic acids are given.
- Physical properties are carboxylic acids are listed.

Practice

Do problems 2, 6, 9, 11, 14, 15, 16, 18, 19, and 20 at the link below:

http://www.docbrown.info/page06/RCOOHderivs/RCOOHderivsQmc.htm

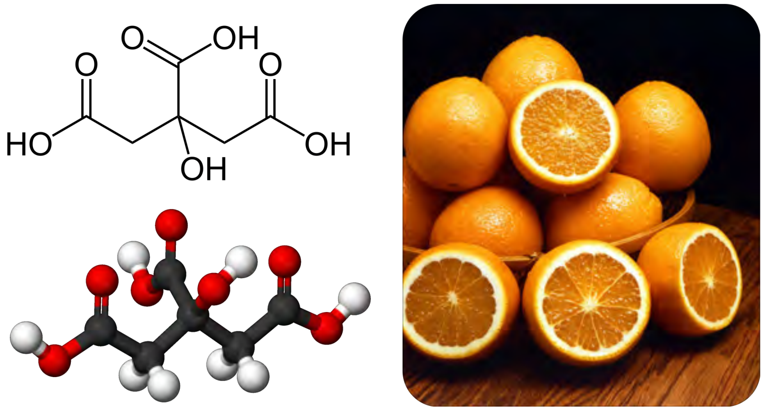


FIGURE 25.8

Citric acid is a large carboxylic acid with three ionizable hydrogen atoms. It is found in citrus fruits and gives them their sour or tart flavor.

Review

1. What is a carboxyl group?
2. Can carboxyl groups form hydrogen bonds?
3. Do carboxylic acids ionize?

- **carboxyl group:** Contains the C=O of the carbonyl group, with the carbon atom also being bonded to a hydroxyl (−OH) group.
- **carboxylic acid:** An organic compound that contains the carboxyl functional group.

25.13 Esters

- Give the generic structure for an ester.
- Describe the rules for naming esters.
- List uses for esters.

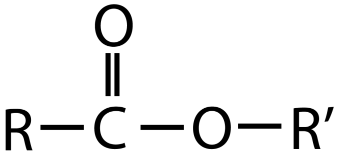
FIGURE 25.9
An ancient perfume flask dating from around 580-550 B.C.

What is that smell?

Perfumes contain ingredients from a number of sources. Musk is obtained from animals, but the vast majority of perfume components are obtained from plants. Approximately 2,000 plant species have been used as sources for perfume materials. The needed chemicals are extracted using solvent extraction or distillation. The oils are diluted with ethanol to varying degrees, depending on the price of the finished product – the less ethanol present (meaning there is a higher percentage of the active odor ingredients), the more expensive the perfume.

Esters

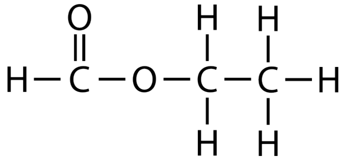
An **ester** is an organic compound that is a derivative of a carboxylic acid in which the hydrogen atom of the hydroxyl group has been replaced with an alkyl group. The structure is the product of a carboxylic acid (the R-portion) and an alcohol (the R'-portion). The general formula for an ester is shown below.



$$R-\overset{\displaystyle O}{\overset{\|}{C}}-O-R'$$

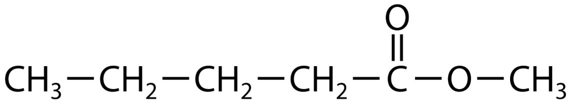
The R group can either be a hydrogen atom or a carbon chain. The R' group must be a carbon chain since a hydrogen atom would make the molecule a carboxylic acid. The steps for naming esters along with two examples are shown below.

1. Identify and name the alkyl group (R') that has replaced the hydrogen of the hydroxyl group. This is the first part of the ester name.
2. Name the carboxylic acid portion of the molecule (R-COO), but change the ending of the name from *–oic acid* to *–oate*. This is the second part of the ester name.
3. Leave a space between the alkyl group name and the name of the carboxylic acid derivative.



$$\mathrm{H-\overset{\overset{O}{\|}}{C}-O-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-H}$$

ethyl methanoate

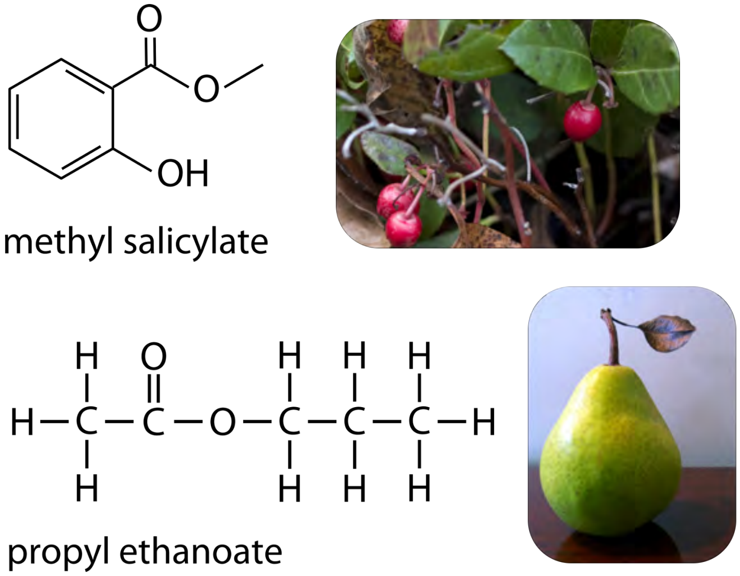


$$\mathrm{CH_3-CH_2-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-O-CH_3}$$

methyl pentanoate

Esters have lower boiling points than the carboxylic acids from which they were derived because they cannot form hydrogen bonds with each other. This is because there are no hydrogen atoms bonded to oxygen atoms, as in the acid. Esters with shorter carbon chains are soluble in water, while those with longer chains are less soluble.

Esters are very commonly found in plants and are responsible for many distinctive odors and flavors. For example, methyl salicylate has the odor and flavor of oil of wintergreen, while propyl ethanoate has that of a pear.



methyl salicylate

propyl ethanoate

FIGURE 25.10

Ester examples.

Summary

- The structure and nomenclature of esters are given.
- Uses for esters are listed.

Practice

Read the material at the link below and answer the following questions:

http://personal.ashland.edu/ bmohney/ket_scholars/esters.html

1. Which ester smells like bananas?
2. What type of ester is found in poisonous secretions of termites?
3. Name two esters that have local anesthetic properties.

Review

1. What two types of molecules form the ester?
2. Do esters boil at lower or higher temperatures than the carboxylic acids they came from?
3. What does propyl ethanoate smell like?

- **ester:** An organic compound that is a derivative of a carboxylic acid in which the hydrogen atom of the hydroxyl group has been replaced with an alkyl group.

25.14 Amines

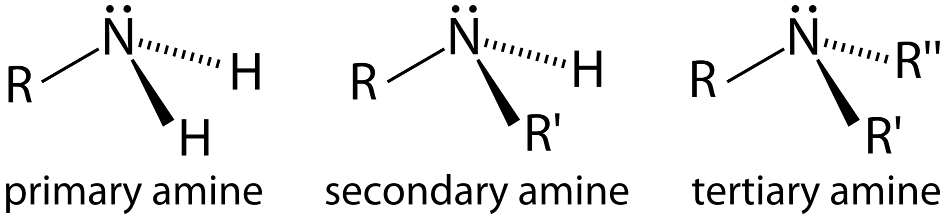
- Describe the structure and naming of amines.
- List the properties of amines.
- Describe uses for amines.

Sunshine and sleep

What does sunshine have to do with sleep (other than the sun shining in your eyes and waking you up)? For many people, their problems in sleeping have to do with an amine that the brain makes called melatonin. This compound affects the sleep-wake cycle and is affected by sunlight. During the winter, the daily cycle of melatonin production may be affected by the shorter time the sun is up. If this cycle is changed, the person may have trouble sleeping. Melatonin supplements are available in pharmacies and health food stores and may be of help for those with sleeping problems.

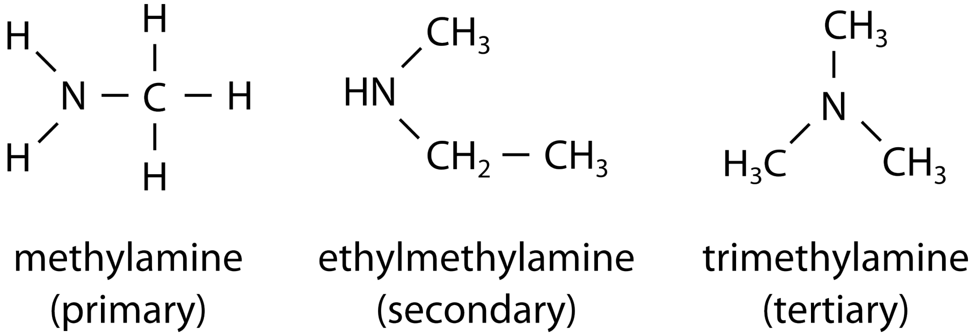
Amines

An **amine** is an organic compound that can be considered to be a derivative of ammonia (NH_3). The general structure of an amine can be abbreviated as $R-NH_2$, where R is a carbon chain. However, similar to alcohols, amines can be primary, secondary, or tertiary.



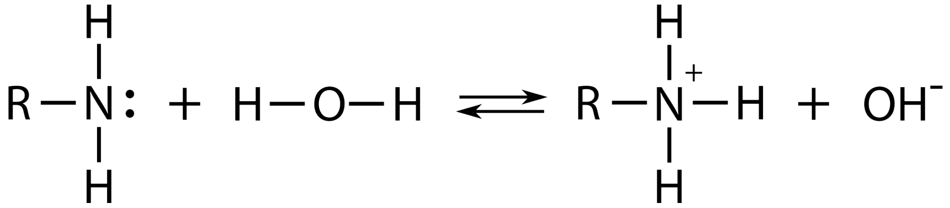
The nitrogen atom of a primary amine is bonded to two hydrogen atoms and one carbon. The nitrogen atom of a secondary amine is bonded to one hydrogen and two carbons. The nitrogen atom of a tertiary amine is bonded to three carbon atoms. Amines are typically named by a common system rather than by IUPAC guidelines. The common system for naming amines along with several examples is shown below.

1. Name the alkyl groups that are attached to the nitrogen atom of the amine. If there is more than one different alkyl group, put them in alphabetical order. If there are two or three of the same alkyl group, use the *di*− or *tri*− prefix.
2. Follow the alkyl group name with the suffix *–amine*, with no spaces.



Properties of Amines

Amines are weak bases due to the presence of a lone pair of electrons on the nitrogen atom. This lone pair can attract the hydrogen atom from a water molecule, causing the bond between it and the oxygen atom to break. The resultant products are the conjugate acid of the amine and the hydroxide ion.



Amines are capable of hydrogen bonding though their boiling points are generally a bit lower than the corresponding alcohol. Methylamine and ethylamine are gases at room temperature, while larger amines are liquids. As with other organic compounds that hydrogen bond, water solubility is reflected in the length of the carbon chains. Smaller amines are soluble, while larger ones are less soluble.

Amines generally have rather pungent or noxious odors. Ammonia can be considered the simplest amine and is very distinctive. Methylamine has an unpleasant odor associated with dead fish. Amines are often formed biologically during the breakdown of proteins in animal cells, and so many have the smell of death and decay. Putrescine and cadaverine are two such amines and are aptly named for their foul odors. The toxins which many animals use as a form of defense are frequently amines. Amines are used industrially as dyes and in many drugs.

Summary

- The structure and nomenclature for amines are described.
- Physical properties of amines are listed.
- Common amines are listed and described.

Practice

Read the material at the link below and answer the first three questions. If you are feeling adventurous, try drawing some of the requested structures:

http://dl.clackamas.cc.or.us/ch106-05/nomencla.htm

Review

1. What is an amine?
2. How many carbon groups are attached to the nitrogen of a secondary amine?
3. Describe the odor of most amines.

- **amine:** An organic compound that can be considered to be a derivative of ammonia (NH_3).

25.15 Substitution Reactions

- Define substitution reaction.
- Give examples of substitution reactions.

Just breathe deeply

Organic compounds can be used for a wide variety of applications. One such compound is halothane, an alkyl halide. This material is used as a general anesthetic for surgical procedures. When it was first developed in 1956, it was very popular, but has had limited use more recently because of toxicity issues, especially liver damage. Halothane is now used mainly as an anesthetic for children since the risk of harm is much less in these patients.

Substitution Reactions

A **substitution reaction** is a reaction in which one or more atoms replace another atom or group of atoms in a molecule. Alkyl halides are formed by the substitution of a halogen atom for a hydrogen atom. When methane reacts with chlorine gas, ultraviolet light can act as a catalyst for the reaction.

$$CH_4(g)+Cl_2(g)\xrightarrow{\text{UV light}}CH_3Cl(g)+HCl(g)$$

The reaction produces chloromethane and hydrogen chloride. When the mixture is allowed to react for longer periods of time further substitution reactions may occur.

$$CH_3Cl(g)+Cl_2(g)\xrightarrow{\text{UV light}}CH_2Cl_2(g)+HCl(g)$$

The product above is dichloromethane. Further substitution produces trichloromethane and tetrachloromethane, commonly called carbon tetrachloride. A mixture of products occurs in the reaction, with the relative amounts dependent upon the time that the reaction is allowed to proceed. Chlorofluorocarbons are produced by reacting chloroalkanes with HF because the fluorine atom bonds preferentially to the carbon.

$$\mathrm{CCl_4}(g)+\mathrm{HF}(g)\xrightarrow{\mathrm{SbF_5}}\mathrm{CCl_3F}(g)+\mathrm{HCl}(g)$$

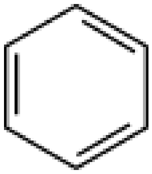
The fluorine atom substitutes for a chlorine atom in the reaction.

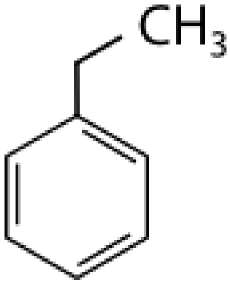
Benzene is a fairly stable and unreactive molecule due to the electron delocalization around the six-membered ring. The treatment of benzene with a halogen in the presence of an iron catalyst causes the substitution of a halogen atom for a hydrogen atom. The resulting molecule is called an aryl halide.

$$\mathrm{C_6H_6}(l)+\mathrm{Br_2}(l)\xrightarrow{\mathrm{FeBr_3}}\mathrm{C_6H_5Br}(l)+\mathrm{HBr}(g)$$

Alkyl groups can be introduced onto a benzene ring by the reaction of benzene with an alkyl halide, using aluminum chloride as the catalyst. In the reaction below, benzene reacts with chloroethane to produce ethylbenzene.

$$\mathrm{C_6H_6}(l)+\mathrm{CH_3CH_2Cl}(g)\xrightarrow{\mathrm{AlCl_3}}\mathrm{C_6H_5CH_2CH_3}(l)+\mathrm{HCl}(g)$$





The reaction of an alkyl halide with an inorganic hydroxide base at elevated temperature produces an alcohol. The molecular reaction to produce methanol from iodomethane and sodium hydroxide is shown below.

$$\mathrm{CH_3I}(l)+\mathrm{NaOH}(aq)\xrightarrow{100^\circ\mathrm{C}}\mathrm{CH_3OH}(l)+\mathrm{NaI}(aq)$$

Summary

- Substitution reaction is defined.
- Examples of substitution reactions are given.

Practice

Check out the substitution reaction possibilities at the link below. Look for reactants and products described in this concept. See what you can predict:

http://www.stolaf.edu/depts/chemistry/courses/toolkits/247/practice/medialib/data/

Review

1. What is common to all the reactions shown above?
2. Name the product of the reaction between ethane and chlorine gas.
3. What would you use to react with benzene if you wanted to make propylbenzene?

- **substitution reaction:** A reaction in which one or more atoms replace another atom or group of atoms in a molecule.

25.16 Addition Reactions

- Define addition reaction.
- Give examples of addition reactions.

What is this yellow stuff?

There is big debate these days about using butter or margarine on your toast (or pancakes or ...). Margarine is less expensive than butter and is lower in fat and cholesterol. Margarine is made from animal or vegetable fats using hydrogenation to reduce the double bonds in the fatty acids, Hydrogen gas is bubbled through the liquid oil and reacts with the carbon-carbon double bonds present in the long-chain fatty acids. The product is less likely to spoil than butter.

Addition Reactions

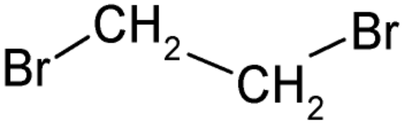
An **addition reaction** is a reaction in which an atom or molecule is added to an unsaturated molecule, making a single product. An addition reaction can be thought of as adding a molecule across the double or triple bond of an alkene or alkyne. Addition reactions are useful ways to introduce a new functional group into an organic molecule.

One type of addition is called hydrogenation. **Hydrogenation** is a reaction that occurs when molecular hydrogen is added to an alkene to produce an alkane. The reaction is typically performed with the use of a platinum catalyst. Ethene reacts with hydrogen to form ethane.

$$\mathrm{CH_2{=}CH_2}(g) + \mathrm{H_2}(g) \xrightarrow{\mathrm{Pt}} \mathrm{CH_3CH_3}(g)$$

Alkyl halides can be produced from an alkene by the addition of either the elemental halogen or the hydrogen halide. When the reactant is the halogen, the product is a disubstituted alkyl halide as in the addition of bromine to ethene.

$$\mathrm{CH_2{=}CH_2}(g) + \mathrm{Br_2}(l) \rightarrow \underset{\text{1,2-dibromoethane}}{\mathrm{CH_2BrCH_2Br}(g)}$$



The addition of bromine to an unknown organic compound is indeed a test for saturation in the compound. Bromine has a distinctive brownish-orange color, while most bromoalkanes are colorless. When bromine is slowly added to the compound, the orange color will fade if it undergoes the addition reaction to the hydrocarbon. If the orange color remains, then the original compound was already saturated and no reaction occurred.

A monosubstituted alkyl halide can be produced by the addition of a hydrogen halide to an alkene. Shown below is the formation of chloroethane.

$$\mathrm{CH_2{=}CH_2}(g) + \mathrm{HCl}(g) \rightarrow \mathrm{CH_3CH_2Cl}(g)$$

A **hydration reaction** is a reaction in which water is added to an alkene. Hydration reactions can take place when the alkene and water are heated to near 100°C in the presence of a strong acid, which acts as a catalyst. Shown below is the hydration of ethene to produce ethanol.

$$\mathrm{CH_2{=}CH_2} + \mathrm{H_2O} \rightarrow \mathrm{CH_3CH_2OH}$$

Under modest reaction conditions, benzene resists addition reactions because to add across a double bond in a benzene ring is to disrupt the ring of delocalized electrons. This greatly destabilizes the molecule. However, under conditions of high temperature and pressure, and with an appropriate catalyst, benzene will slowly react with three molecules of hydrogen to produce cyclohexane.

$$\mathrm{C_6H_6} + 3\mathrm{H_2} \xrightarrow{\mathrm{Pt}} \mathrm{C_6H_{12}}$$

Summary

- Addition reaction is defined.
- Examples of addition reactions are given.

Practice

Draw structures of the products of the reactions in the “It is a helpful exercise to predict...” box partway down the page.

Review

1. What type of compound is needed for an addition reaction?
2. Name the compound formed in the reaction of $CH_3CH_2CH=CH_2$ and HCl.
3. What is the product of a hydration reaction?

- **addition reaction:** A reaction in which an atom or molecule is added to an unsaturated molecule, making a single product.
- **hydration reaction:** A reaction in which water is added to an alkene.
- **hydrogenation:** A reaction that occurs when molecular hydrogen is added to an alkene to produce an alkane.

25.17 Oxidation Reactions

- Define organic oxidation reaction.
- Give examples of organic oxidation reactions.

Keeping food safe

Benzoic acid crystals in polarized light are pictured above. Benzoic acid is widely used as a food preservative, either as the carboxylic acid or as the sodium benzoate salt. This compound is most effective when added to acidic foods such as fruit juices and soft drinks. The major industrial source of benzoic acid is the partial oxidation of toluene with oxygen. The process is inexpensive and environmentally benign.

Oxidation Reactions

Oxidation can be defined as the addition of oxygen to a molecule or the removal of hydrogen. When an alkane is heated in the presence of an appropriate catalyst, it can be oxidized to the corresponding alkene in a reaction called a dehydrogenation reaction. Two hydrogen atoms are removed in the process. The alkene can be further oxidized to an alkyne by the removal of two more hydrogen atoms.

$$\text{oxidation} \qquad CH_3CH_3 \xrightarrow{-H_2} CH_2{=}CH_2 \xrightarrow{-H_2} CH{\equiv}CH$$

The reactions are reversible, and so an alkyne can be reduced first to an alkene and then to an alkane.

$$\text{reduction} \qquad CH{\equiv}CH \xrightarrow{+H_2} CH_2{=}CH_2 \xrightarrow{+H_2} CH_3CH_3$$

So the alkane is the most reduced form of a hydrocarbon, while the alkyne is the most oxidized form.

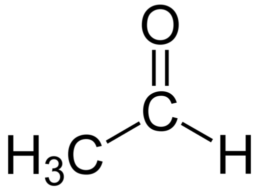
Oxidation reactions in organic chemistry often involve the addition of oxygen to a compound, which changes the particular functional group of that compound. The following sequence shows how methane can be oxidized first to methanol, then to methanal, then to methanoic acid, and finally to carbon dioxide.

$$\underset{\text{methane}}{CH_4} \xrightarrow{\text{gain of oxygen}} \underset{\text{methanol}}{CH_3OH} \xrightarrow{\text{loss of hydrogen}} \underset{\text{methanal}}{CH_2O} \xrightarrow{\text{gain of oxygen}} \underset{\text{methanoic acid}}{HCOOH} \xrightarrow{\text{loss of hydrogen}} CO_2$$

Each step in the process is either a gain of oxygen or a loss of hydrogen. Each step also releases energy, which explains why the complete combustion of alkanes to carbon dioxide is an extremely exothermic reaction.

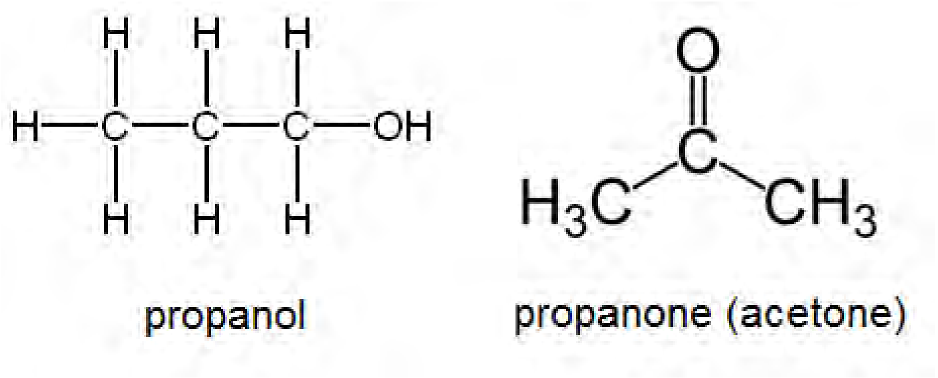
The oxidation of an alcohol can produce either an aldehyde or a ketone. Ethanol can be oxidized in the laboratory by slight warming combined with the addition of an oxidizing agent such as dichromate ion, which catalyzes the reaction in acidic solution. The reaction produces the aldehyde ethanal (acetaldehyde).

$$CH_3CH_2OH \xrightarrow[H^+]{Cr_2O_7^{2-}} CH_3CHO$$



When the alcohol to be oxidized is a secondary alcohol, the oxidation product is a ketone rather than an aldehyde. The oxidation of the simplest secondary alcohol, 2-propanol, yields propanone.

$$CH_3CHOHCH_3 \xrightarrow[H^+]{Cr_2O_7^{2-}} CH_3COCH_3$$



Tertiary alcohols cannot be oxidized in this way because the carbon to which the hydroxyl group is attached does not have another hydrogen atom attached to it.

When a primary alcohol is oxidized to an aldehyde, the reaction is difficult to stop because the aldehyde is easily oxidized further to the corresponding carboxylic acid. The oxidation of ethanal produces ethanoic (acetic) acid.

$$CH_3CHO \xrightarrow[H^+]{Cr_2O_7^{2-}} CH_3COOH$$

Ethanol-containing beverages such as wine are susceptible to such oxidation if kept for long periods of time after having been opened and exposed to the air. Wine that has become oxidized will have an unpleasant vinegary taste due to the production of acetic acid.

Unlike aldehydes, ketones are resistant to further oxidation because the carbonyl group is in the middle of the carbon chain and so the ketone cannot be converted to a carboxylic acid.

Summary

- Oxidation reactions are described.
- Examples of oxidation reactions are given.

Practice

Read the material at the link below and answer the following questions:

http://www.chemguide.co.uk/organicprops/alcohols/oxidation.html

1. What happens to a primary alcohol that is completely oxidized?
2. How can you get an aldehyde from a primary alcohol?
3. What would you use to convert a secondary alcohol to a ketone?

Review

1. What is the product of oxidation of a primary alcohol?
2. What type of compound gives a ketone when oxidized?
3. What will produce acetic acid when completely oxidized?

25.18 Condensation Reactions

- Define condensation reaction.
- Give examples of condensation reactions.

A new way to lubricate machinery

Vegetable oils are being explored for a variety of uses that could replace petroleum products. One such application is in the field of lubricants. Every moving part (such as engine pistons) needs lubrication to decrease friction and prolong the life of the equipment. Petroleum products serve this purpose now, but are not good for the environment. New techniques for making specialized esters from vegetable oil are being explored that will make the compounds more stable and more useful as lubricants.

Condensation Reactions

A **condensation reaction** is a reaction in which two molecules combine to form a single molecule. A small molecule, often water, is usually removed during a condensation reaction. Amino acids are important biological molecules that have an amine functional group on one end of the molecule and a carboxylic acid functional group on the other end. When two amino acids combine in a condensation reaction, a covalent bond forms between the amine nitrogen of one amino acid and the carboxyl carbon of the second amino acid. A molecule of water is the removed as a second product.

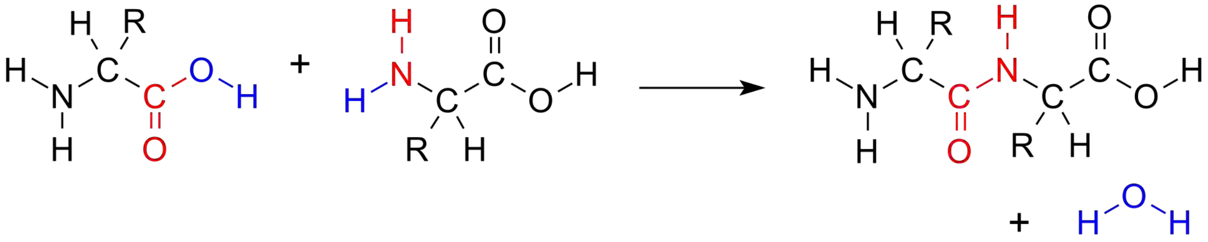


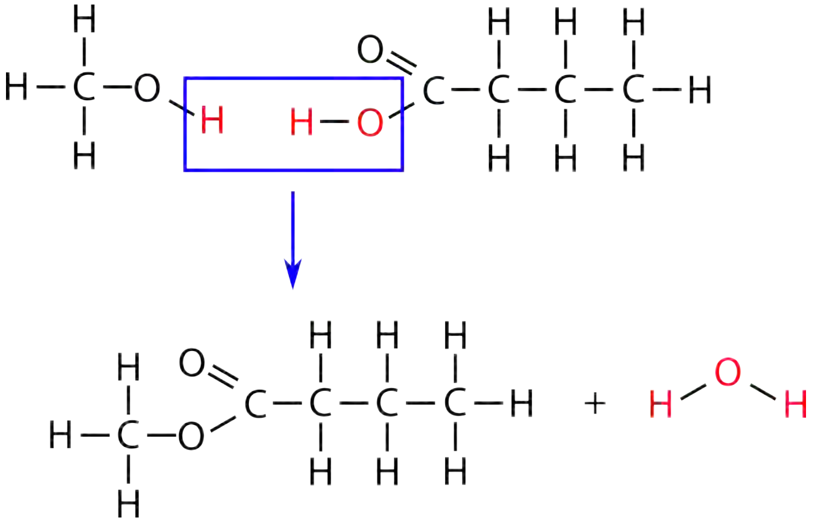
FIGURE 25.11

Amino acids join together to form a molecule called a dipeptide. The –OH from the carboxyl group of one amino acid combines with a hydrogen atom from the amino group of the other amino acid to produce water (blue).

This reaction forms a molecule called a dipeptide and the carbon-nitrogen covalent bond is called a peptide bond. When repeated numerous times, a length molecule called a protein is eventually produced.

Esterification

An **esterification** is a condensation reaction in which an ester is formed from an alcohol and a carboxylic acid. Esterification is a subcategory of condensation reactions because a water molecule is produced in the reaction. The reaction is catalyzed by a strong acid, usually sulfuric acid. When the carboxylic acid butanoic acid is heated with an excess of methanol and a few drops of sulfuric acid, the ester methyl butanoate is produced. Methyl butanoate has the scent of pineapples. The reaction is shown below with both molecular and structural formulas.



The esterification reaction is reversible. When an ester is heated in the presence of a strong base such as sodium hydroxide, the ester breaks down. The products are an alcohol and the conjugate base of the carboxylic acid as a salt.

$$\underset{\text{ethyl ethanoate}}{CH_3COOCH_2CH_3} + NaOH \rightarrow \underset{\text{sodium acetate}}{CH_3COO^-Na^+} + \underset{\text{ethanol}}{CH_3CH_2OH}$$

The sodium hydroxide is not acting as a catalyst, but is consumed in the reaction.

Saponification describes the alkaline hydrolysis reaction of an ester. The term saponification originally described the hydrolysis of long-chain esters called fatty acid esters to produce soap molecules, which are the salts of fatty acids. One such soap molecule is sodium stearate, formed from the hydrolysis of ethyl stearate.

$$\underset{\text{ethyl stearate}}{C_{17}H_{35}COOC_2H_5} + NaOH \rightarrow \underset{\text{sodium stearate (soap)}}{C_{17}H_{35}COO^-Na^+} + C_2H_5OH$$

Summary

- Condensation reaction is defined and an example is given.
- Esterification reaction is defined and an example is given.

Practice

Read the material at the link below and answer the following questions:

http://www.chemguide.co.uk/organicprops/esters/preparation.html

1. What is the catalyst for the ester synthesis reaction using a carboxylic acid and an alcohol?
2. How can you get more ester and keep the reverse reaction from occurring?
3. What other compounds could you react with alcohols acids to form esters?

Review

1. What is a condensation reaction?
2. What are the starting materials for an esterification reaction?
3. How can an ester be saponified?

- **condensation reaction:** A reaction in which two molecules combine to form a single molecule.
- **esterification:** A reaction in which an ester is formed from an alcohol and a carboxylic acid.
- **saponification:** The alkaline hydrolysis reaction of an ester.

25.19 Polymerization – Addition Polymers

- Define polymer.
- Define addition polymer.
- Write reactions for the synthesis of addition polymers.
- Give examples of addition polymers.

Will it ever go away?

We enjoy the benefits of Styrofoam® containers, but don't often think about where they end up. These materials do not break down quickly under exposure to the elements. When buried in a landfill, it will be with us for a long time. The good news is that there is not a lot of this pollutant found in landfills (maybe about 0.5% by weight) of the total mass of garbage. There is no good way to recycle Styrofoam® at present, but someday a creative scientist may come up with one.

Polymerization – Addition Polymers

Polymers are very different from the other kinds of organic molecules that you have seen so far. Whereas other compounds are of relatively low molar mass, polymers are giant molecules of very high molar mass. Polymers are the primary components of all sorts of plastics and related compounds. A **polymer** is a large molecule formed of many smaller molecules covalently bonded in a repeating pattern. The small molecules which make up the polymer are called **monomers**. Polymers generally form either from an addition reaction or a condensation reaction.

Addition Polymers

An **addition polymer** is a polymer formed by chain addition reactions between monomers that contain a double bond. Molecules of ethene can polymerize with each other under the right conditions to form the polymer called polyethylene.

$$n\,CH_2{=}CH_2 \rightarrow (CH_2\text{-}CH_2)_n$$

The letter *n* stands for the number of monomers that are joined in repeated fashion to make the polymer and can have a value in the hundreds or even thousands.

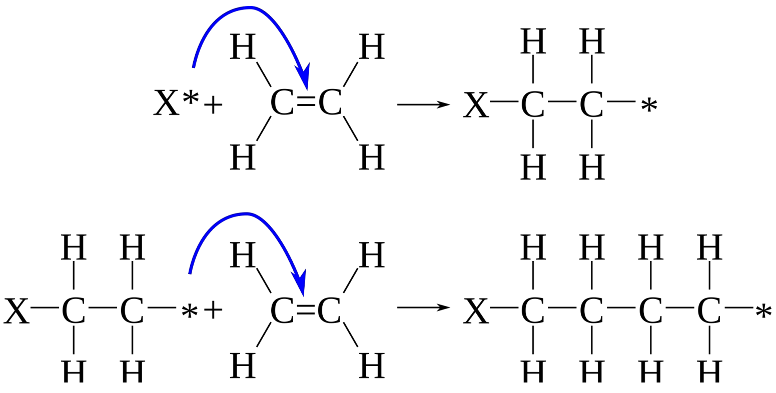


FIGURE 25.12

Polyethylene synthesis.

The reactions above show the basic steps to form an addition polymer:

1. Initiation - a free radical initiator (X^*) attacks the carbon-carbon double bond (first step above). The initiator can be something like hydrogen peroxide. This material can easily split to form two species with a free electron attached to each: H-O-O-H → 2 H-O•. This free radical attacks a carbon-carbon double bond. One of the pi electrons forms a single bond with the initiator while the other pi electron forms a new free radical on the carbon atom.
2. Propagation - the new free radical compound interacts with another alkene, continuing the process of chain growth (second step above).
3. Termination occurs whenever two free radicals come in contact with one another (not shown). The two free electrons form a covalent bond and the free radical on each molecule no longer exists.

Polyethylene can have different properties depending on the length of the polymer chains and on how efficiently they pack together. Some common products made from different forms of polyethylene include plastic bottles, plastic bags, and harder plastic objects such as milk crates.

Several other kinds of unsaturated monomers can be polymerized and find use in common household products. Polypropylene is stiffer than polyethylene and finds use as plastic utensils and some other kinds of containers.

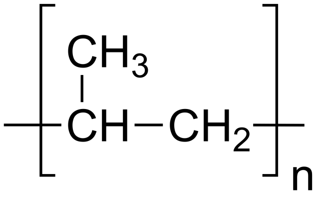


FIGURE 25.13

Polypropylene structure.

Polystyrene is used in insulation and in molded items such as coffee cups.

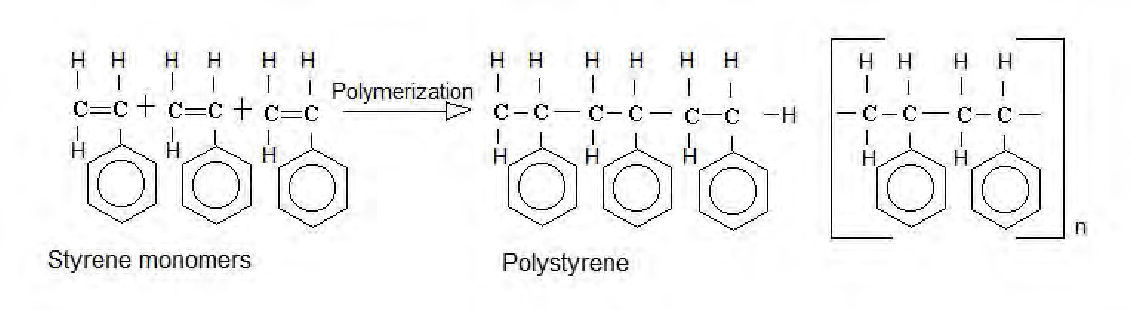


FIGURE 25.14

Polystyrene synthesis and structure

Polyvinyl chloride (PVC) is extensively used for plumbing pipes.

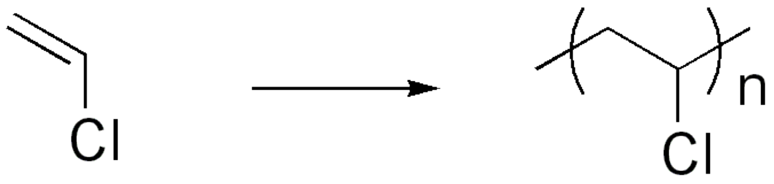
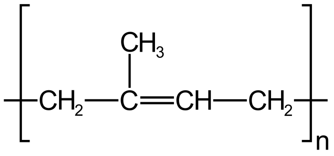


FIGURE 25.15

Polyvinyl chloride

Polyisoprene is a polymer of isoprene and is better known as rubber. It is produced naturally by rubber trees, but several variants have been developed which demonstrate improvements on the properties of natural rubber.



$$\left[-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-\right]_n$$

FIGURE 25.16

Polyisoprene

Summary

- Polymer is defined.
- Addition polymer is defined and the general synthesis of an addition polymer is shown.
- Examples of addition polymers are listed.

Practice

Read the material at the link below and answer the following questions:

http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/polymers.htm

1. Who won the 1953 Nobel Prize in Chemistry for his work with polymers?
2. What is the molecular weight range for polyethylene?
3. What is the monomer for Teflon?

Review

1. What is an addition polymer?
2. What is the first step in the synthesis of a polymer?
3. What is the final step in the synthesis of a polymer?

- **addition polymer:** A polymer formed by chain addition reactions between monomers that contain a double bond.
- **monomer:** The small molecules which make up the polymer.
- **polymer:** A large molecule formed of many smaller molecules covalently bonded in a repeating pattern.

25.20 Polymerization – Condensation Polymers

- Define condensation polymer.
- Describe condensation polymer reactions.
- List typical condensation polymers.

A different sound and feel

Animal gut and silk were used for all guitar strings for centuries until modern technology and changes in musical taste brought about significant changes. There are two major types of guitar strings in use today. Steel strings (first developed around 1900) are found on acoustic and electric guitars. They have a bright, crisp sound that lends itself well to such diverse music as jazz, rock and roll, and bluegrass. Nylon strings are a more recent development. During World War II, the silk and animal products needed for guitar strings were not available. Nylon quickly proved to be a more than adequate substitute. Now nylon strings are found on all classical guitars. Their sound is somewhat softer than the steel strings and the tone quality suits that genre of music better.

Polymerization - Condensation Polymers

A **condensation polymer** is a polymer formed by condensation reactions. Monomers of condensation polymers must contain two functional groups so that each monomer can link up with two other monomers. One type of a condensation polymer is called a polyamide. An amide is characterized by the functional group shown below wherein the carbon of a carbonyl group is bonded to the nitrogen of an amine.

One pair of monomers that can form a polyamide is adipic acid and hexanediamine. Adipic acid is a carboxylic acid with two carboxyl groups on either end of the molecule. Hexanediamine has amino groups on either end of

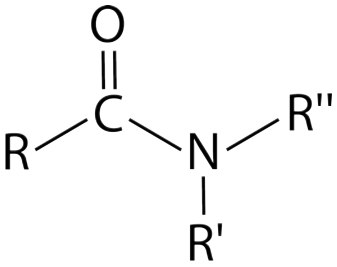


FIGURE 25.17
Amide

a six-carbon chain. When these molecules react with each other, a molecule of water is eliminated, making it a condensation reaction (**Figure** 25.18).

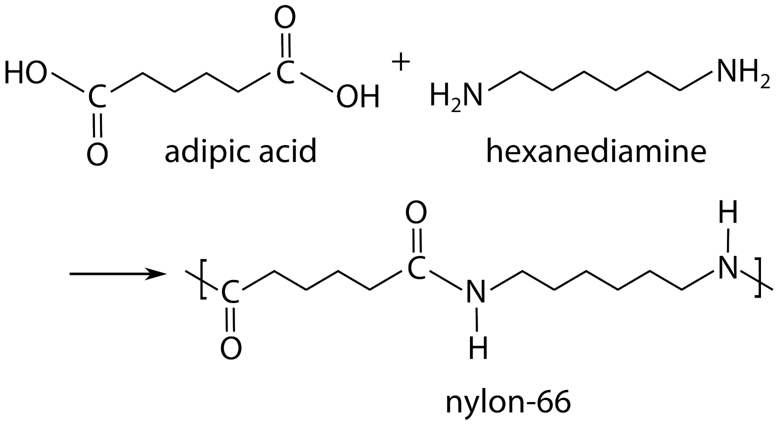
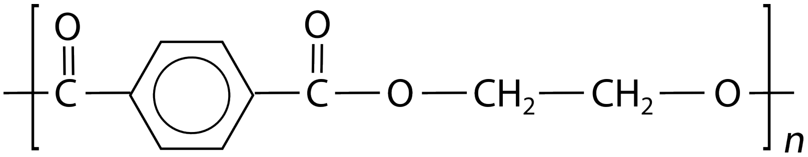


FIGURE 25.18
Nylon synthesis

The polymer that results from the repetition of the condensation reaction is a polyamide called nylon 66. Nylon 66 was first invented in 1935 and has been used for all sorts of products. It and other polyamides are commonly found in fibers and clothing, fishing line, and carpeting among many applications (**Figure** 25.19).

FIGURE 25.19
Nylon spatula.

Polyester is another common type of condensation polymer. Recall that esters are formed from the reaction of an alcohol with a carboxylic acid. When both the acid and alcohol have two functional groups, the ester is capable of being polymerized. One such polyester is called polyethylene terephthalate (PET) and is formed from the reaction of ethylene glycol with terephthalic acid. The structure of PET is shown below.



PET is used in tires, photographic film, food packaging, and clothing. Polyester fabric is used in permanent-press clothing. Its resistance to wrinkling comes from cross-linking of the polymer strands.

Summary

- Polymer condensation reaction is defined.
- Examples of condensation reactions are shown.
- Examples of condensation polymers are described.

Practice

Read the material at the link below and answer the following questions:

http://www.amazingwomeninhistory.com/stephanie-kwolek-inventor-kevlar/

1. Who invented Kevlar and when?
2. What started the project that led to the development of Kevlar?
3. What is a major use for Kevlar today?

Review

1. What is a condensation reaction?
2. What structural characteristics do the two monomers need to have?
3. What monomers compose nylon 66?

- **condensation polymer:** A polymer formed by condensation reactions.

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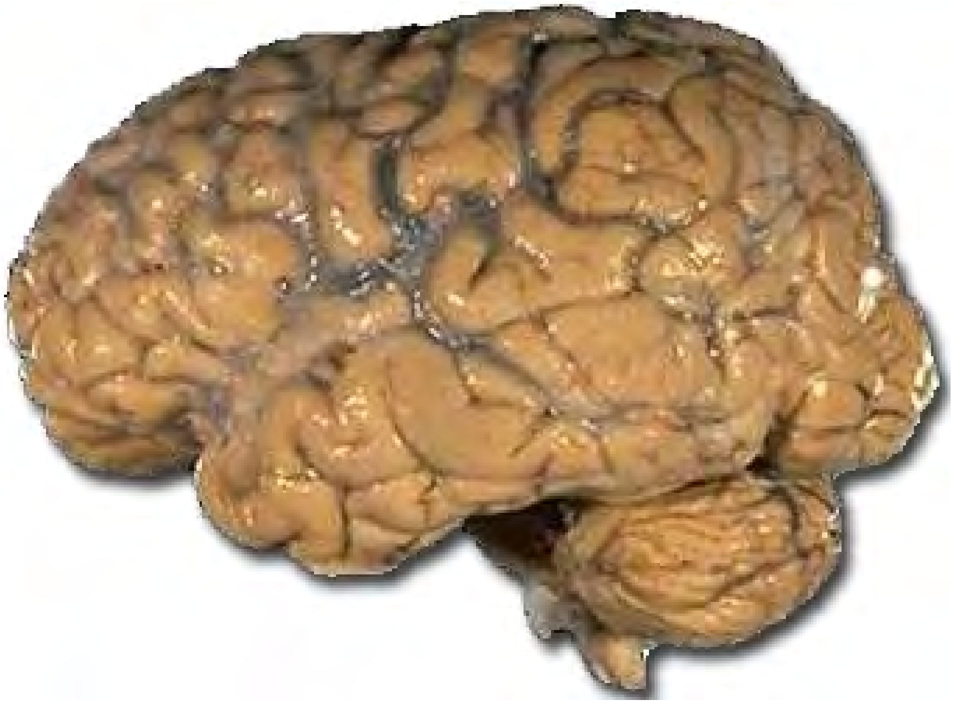
CHAPTER 26 Biochemistry

Chapter Outline

26.1 Monosaccharides

- Define carbohydrate.
- Define monosaccharide.
- Give structures for important monosaccharides.



What's on your mind?

The brain is a marvelous organ. And it's a hungry one, too. The major fuel for the brain is the carbohydrate glucose. The average adult brain represents about 2% of our body's weight, but uses 25% of the glucose in the body. Moreover, specific areas of the brain use glucose at different rates. If you are concentrating hard (taking a test, for example) certain parts of the brain need a lot of extra glucose while other parts of the brain only use their normal amount. Something to think about.

Monosaccharides

Some foods that are high in carbohydrates include bread, pasta, and potatoes. Endurance athletes often prepare for competition by consuming large amounts of carbohydrate-heavy foods to allow them to perform at a high level for long periods of time.

The term carbohydrate comes from the fact that the majority contain carbon, hydrogen, and oxygen in a ratio of 1:2:1, making for an empirical formula of CH_2O. This is somewhat misleading because the molecules are not actually hydrates of carbon at all. **Carbohydrates** are monomers and polymers of aldehydes and ketones that have multiple hydroxyl groups attached.

Carbohydrates are the most abundant source of energy found in most foods. The simplest carbohydrates are also called simple sugars and are plentiful in fruits. A **monosaccharide** is a carbohydrate consisting of one sugar unit.

FIGURE 26.1

Foods that serve as carbohydrate sources.

Common examples of simple sugars or monosaccharides are glucose and fructose. Both of these monosaccharides are referred to as hexoses since they have six carbons. Glucose is also referred to as corn sugar or grape sugar and is abundant in plants and animals. Fructose occurs in a great many fruits and is also found in honey. They are structural isomers of one another, with the difference being that glucose contains an aldehyde functional group, whereas fructose contains a ketone functional group.

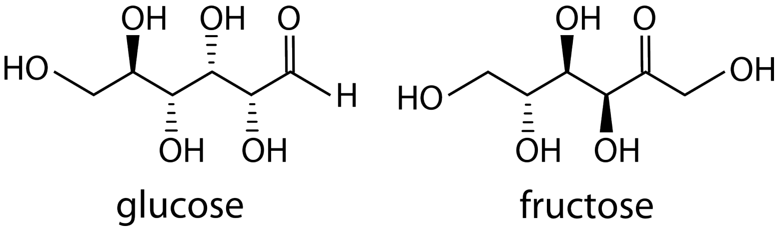


FIGURE 26.2

Glucose and fructose are monosaccharides, or simple sugars.

Glucose and fructose are both very soluble in water. In aqueous solution, the predominant forms are not the straight-chain structure shown above. Rather, they adopt a cyclic structure (see **Figure** 26.3). Glucose is a six-membered ring, while fructose is a five-membered ring. Both rings contain an oxygen atom.

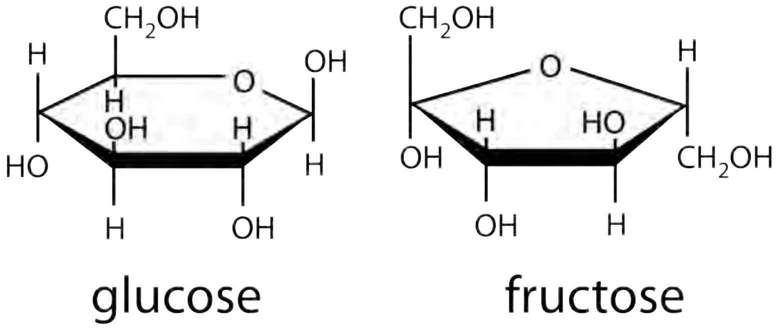


FIGURE 26.3

The cyclic form of sugars is the favored form in aqueous solution.

Another important group of monosaccharides are the pentoses, containing five carbons in the chain. Ribose and deoxyribose are two pentoses that are components of the structures of DNA and RNA.

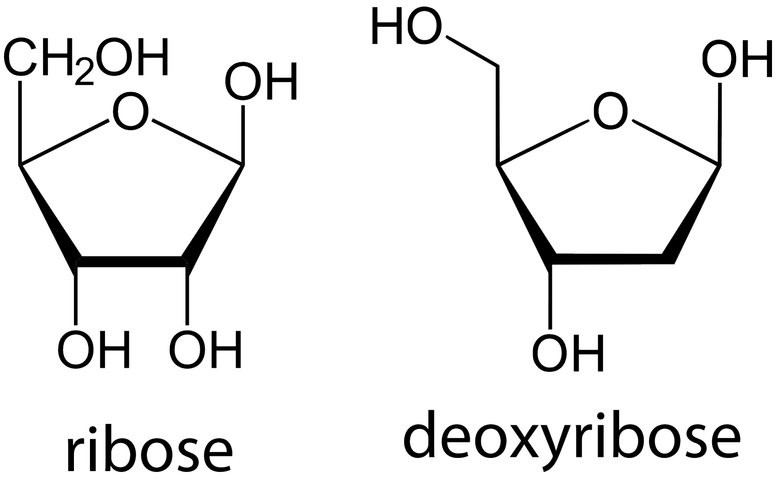


FIGURE 26.4
Ribose and deoxyribose

Summary

- Monosaccharide is defined.
- Structures of common monosaccharides are given.

Practice

Read the material at the link below and answer the following questions.

1. What is the general formula for a monosaccharide?
2. What type of monosaccharide is glucose?
3. What type of monosaccharide is fructose?

Review

1. What functional groups are on glucose?
2. What functional groups are on fructose?
3. Which form is favored in aqueous solution?

- **carbohydrates:** Monomers and polymers of aldehydes and ketones that have multiple hydroxyl groups attached.
- **monosaccharide:** A carbohydrate consisting of one sugar unit.

26.2 Disaccharides

- Define disaccharide.
- Give examples of common disaccharides.

Got milk?

Milk is one of the basic foods needed for good nutrition, especially for growing children. It contains vitamins and minerals necessary for healthy development. Unfortunately, milk also contains lactose, a carbohydrate that can make some people very ill. Lactose intolerance is a condition in which the lactose in milk cannot be digested well in the small intestine. The undigested lactose then moves into the large intestine where bacteria attack it, forming large amounts of gas. Symptoms of lactose intolerance include bloating, cramps, nausea, and vomiting. Often, the individual will outgrow this problem. Avoidance of foods containing lactose is recommended. Since children need mill, tablets can be taken that provide the needed digestive materials in the small intestine. Lactose-free milk is also readily available.

Disaccharides

The simple sugars form the foundation for more complex carbohydrates. The cyclic forms of two sugars can be linked together by means of a condensation reaction. The figure below shows how a glucose molecule and a fructose molecule combine to form a sucrose molecule. A hydrogen atom from one molecule and a hydroxyl group from the other molecule are eliminated as water, with a resulting covalent bond linking the two sugars together at that point.

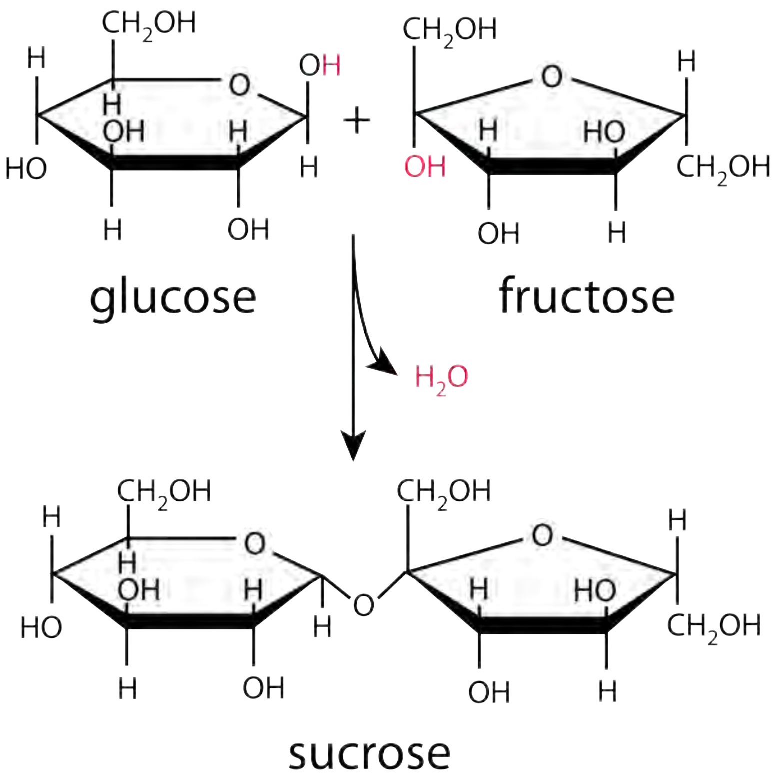


FIGURE 26.5

Glucose and fructose combine to produce the disaccharide sucrose in a condensation reaction.

Sucrose, commonly known as table sugar, is an example of a disaccharide. A **disaccharide** is a carbohydrate formed by the joining of two monosaccharides. Other common disaccharides include lactose and maltose. Lactose, a component of milk, is formed from glucose and galactose, while maltose is two glucose molecules.

During digestion, these disaccharides are hydrolyzed in the small intestine to form the component monosaccharides, which are then absorbed across the intestinal wall and into the bloodstream to be transported to the cells.

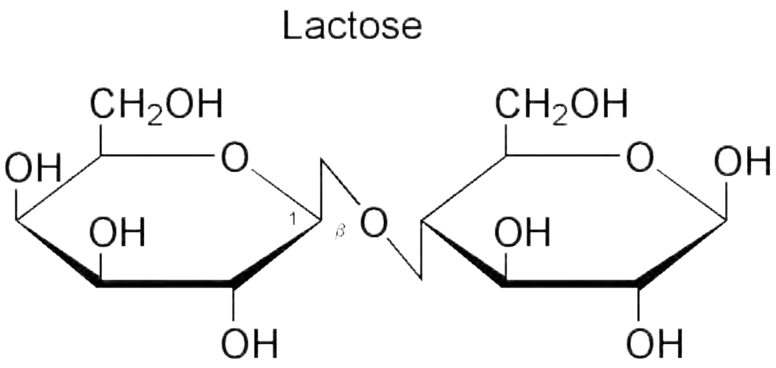


FIGURE 26.6

Lactose

Summary

- Disaccharide is defined.
- Examples of common disaccharides are given.

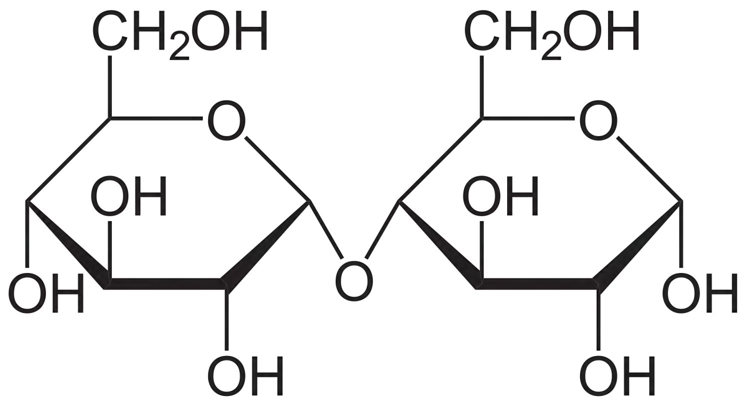


FIGURE 26.7

Maltose

Practice

Read the material at the link below and answer the following questions:

http://www.wisegeek.com/what-are-disaccharides.htm

1. What type of reaction leads to the formation of disaccharides?
2. What molecule is removed in the process?
3. What is one example of sucrose?

Review

1. What is the bridge between two monosaccharides in a disaccharide?
2. What is sucrose composed of?
3. What is lactose composed of?
4. What is maltose composed of?

- **disaccharide:** A carbohydrate formed by the joining of two monosaccharides.

26.3 Polysaccharides

- Define polysaccharide.
- List common polysaccharides and their uses.

Are we there yet?

As the weather warms up, the runners come out. Not just the casual joggers, but those really serious ones who actually enjoy running all 26.2 miles of a marathon. Prior to these races (and a lot of shorter ones), you hear a lot about carbo-loading. This practice involves eating a lot of starch in the days prior to the race. The starch is converted to glucose, which is normally used for biochemical energy. Excess glucose is stored as glycogen in liver and muscle tissue to be used when needed. If there is a lot of glycogen available, the muscles will have more biochemical energy to draw on when needed for the long run. The rest of us will just sit at the sidewalk restaurant eating our spaghetti and enjoying watching other people work hard.

Polysaccharides

Many simple sugars can combine by repeated condensation reactions until a very large molecule is formed. A **polysaccharide** is a complex carbohydrate polymer formed from the linkage of many monosaccharide monomers. One of the best known polysaccharides is starch, the main form of energy storage in plants. Starch is a staple in most human diets, with foods such as corn, potatoes, rice, and wheat having high starch content. Starch is made of glucose monomers and occurs in both straight-chain and branched forms. Amylose is the straight-chain form and consists of hundreds of linked glucose molecules. The branched form of starch is called amylopectin. In the small intestine, starch is hydrolyzed to form glucose. The glucose can then be converted to biochemical energy or stored for later use.

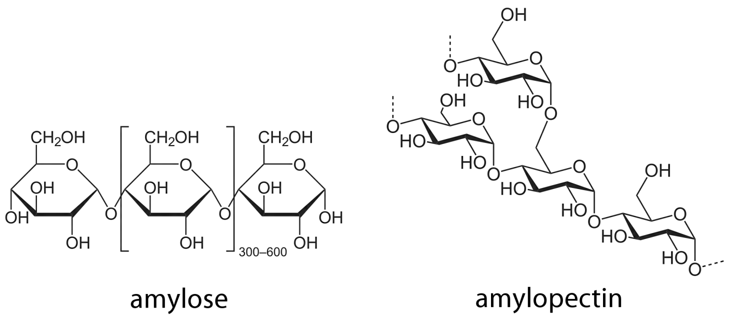


FIGURE 26.8

Amylose and amylopectin are the two most common components of naturally occurring starch. Both consist of many glucose monomers connected into a polymer. Starch serves as energy storage in plants.

Glycogen is an even more highly branched polysaccharide of glucose monomers that serves a function of energy storage in animals. Glycogen is made and stored primarily in the cells of the liver and muscles.

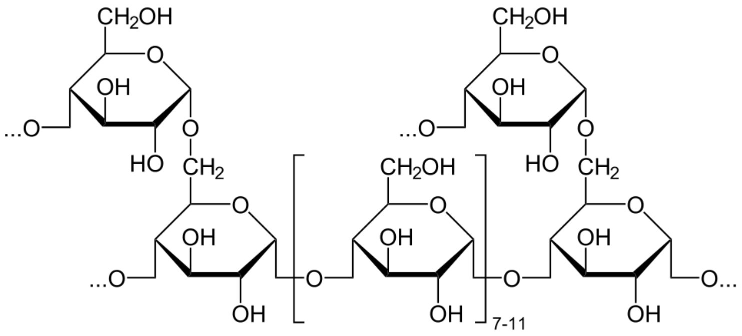


FIGURE 26.9

Glycogen is a branched polymer of glucose and stores energy in animals.

Cellulose is another polymer of glucose, consisting of anywhere from hundreds to over ten thousand monomers. It is the structural component of the cell walls of green plants and is the single most common organic molecule on Earth. Roughly 33% of all plant matter is cellulose. The linkage structure in cellulose is different than that of starch, and cellulose is indigestible except by a few microorganisms that live in the digestive tracts of cattle and termites. The figure below shows a triple strand of cellulose. There is no branching and the fibers adopt a very stiff rod-like structure with numerous hydrogen bonds between the fibers adding to its strength. Cellulose is the main component of paper, cardboard, and textiles made from cotton, linen, and other plant fibers.

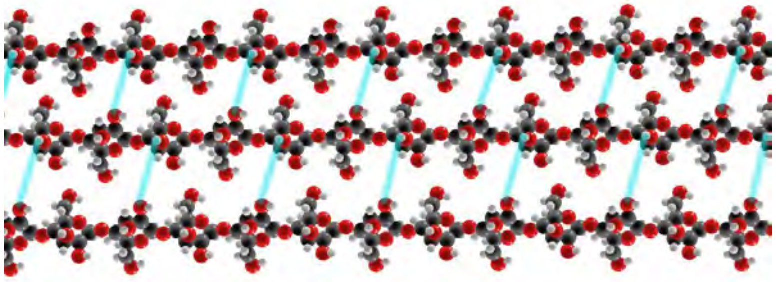


FIGURE 26.10

Cellulose is composed of very long strands of glucose monomers that are hydrogen bonded to one another. Cellulose is largely indigestible and comprises the cell walls of plants.

Summary

- Polysaccharide is defined.
- Common examples of polysaccharides are listed.

Practice

Read the material at the link below and answer the following questions:

http://www.nytimes.com/2008/11/14/science/14visuals.html

1. Do termites actually digest the wood they eat?
2. What role does the amoeba play in termite nutrition?
3. Why is understanding this process important?

Review

1. What monomer composes all the polysaccharides mentioned?
2. What is the storage form of energy for plants?
3. What is the storage form of energy for animals?

- **polysaccharide:** A complex carbohydrate polymer formed from the linkage of many monosaccharide monomers.

26.4 Amino Acids

- Define amino acid.
- Draw the generic structure for an amino acid.
- List the twenty common amino acids.

Will it really help?

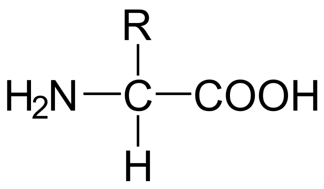
Athletics is very competitive these days at all levels, from school to the pros. Everybody is looking for that edge that will make them faster, stronger, more physically fit. One approach taken by many athletes is the use of amino acid supplements. The theory is that the increase in amino acids in the diet will lead to increased protein for muscles. However, the only real benefit comes to the people who make and sell the pills. There does not seem to be any advantage obtained by the athletes themselves. You're much better off just eating a healthy diet.

Amino Acids

An **amino acid** is a compound that contains both an amino group ($-NH_2$) and a carboxyl group ($-COOH$) in the same molecule. While any number of amino acids can possibly be imagined, biochemists generally reserve the term for a group of 20 amino acids which are formed and used by living organisms. The **Figure** 26.11 shows the general structure of an amino acid.

The amino and carboxyl groups of an amino acid are both covalently bonded to a central carbon atom. That carbon atom is also bonded to a hydrogen atom and an R group. It is this R group which varies from one amino acid to another and is called the amino acid side chain.

The nature of the side chains accounts for the variability in physical and chemical properties of the different amino acids. Some side chains consist of nonpolar aliphatic or aromatic hydrocarbons. Other side chains are polar, while some are acidic or basic.



$$H_2N-\overset{\displaystyle R}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-COOH$$

FIGURE 26.11

An amino acid is an organic molecule that contains an amino group, a carboxyl group and a side chain (R), all bonded to a central carbon atom.

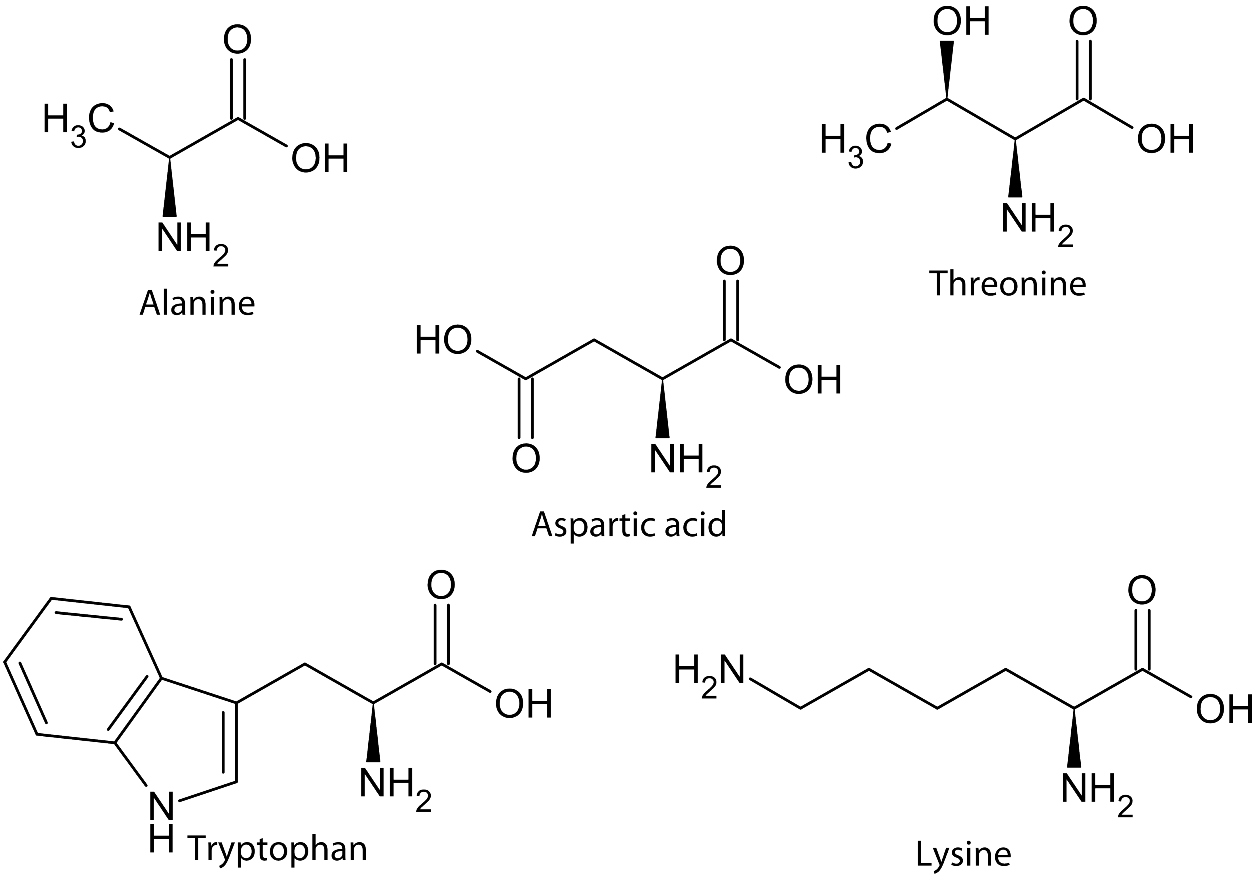


FIGURE 26.12

Five of the twenty biologically relevant amino acids, each having a distinctive side chain (R). Alanine's side chain is nonpolar, while threonine's is polar. Tryptophan is one of several amino acids whose side chain is aromatic. Aspartic acid has an acidic side chain, while lysine has a basic side chain.

The **Table** 26.1 lists the names of the 20 naturally occurring amino acids along with a three-letter abbreviation which is used to describe sequences of linked amino acids.

TABLE 26.1: **Amino Acids and Abbreviations**

Amino acid	Abbreviation	Amino acid	Abbreviation
Alanine	Ala	Leucine	Leu
Arginine	Arg	Lysine	Lys

TABLE 26.1: (continued)

Asparagine	Asn	Methionine	Met
Aspartic acid	Asp	Phenylalanine	Phe
Cysteine	Cys	Proline	Pro
Glutamine	Gln	Serine	Ser
Glutamic acid	Glu	Threonine	Thr
Glycine	Gly	Tryptophan	Trp
Histidine	His	Tyrosine	Tyr
Isoleucine	Ile	Valine	Val

Another more recent set of abbreviations employs only one letter. Leucine would be designated by L, serine by S, tyrosine by Y. The advantage of this system comes when listing the amino acid sequence of a protein that may contain over 100 amino acids in its chain.

Summary

- Amino acid is defined.
- The generic amino acid structure is shown.
- Common amino acids are listed.

Practice

Read the material at the link below and answer the following questions:

http://hyperphysics.phy-astr.gsu.edu/hbase/organic/essam.html

1. What are essential amino acids?
2. What are nonessential amino acids?
3. What happens if you are deficient in an amino acid?

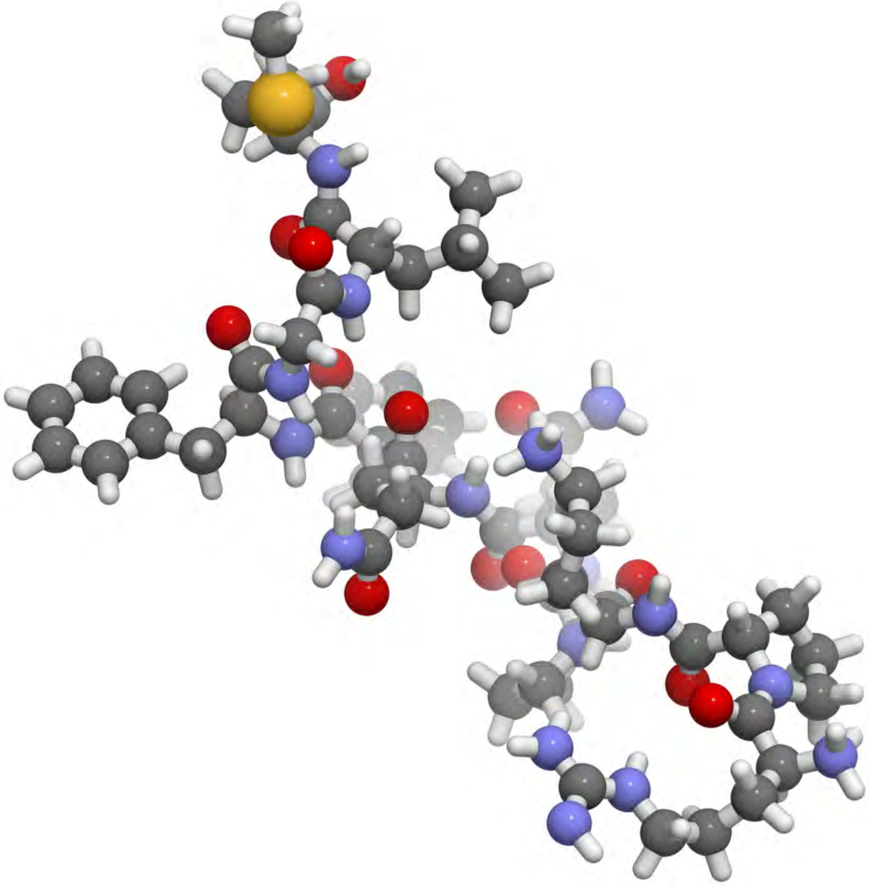
Review

1. What is an amino acid?
2. What is the three-letter abbreviation for histidine?
3. Why would the one-letter abbreviation system have an advantage?

- **amino acid:** A compound that contains both an amino group ($-NH_2$) and a carboxyl group ($-COOH$) bonded to a central carbon in the same molecule.

26.5 Peptides

- Define peptide.
- Describe the formation of the peptide bond.



How did you do that?

The cells have an intricate mechanism for the manufacture of proteins. Humans have to use other techniques in order to make the same proteins. The chemistry of peptide synthesis is complicated. Both active groups on an amino acid can react and the amino acid sequence must be the proper one in order for the protein to function. Robert Merrifield developed the first synthetic approach for making proteins in the lab (and won the Nobel Prize in Chemistry in 1984 for his work). The manual approach which he used was lengthy and tedious. Today, automated systems can crank out a peptide in a very short period of time.

Peptides

A **peptide** is a combination of amino acids in which the amino group of one amino acid has undergone a reaction with the carboxyl group of another amino acid. The reaction is a condensation reaction, forming an amide group (CO−N), shown below.

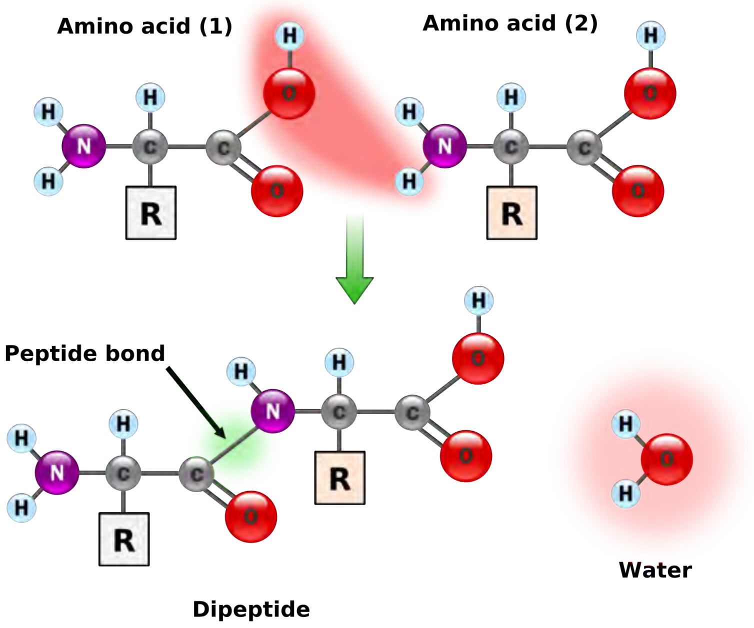


FIGURE 26.13
Amino acids join together to form a molecule called a dipeptide. The C–N bond is called a peptide bond. The order of amino acids is by convention shown with the free amino group on the left and the free carboxyl group on the right.

A **peptide bond** is the amide bond that occurs between the amino nitrogen of one amino acid and the carboxyl carbon of another amino acid. The resulting molecule is called a dipeptide. Notice that the particular side chains of each amino acid are irrelevant since the R groups are not involved in the peptide bond.

The dipeptide has a free amino group on one end of the molecule and a free carboxyl group on the other end. Each is capable of extending the chain through the formation of another peptide bond. The particular sequence of amino acids in a longer chain is called an amino acid sequence. By convention, the amino acid sequence is listed in the order such that the free amino group is on the left end of the molecule and the free carboxyl group is on the right end of the molecule. For example, suppose that a sequence of the amino acids glycine, tryptophan, and alanine is formed with the free amino group as part of the glycine and the free carboxyl group as part of the alanine. The amino acid sequence can be easily written using the abbreviations as Gly-Trp-Ala. This is a different sequence from Ala-Trp-Gly because the free amino and carboxyl groups would be on different amino acids in that case.

Summary

- Peptide is defined.
- The peptide bond is described.

Practice

Read the material at the link below and answer the following questions:

http://www.sciencedaily.com/articles/p/peptide_bond.htm

1. What class of reaction leads to formation of a peptide bond?
2. What molecule is eliminated in this reaction?
3. What class of organic compound is the product of this reaction?

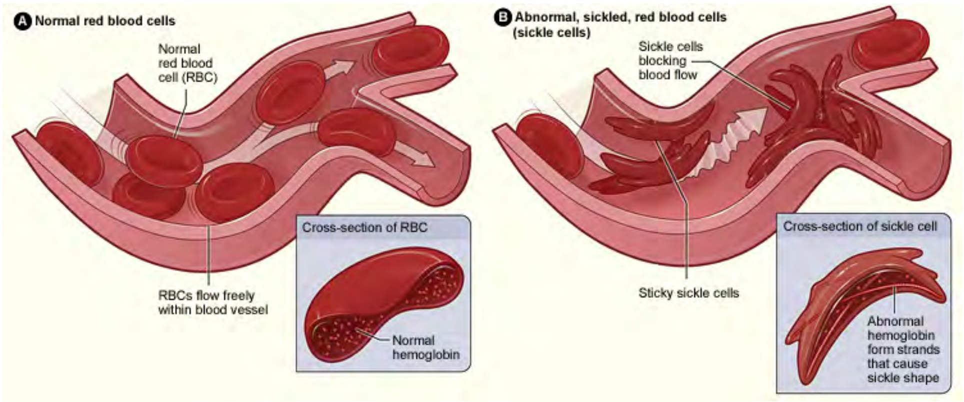
Review

1. What is a peptide bond?
2. How is this different from an ester?
3. You mix two amino acids together: glu and ser. If you reacted them, how many different dipeptides would you expect to get? List them.

- **peptide:** A combination of amino acids in which the amino group of one amino acid has undergone a reaction with the carboxyl group of another amino acid.
- **peptide bond:** The amide bond that occurs between the amino nitrogen of one amino acid and the carboxyl carbon of another amino acid.

26.6 Proteins

- Define polypeptide.
- Define protein.
- List and describe the four levels of protein structure.



A serious shift

Hemoglobin is a complex protein with a quaternary structure and containing iron. There are four subunits in the hemoglobin molecule – two alpha subunits and two beta subunits. Each subunit contains one iron ion, whose oxidation state changes from +2 to +3 and back again, depending upon the environment around the iron. When 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 again.

With hemoglobin of normal structure, this shift in conformation does not present any problems. However, individuals with hemoglobin S do experience serious complications. This hemoglobin has one amino acid in the two beta chains that is different from the amino acid at that point in the primary structure of normal hemoglobin. The result of this one structural change is aggregation of the individual protein molecules when oxygen is released. Adjacent hemoglobin molecules come in contact with one another and clump up, causing the reds cell to deform and break.

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, a very serious condition.

Proteins

A **polypeptide** is a sequence of amino acids between ten and one hundred in length. A **protein** is a peptide that is greater than one hundred amino acids in length. Proteins are very prevalent in living organisms. Hair, skin, nails, muscles, and the hemoglobin in red blood cells are some of the important parts of your body that are made of different proteins. The wide array of chemical and physiological properties of proteins is a function of their amino acid sequences. Since proteins generally consist of one hundred or more amino acids, the number of amino acid sequences that are possible is virtually limitless.

The three-dimensional structure of a protein is very critical to its function. This structure can be broken down into four levels. The **primary structure** is the amino acid sequence of the protein. The amino acid sequence of a given protein is unique and defines the function of that protein. The **secondary structure** is a highly regular sub-structure of the protein. The two most common types of protein secondary structure are the alpha helix and the beta sheet. An alpha helix consists of amino acids that adopt a spiral shape. A beta sheet is alternating rows of amino acids that line up in a side-by-side fashion. In both cases, the secondary structures are stabilized by extensive hydrogen bonding between the side chains.

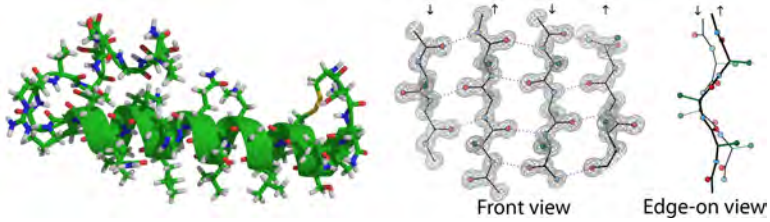


FIGURE 26.14
Alpha helix and beta sheet.

The interaction of the various side chains in the amino acid, specifically hydrogen bonding, leads to the adoption of a particular secondary structure. The **tertiary structure** is the overall three-dimensional structure of the protein. A typical protein consists of several sections of a specific secondary structure (alpha helix or beta sheet) along with other areas in which a more random structure occurs. These areas combine to produce the tertiary structure.

Some protein molecules consist of multiple protein subunits. The **quaternary structure** of a protein refers to the specific interaction and orientation of the subunits of that protein Hemoglobin is a very large protein found in red blood cells and whose function is to bind and carry oxygen throughout the bloodstream. Hemoglobin consists of four subunits – two α subunits (yellow) and two β subunits (gray) – which then come together in a specific and defined way through interactions of the side chains (see **Figure** 26.15). Hemoglobin also contains four iron atoms, located in the middle of each of the four subunits. The iron atoms are part of a structure called a porphyrin, shown in red in the figure.

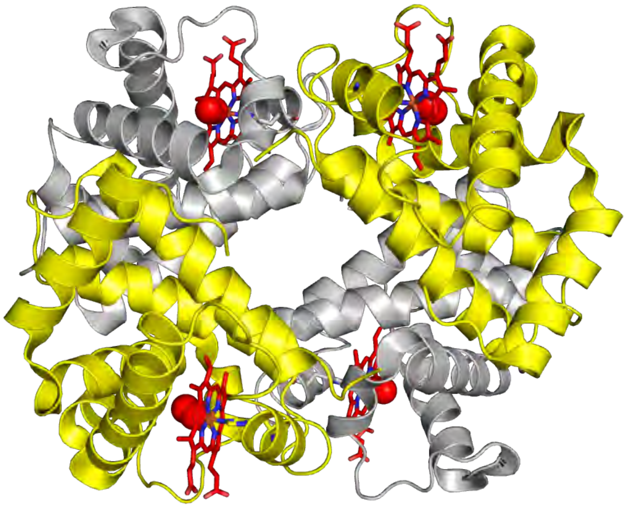


FIGURE 26.15
Hemoglobin

Some proteins consist of only one subunit and thus do not have a quaternary structure. The **Figure** 26.16 diagrams the interaction of the four levels of protein structure.

Summary

- Peptide and proteins are defined.

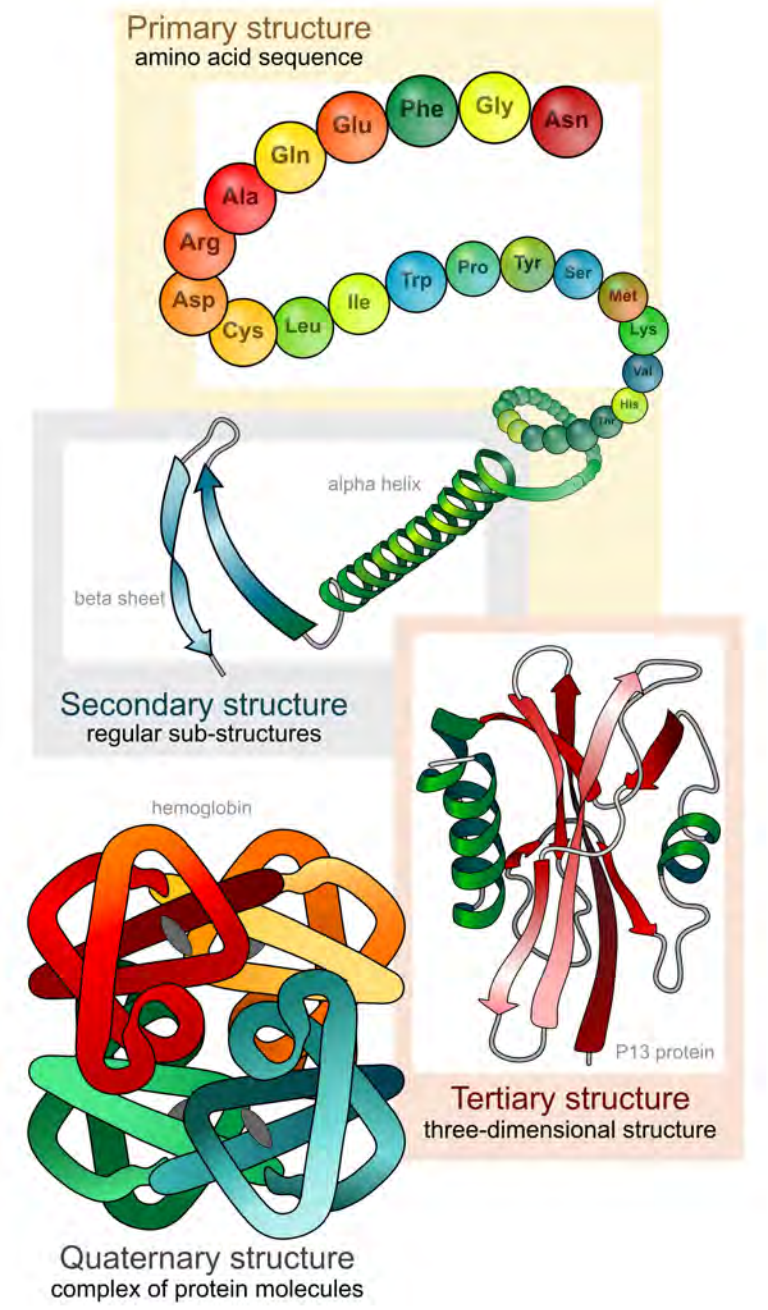
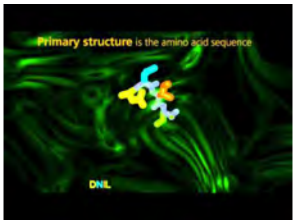


FIGURE 26.16
The four levels of protein structure.

- The four levels of protein structure are listed and defined.

Practice

Watch the video at the link below and answer the following questions:



MEDIA

Click image to the left for more content.

http://www.youtube.com/watch?v=Q7dxi4ob2O4

1. What is part of what determines how a protein folds?
2. What holds secondary structure together?
3. What holds the tertiary structure together?

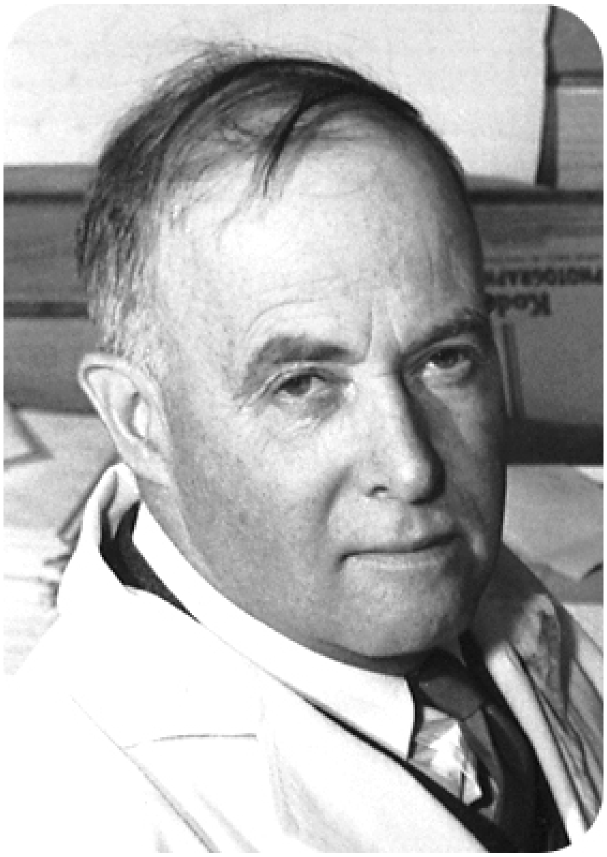
Review

1. A protein has the following sequence: ser-his-thr-tyr. What component of protein structure is this?
2. What do we call the overall three-dimensional shape of a protein?
3. A protein has one subunit. Would it have a quaternary structure?

- **polypeptide:** A sequence of amino acids between ten and one hundred in length.
- **primary structure:** The amino acid sequence of the protein.
- **protein:** A peptide that is greater than one hundred amino acids in length.
- **quaternary structure:** The specific interaction and orientation of the subunits of that protein.
- **secondary structure:** A highly regular sub-structure of the protein.
- **tertiary structure:** The overall three-dimensional structure of the protein.

26.7 Enzymes

- Define enzyme.
- Define active site.
- Describe the process of an enzyme reaction.
- Describe the process by which a competitive inhibitor alters the rate of an enzyme reaction.
- Describe the process by which a non-competitive inhibitor alters the rate of an enzyme reaction.
- Explain the role of cofactors in enzyme reactions.



What did he discover?

The first enzyme to be isolated was discovered in 1926 by American chemist James Sumner, who crystallized the protein. The enzyme was urease, which catalyzes the hydrolytic decomposition of urea, a component of urine, into ammonia and carbon dioxide.

$$H_2NCONH_2(aq)+H_2O(l)\xrightarrow{\text{urease}}2NH_3(g)+CO_2(g)$$

His discovery was ridiculed at first because nobody believed that enzymes would behave the same way that other chemicals did. Sumner was eventually proven right and won the Nobel Prize in Chemistry in 1946.

Enzymes

An **enzyme** is a protein that acts as a biological catalyst. Recall that a catalyst is a substance that increases the rate of a chemical reaction without itself being consumed in the reaction. Cellular processes consist of many chemical reactions that must occur quickly in order for the cell to function properly. Enzymes catalyze most of the chemical reactions that occur in a cell. A **substrate** is the molecule or molecules on which the enzyme acts. In the urease catalyzed reaction above, urea is the substrate. The **Figure ??** diagrams a typical enzymatic reaction.

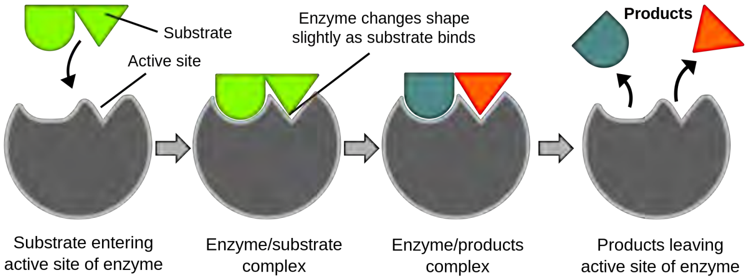


FIGURE 26.17

The sequence of steps for a substrate binding to an enzyme in its active site, reacting, then being released as products.

The first step in the reaction is that the substrate binds to a specific part of the enzyme molecule. The binding of the substrate is dictated by the shapes of each molecule. Side chains on the enzyme interact with the substrate in a specific way, resulting in the making and breaking of bonds. The **active site** is the place on an enzyme where the substrate binds. An enzyme folds in such a way that it typically has one active site, usually a pocket or crevice formed by the folding pattern of the protein. Because the active site of an enzyme has such a unique shape, only one particular substrate is capable of binding to that enzyme. In other words, each enzyme catalyzes only one chemical reaction with only one substrate. Once the enzyme/substrate complex is formed, the reaction occurs and the substrate is transformed into products. Finally, the product molecule or molecules are released from the active site. Note that the enzyme is left unaffected by the reaction and is now capable of catalyzing the reaction of another substrate molecule.

Inhibitors

An **inhibitor** is a molecule, which interferes with the function of an enzyme, either slowing or stopping the chemical reaction. Inhibitors can work in a variety of ways, but one of the most common is illustrated in below.

The inhibitor binds competitively at the active site and blocks the substrate from binding. Since no reaction occurs with the inhibitor, the enzyme is prevented from catalyzing the reaction. Cyanide is a potent poison which acts as a competitive inhibitor. It binds to the active site of the enzyme *cytochrome c oxidase* and interrupts cellular respiration. The binding of the cyanide to the enzyme is irreversible and the affected organism dies quickly.

Non-competitive inhibition

A non-competitive inhibitor does not bind at the active site. It attaches at some other site on the enzyme and changes the shape of the protein. This shift in three-dimensional structure alters the shape of the active site so that the substrate will no longer fit in the site properly.

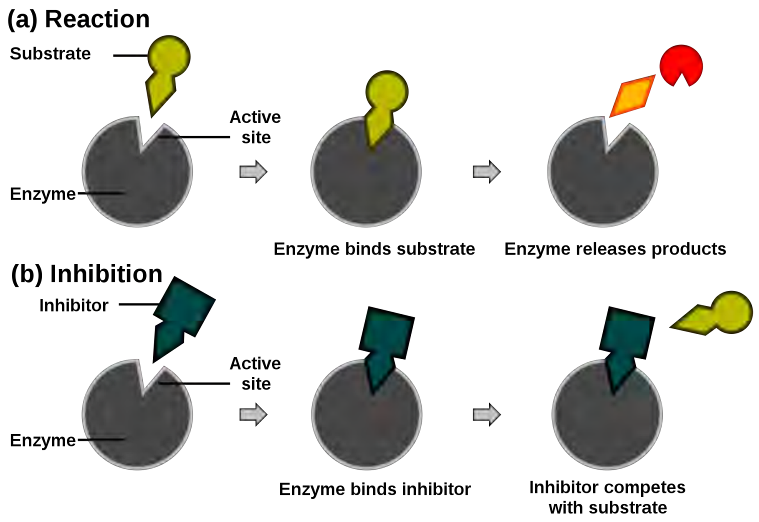


FIGURE 26.18

A competitive inhibitor is a molecule that binds to the active site of an enzyme without reacting, thus preventing the substrate from binding.

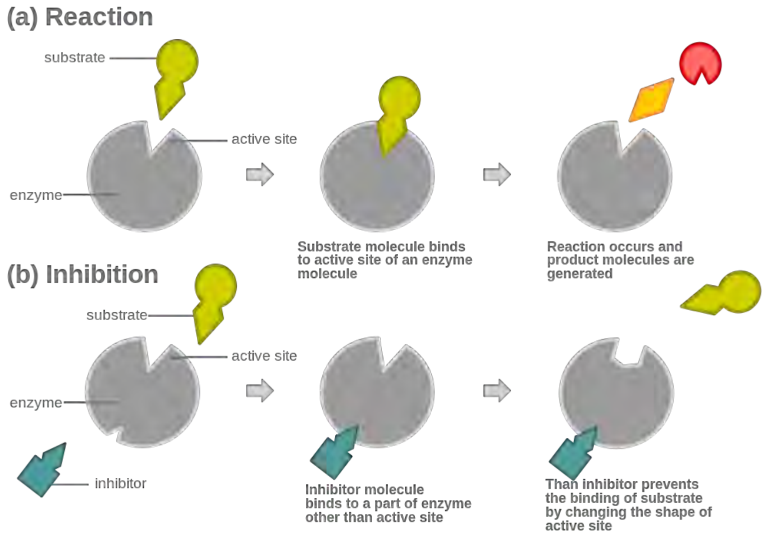


FIGURE 26.19

Non-competitive inhibition

Cofactors

Some enzymes require the presence of a non-protein molecule called a cofactor in order to function properly. Cofactors can be inorganic metal ions or small organic molecules. Many vitamins, such as B vitamins, act as cofactors. Some metal ions which function as cofactors for various enzymes include zinc, magnesium, potassium, and iron.

Summary

- Enzyme is defined.
- An overview of the enzyme reaction process is illustrated.
- Competitive and non-competitive inhibitors are described.
- The role of a cofactor is described.

Practice

Watch the animation at the site below and take the quiz:

http://highered.mcgraw-hill.com/sites/0072495855/student_view0/chapter2/animation__how_enzymes_work.html

Review

1. What is the substrate?
2. How does a competitive inhibitor work?
3. How does a non-competitive inhibitor work?

- **active site:** The place on an enzyme where the substrate binds.
- **enzyme:** A protein that acts as a biological catalyst.
- **inhibitor:** A molecule which interferes with the function of an enzyme, either slowing or stopping the chemical reaction.
- **substrate:** The molecule or molecules on which the enzyme acts.

26.8 Triglycerides

- Describe the structure of saturated and unsaturated fatty acids.
- Describe the structure of a triglyceride.
- Describe the role of triglycerides in diet.

Omega-3 fatty acids

Eat right or take a pill?

There is a lot of interest these days on healthy diets and concerns about heart problems. There is also a strong market for the sales of omega-3 fatty acids, said to be helpful in lowering fat levels in blood. But too many people rely on the pills to help their hearts and don't understand the chemistry behind it all. Yes, taking omega-3 fatty acids will give you some needed fatty acids. No, this is not a substitute for eating a healthy diet and exercising. You can't sit in front of the TV set, eating your large pizza, and expect these pills to make you healthy. You've got to do things the hard way – eat your vegetables and get some exercise. Yes, mother.

Triglycerides

A **lipid** is a member of a class of water-insoluble compounds that includes oils, fats, and waxes. Oils and fats are based on the same general structure, but fats are solids at room temperature, while oils are liquids. Butter is an example of a fat and is derived from animals. Some oils include olive oil and canola oil, which are obtained from plants. Lipids are an essential part of a healthy diet, though excess dietary fat can be harmful. Lipids store energy in the body and are also needed to keep cell membranes healthy.

One type of lipid is called a **triglyceride**, an ester derived from glycerol combined with three fatty acid molecules.

Glycerol is a triol, an alcohol which contains three hydroxyl functional groups. A fatty acid is a long carbon chain, generally from 12 to 24 carbons in length, with an attached carboxyl group. Each of the three fatty acid molecules

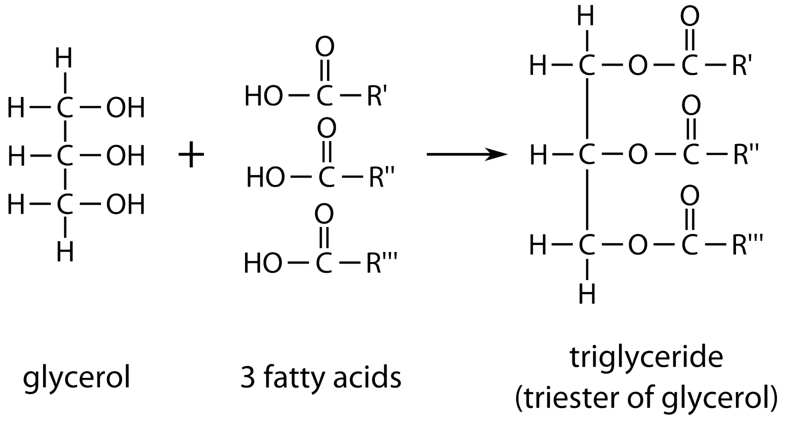


FIGURE 26.20
Triglyceride components

undergoes an esterification with one of the hydroxyl groups of the glycerol molecule. The result is a large triester molecule referred to as a triglyceride.

Triglycerides function as a long-term storage form of energy in the human body. Because of the long carbon chains, triglycerides are nearly nonpolar molecules and thus do not dissolve readily in polar solvents such as water. Instead, oils and fats are soluble in nonpolar organic solvents such as hexane and ethers.

Fats may be either saturated or unsaturated. A **saturated fat** is a fat that consists of triglycerides whose carbon chains consist entirely of carbon-carbon single bonds. Therefore, the carbon chains are saturated with the maximum number of hydrogen atoms possible. An **unsaturated fat** is a fat that consists of triglycerides whose carbon chains contain one or more carbon-carbon double bonds. A fat with one double bond is called monounsaturated, while a fat with multiple double bonds is called polyunsaturated (see **Figure** 26.21).

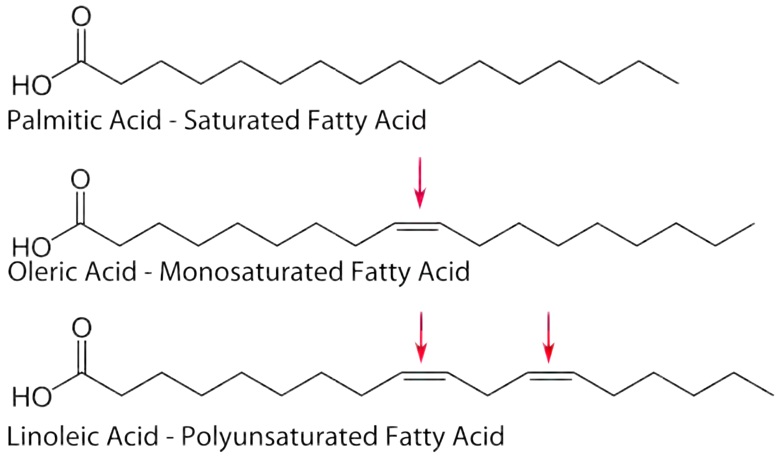


FIGURE 26.21
Saturated and unsaturated fatty acids

Unsaturated fats are generally considered to be healthier because they contain fewer calories than an equivalent amount of saturated fats. Additionally, high consumption of saturated fats is linked to an increased risk of cardiovascular disease. Some examples of foods with high concentrations of saturated fats include butter, cheese, lard, and some fatty meats. Foods with higher concentrations of unsaturated fats include nuts, avocado, and those that contain various vegetable oils such as canola oil and olive oil. The **Figure** 26.22 shows the percentages of fat types in some common foods.

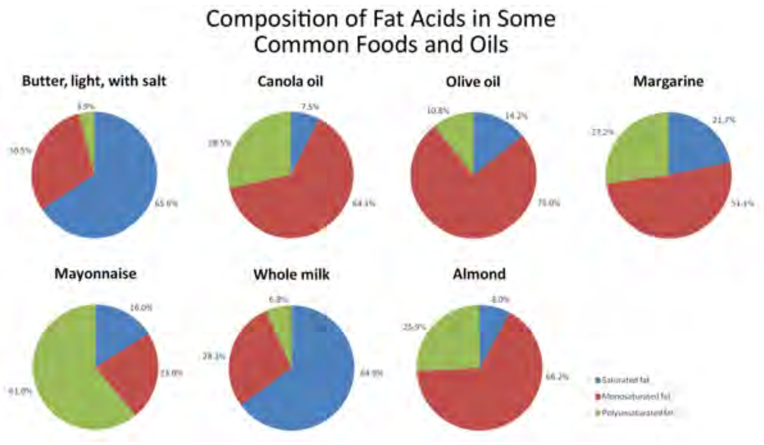


FIGURE 26.22

Some common foods and oils along with their percentages of saturated, monounsaturated, and polyunsaturated fats.

Summary

- The structures of saturated and unsaturated fatty acids are given.
- The structure of a triglyceride is given.
- The role of triglycerides in our diet is described.

Practice

Read the material at the link below and answer the following questions:

http://www.heart.org/HEARTORG/GettingHealthy/NutritionCenter/Triglycerides_UCM_306029_Article.jsp

1. What are normal blood triglyceride levels?
2. What exercise levels are recommended to help lower blood triglycerides?
3. What types of cooking oils are healthier?

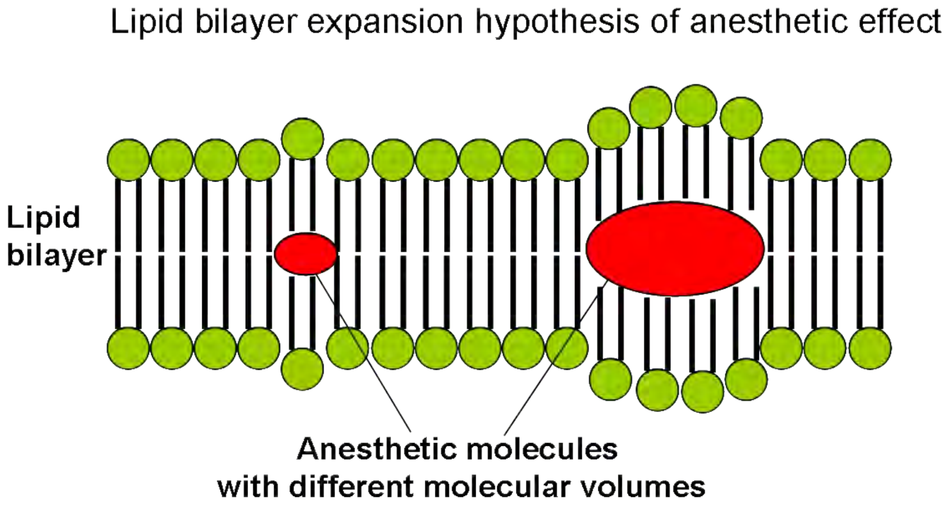
Review

1. What is a fatty acid?
2. What is a triglyceride?
3. Why are unsaturated fatty acids important?

- **lipid:** A member of a class of water-insoluble compounds that includes oils, fats, and waxes.
- **saturated fat:** A fat that consists of triglycerides whose carbon chains consist entirely of carbon-carbon single bonds.
- **triglyceride:** An ester derived from glycerol combined with three fatty acid molecules.
- **unsaturated fat:** A fat that consists of triglycerides whose carbon chains contain one or more carbon-carbon double bonds.

26.9 Phospholipids

- Describe the structure of a phospholipid.
- Describe the structure of a membrane.



Do you feel anything now?

When you go to the dentist to get a tooth pulled, you really don't want to feel the pain. The dentist injects an anesthetic into your gum and it eventually gets numb. One theory as to why anesthetics work deals with the movement of ions across the cell membrane. The anesthetic gets into the membrane structure and causes shifts in how ions move across the membrane. If ion movement is disrupted, nerve impulse will not be transmitted and you will not sense pain – at least not until the anesthetic wears off.

Phospholipids

A **phospholipid** is a lipid that contains a phosphate group and is a major component of cell membranes. A phospholipid consists of a hydrophilic (water-loving) head and hydrophobic (water-fearing) tails (see **Figure** 26.23). The phospholipid is essentially a triglyceride in which n fatty acid has been replaced by a phosphate group of some sort.

Following the rule of "like dissolves like", the hydrophilic head of the phospholipid molecule dissolves readily in water. The long fatty acid chains of a phospholipid are nonpolar and thus avoid water because of their insolubility. In water, phospholipids spontaneously form a double layer called a lipid bilayer in which the hydrophobic tails of phospholipid molecules are sandwiched between two layers of hydrophilic heads (see **Figure** 26.25). In this way, only the heads of the molecules are exposed to the water, while the hydrophobic tails interact only with each other.

Phospholipid bilayers are critical components of cell membranes. The lipid bilayer acts as a barrier to the passage of molecules and ions into and out of the cell. However, an important function of the cell membrane is to allow selective passage of certain substances into and out of cells. This is accomplished by the embedding of various protein molecules in and through the lipid bilayer (see **Figure** 26.25). These proteins form channels through which certain specific ions and molecules are able to move. Many membrane proteins also contain attached carbohydrates on the outside of the lipid bilayer, allowing it to form hydrogen bonds with water.

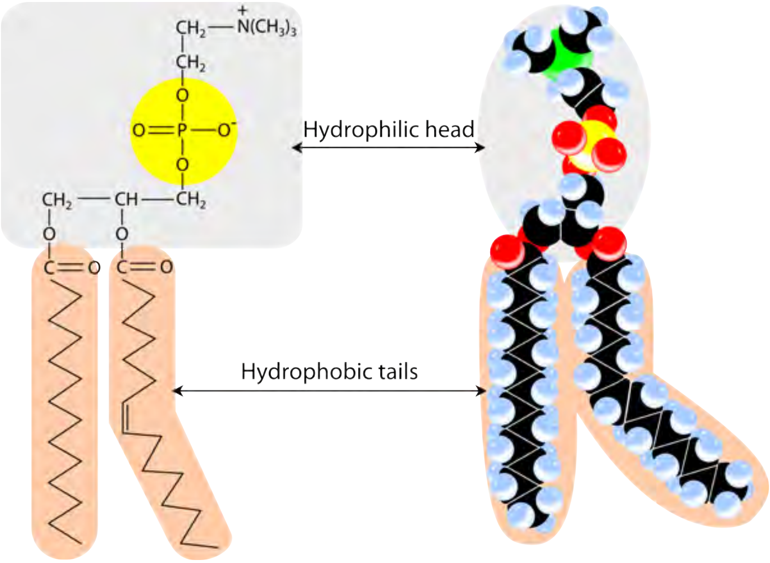


FIGURE 26.23

A phospholipid consists of a head and a tail. The "head" of the molecule contains the phosphate group and is hydrophilic, meaning that it will dissolve in water. The "tail" of the molecule is made up of two fatty acids, which are hydrophobic and do not dissolve in water.

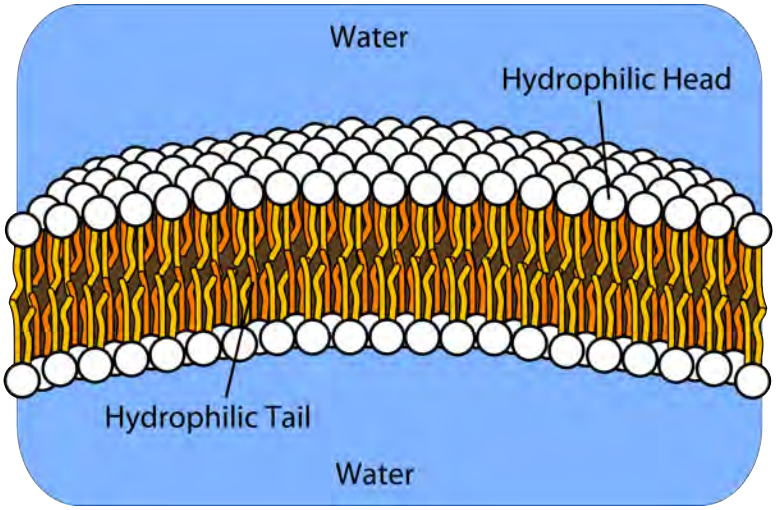


FIGURE 26.24

In a water solution, phospholipids form a bilayer where the hydrophobic tails point towards each other on the interior and only the hydrophilic heads are exposed to the water.

Summary

- The structure of phospholipids is described.
- The structure of the cell membrane is described.

Practice

Read the material at the link below and answer the following questions:

http://hyperphysics.phy-astr.gsu.edu/hbase/organic/phoslip.html

1. What is the phospholipid backbone?
2. What is the consistency of a phospholipid double-layered membrane?
3. Is the membrane rigid or fluid?

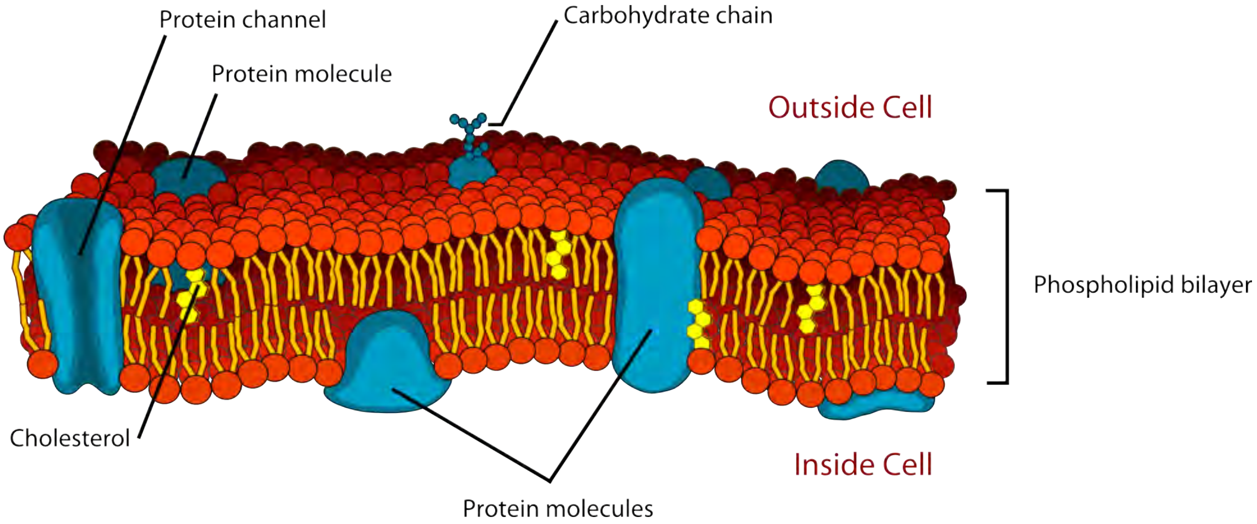


FIGURE 26.25

The phospholipid bilayer of a cell membrane contains embedded protein molecules which allow for selective passage of ions and molecules through the membrane.

Review

1. What is a phospholipid?
2. Which part of the phospholipid molecule is water-soluble?
3. Which part is not water-soluble?

- **phospholipid:** A lipid that contains a phosphate group and is a major component of cell membranes.

26.10 Waxes

- Define wax.
- Describe properties of waxes.
- List common waxes.

Thar she blows!

From the 1700s up to the late 1900s, whalers searched the ocean for the sperm whale. Whaling was a dangerous occupation – the prey would average about fifty feet in length. But the search was worth it if successful. One large whale could produce up to 500 gallons of oil, valuable for making candles, ointments, cosmetic creams, and industrial lubricants. In 1988, sperm whales (and other whale species) were place under international protection because their numbers were diminishing rapidly. Today, various vegetable oils are used in place of whale oils.

Waxes

Another type of lipid molecule is waxes. **Waxes** are esters of long-chain fatty acids and long-chain alcohols. Waxes are soft solids with generally low melting points and are insoluble in water. The **Figure** 26.26 shows the structure of cetyl palmitate, a natural wax present in sperm whales.

One of the best known natural waxes is beeswax, though many other animals and plants synthesize waxes naturally. Waxes can be found on leaves of plants and on the skin, hair, or feathers of animals, where they function to keep these structures pliable and waterproof. Humans take advantage of the protective properties of natural and synthetic waxes in such applications as floor polish and car wax.

Summary

- The structure of waxes is shown.

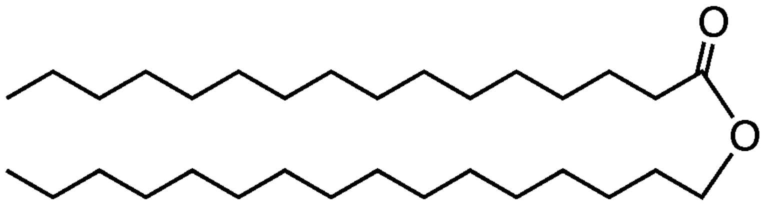


FIGURE 26.26

Cetyl palmitate belongs to the category of compounds called waxes. It is derived from a fatty acid that is 15 carbons in length and an alcohol that contains 16 carbon atoms.

- Properties of waxes are described.
- Common waxes are listed.

Practice

Read the material at the link below and answer the following questions:

http://lipidlibrary.aocs.org/lipids/waxes/index.htm

1. Besides wax esters, what other organic components can be found in waxes?
2. What is another name for wool wax?
3. What are the three major non-polar lipids on the skin surface of humans?

Review

1. What is a wax?
2. Name two properties of waxes.
3. Name a wax found in sperm whales.

- **wax:** Ester of long-chain fatty acids and long-chain alcohols.

26.11 Nucleic Acids

- Define nucleic acid.
- Define nucleotide.
- Describe the structures of common nucleotides.

Treating cancer with chemistry.

Cancer treatment is a complex and challenging effort. Cancer cells grow without the normal controls that exist. One approach is to alter the structure of the DNA to slow down or stop the growth of the abnormal cells. Compounds that structurally resemble the normal building blocks of DNA have been shown to be very effective in stopping the spread of some forms of cancer.

Nucleic Acids

Swiss biochemist Friedrich Miescher first discovered nitrogen-containing compounds in the nuclei of cells in 1869. The term nucleic acid was used to describe these molecules because of their discovery within the cell nucleus and because of the presence of phosphate groups and their relationship to phosphoric acid. A **nucleic acid** is a large biopolymer consisting of many nucleotides. The two primary nucleic acids which are found in cells are deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). DNA is the carrier of genetic information and is ultimately responsible for how cells produce proteins in order to carry out all the functions necessary for life. RNA is a related molecule that is involved in the mechanism by which the information stored in DNA is eventually converted into protein molecules.

The basic components of nucleic acids are nucleotides. A **nucleotide** is a molecule that contains a five-carbon sugar, a phosphate group, and a nitrogen containing base. The five-carbon sugar is either ribose, in the case of RNA, or deoxyribose, in the case of DNA. The only difference between the two molecules is the presence of a hydroxyl group attached to one member of the carbon ring in RNA. In DNA, that same carbon atom is attached only to a hydrogen atom (see **Figure** 26.27).

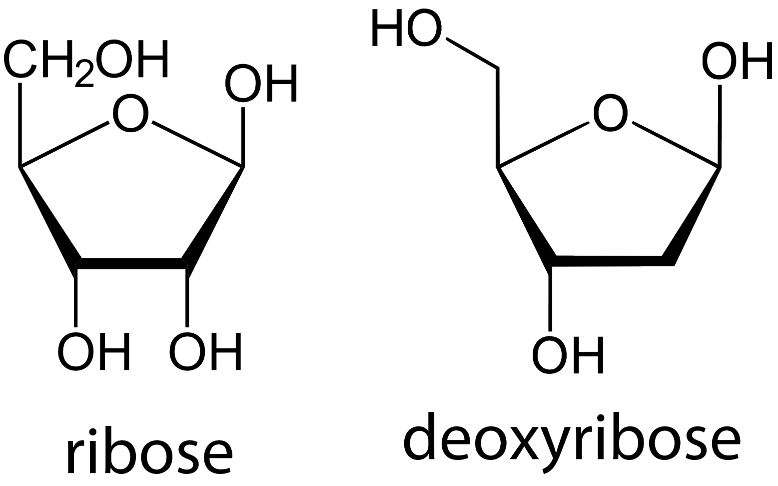


FIGURE 26.27

The sugars ribose and deoxyribose are components of RNA and DNA respectively.

The nucleotides form the backbone of RNA and DNA. Each nucleotide consists of a base, a pentose (either ribose or deoxyribose) and phosphate groups. Three of the bases in RNA and DNA are identical (adenine, cytosine, and guanine). Thymine is found in DNA while uracil is in RNA.

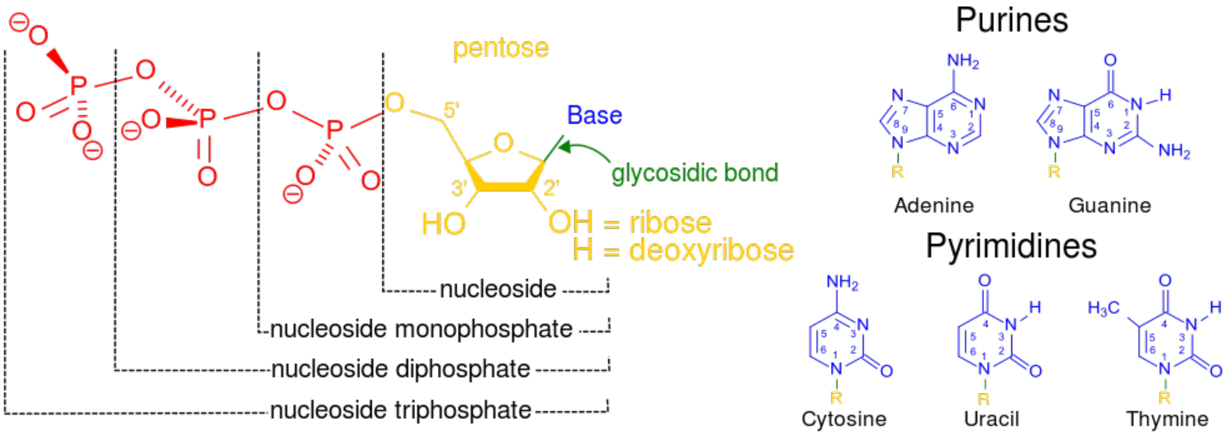


FIGURE 26.28

Nucleotides

Summary

- The definition of a nucleic acid is given.
- The definition of a nucleotide and structures of the five nucleotides are provided.

Practice

Read the material at the link below and answer the following questions:

http://www.ncbi.nlm.nih.gov/pubmed/17901982

1. What was Miescher studying in 1868-1869?
2. What was interesting about the chemical composition of the material he isolated?
3. What did he call it and why?

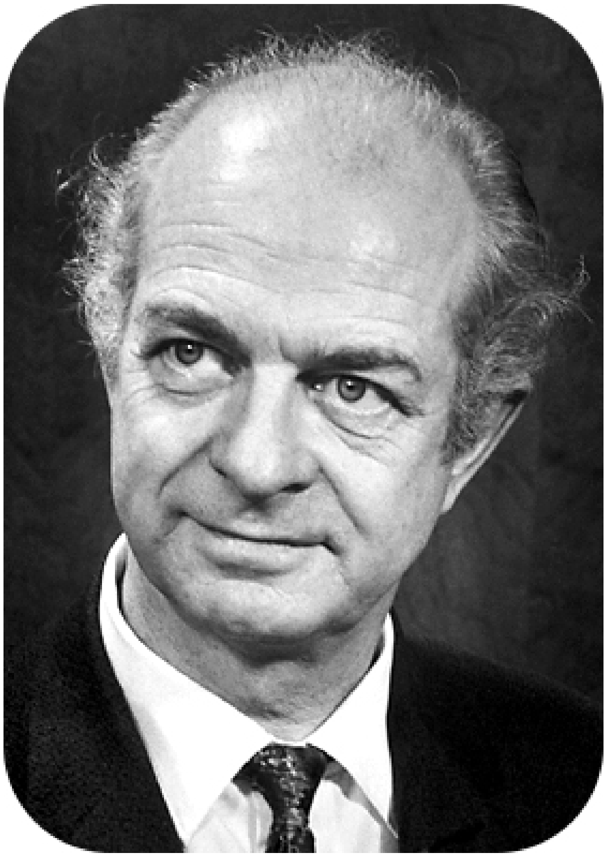
Review

1. What is a nucleic acid?
2. What is a nucleotide?
3. Which pentose is in DNA and which is in RNA?

- **nucleic acid:** A large biopolymer consisting of many nucleotides.
- **nucleotide:** A molecule that contains a five-carbon sugar, a phosphate group, and a nitrogen containing base.

26.12 DNA and RNA

- Describe the structure of a nucleotide.
- List the bases found in DNA.
- List the bases found in RNA.
- Describe the double helical structure of DNA.



You can't win them all.

Linus Pauling was one of the greatest scientists of the twentieth century. A two-time Nobel Prize winner (in chemistry in 1954 and the peace prize in 1962). However, he didn't always come in first. In the 1950s, there was a great deal of interest in the structure of DNA. Pauling spent some time on this puzzle, although he was primarily interested in proteins. The inadequate amount of information he had led him to propose a DNA structure where the bases were on the outside and the phosphate groups were on the inside. It turns out that he was in error about this idea, but it certainly did not take away from his outstanding scientific reputation.

DNA and RNA

The three parts of a DNA nucleotide are assembled as shown below.

Every DNA and RNA polymer consists of multiple nucleotides strung together into extremely long chains. The only variation in each nucleotide is the identity of the nitrogenous base. The figure above shows one example of a nitrogenous base, called adenine. There are only five different nitrogenous bases found in all nucleic acids. The four

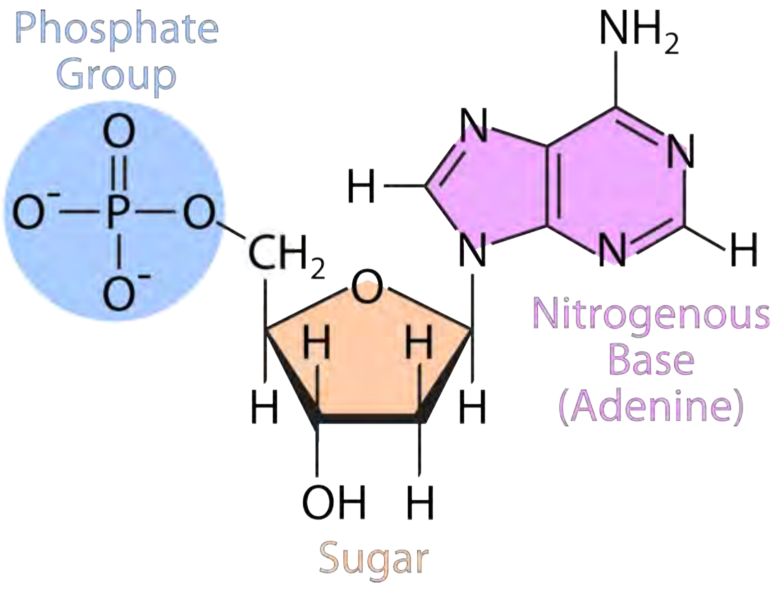


FIGURE 26.29
Nucleotides are composed of a phosphate group, a sugar, and one of five different nitrogenous bases.

bases of DNA are adenine, thymine, cytosine, and guanine, abbreviated A, T, C, and G respectively. In RNA, the base thymine is not found and is instead replaced by a different base called uracil, abbreviated U. The other three bases are present in both DNA and RNA.

The specific structure of DNA proved elusive to scientists for many years. In 1953, James Watson and Francis Crick proposed that the structure of DNA consists of two side-by-side polynucleotide chains wrapped into the shape of a **double helix**. One aspect of this structure is that each nitrogenous base on one of the DNA strands must be paired up with another base on the opposite strand. The **Figure** 26.30 illustrates the base pairing. Each adenine base is always paired with a thymine, while each cytosine is paired with a guanine. The bases fit together perfectly from one strand to the other and are also held together by hydrogen bonds. The A-T pairing contains two hydrogen bonds, while the C-G pairing contains three hydrogen bonds. The ends of each strand are labeled either 3' or 5' based on a numbering of the deoxyribose sugar ring.

The double helical structure of DNA is shown below.

Summary

- The nucleotide structures of DNA and RNA are described.
- Base pairing in DNA is illustrated.
- The DNA double helix is shown.

Practice

Read the material at the link below and answer the following questions:

www.accessexcellence.org/RC/AB/BC/Rosalind_Franklin.php

1. Where did Rosalind Franklin do her research?
2. What important data about DNA structure did she have?
3. Did she know that Watson and Crick had seen her research data?

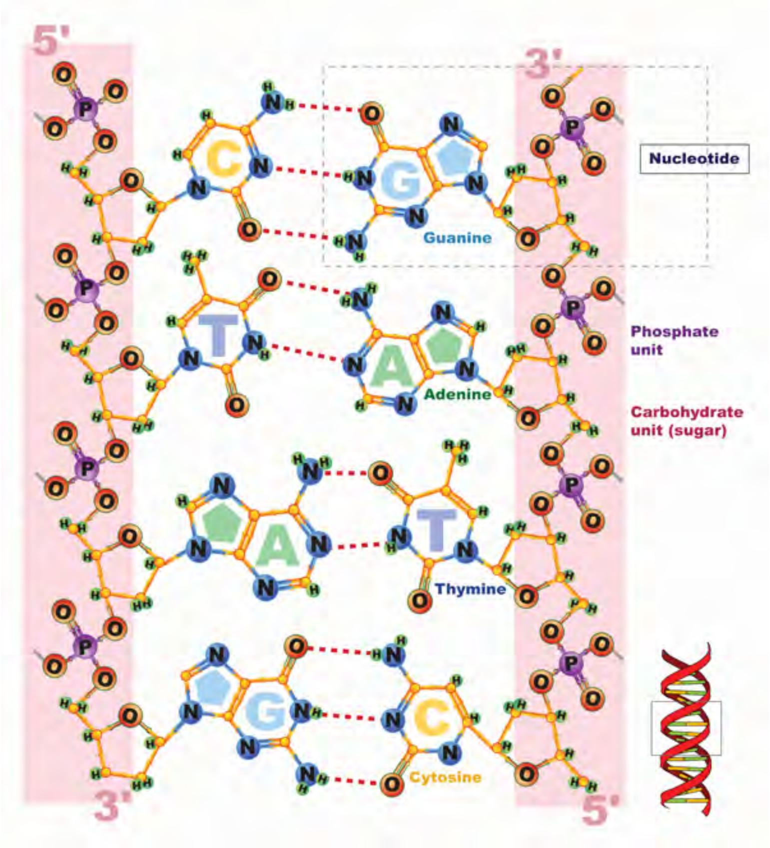


FIGURE 26.30
Base pairing in DNA

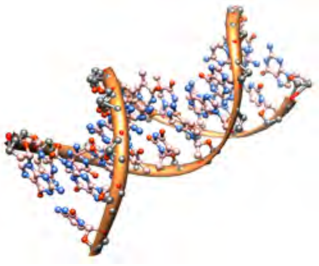


FIGURE 26.31
The DNA double helix

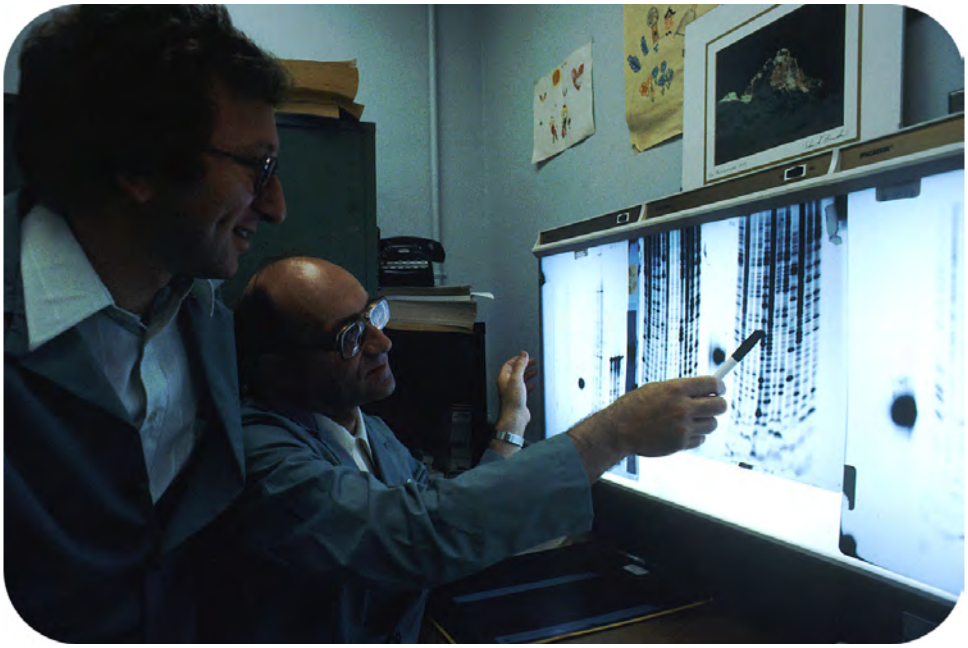
Review

1. What four bases make up the DNA chain?
2. How are these bases held together?
3. What is the resulting structure called?

- **double helix:** The three-dimensional structure of DNA.

26.13 Genetic Code

- Define gene.
- Describe the DNA triplet codes for amino acids.



Still working on it.

The Human Genome Project started in 1990 with the lofty goal of sequencing the complete set of human DNA. This project was completed in April 2003, ahead of schedule and under the budget set for it (a rare occurrence for a government project). With this knowledge, we can now identify genetic disorders quickly and personalize treatment for many diseases. Much work still remains to understand the connections between specific DNA sequences and specific diseases.

The Genetic Code

Each particular organism contains many protein molecules that are specific to that organism. The particular base sequence of DNA is responsible for the production of all of the different proteins that are present in each and every living thing that has ever inhabited the Earth. How does that work? Cells use the unique sequence of DNA bases to decide which proteins to synthesize. A **gene** is a segment of DNA that carries a code for making a specific polypeptide chain. The cell essentially decodes the DNA in order to make whatever peptides and proteins are needed by that organism.

The **genetic code** works as a series of three-letter codes. Each sequence of three letters, called a triplet, corresponds to one of the twenty common amino acids. The triplets are read by the cell, one after the other, in the process of protein synthesis. The **Table** 26.2 shows all of the possible triplets and the amino acids that result from each three-letter code.

TABLE 26.2: **DNA Triplet Codes for Amino Acids**

AAA	Phe	GAA	Leu	TAA	Ile	CAA	Val
AAG	Phe	GAG	Leu	TAG	Ile	CAG	Val
AAT	Leu	GAT	Leu	TAT	Ile	CAT	Val
AAC	Leu	GAC	Leu	TAC	Met	CAC	Val
AGA	Ser	GGA	Pro	TGA	Thr	CGA	Ala
AGG	Ser	GGG	Pro	TGG	Thr	CGG	Ala
AGT	Ser	GGT	Pro	TGT	Thr	CGT	Ala
AGC	Ser	GGC	Pro	TGC	Thr	CGC	Ala
ATA	Tyr	GTA	His	TTA	Asn	CTA	Asp
ATG	Tyr	GTG	His	TTG	Asn	CTG	Asp
ATT	End	GTT	Gln	TTT	Lys	CTT	Glu
ATC	End	GTC	Gln	TTC	Lys	CTC	Glu
ACA	Cys	GCA	Arg	TCA	Ser	CCA	Gly
ACG	Cys	GCG	Arg	TCG	Ser	CCG	Gly
ACT	End	GCT	Arg	TCT	Arg	CCT	Gly
ACC	Trp	GCC	Arg	TCC	Arg	CCC	Gly

The DNA code word GCA corresponds to the amino acid arginine, while the DNA code word TCG corresponds to the amino acid serine. Most amino acids are represented by more than one possible triplet code, but each triplet code yields only one amino acid. Three of the DNA code words (ATT, ATC, and ACT) are end or termination code words. The translation of a DNA base sequence begins immediately after one termination code word and runs until another termination code word is reached.

Even with only four different bases, the number of possible nucleotide sequences in a DNA chain is virtually limitless. The particular DNA sequence of a particular organism constitutes the genetic blueprint for that organism. This genetic blueprint is found in the nucleus of each cell of the organism and is passed on from parents to offspring. The incredible diversity of life on Earth stems from the differences in the genetic code of every living thing.

Summary

- A gene is defined.
- The genetic code is described.

Practice

Read the material at the link below and answer the following questions:

http://nihrecord.od.nih.gov/newsletters/2010/02_05_2010/story3.htm

1. What did Marshall Nirenberg do?
2. When did he first report his results?
3. What did he win for his discovery?

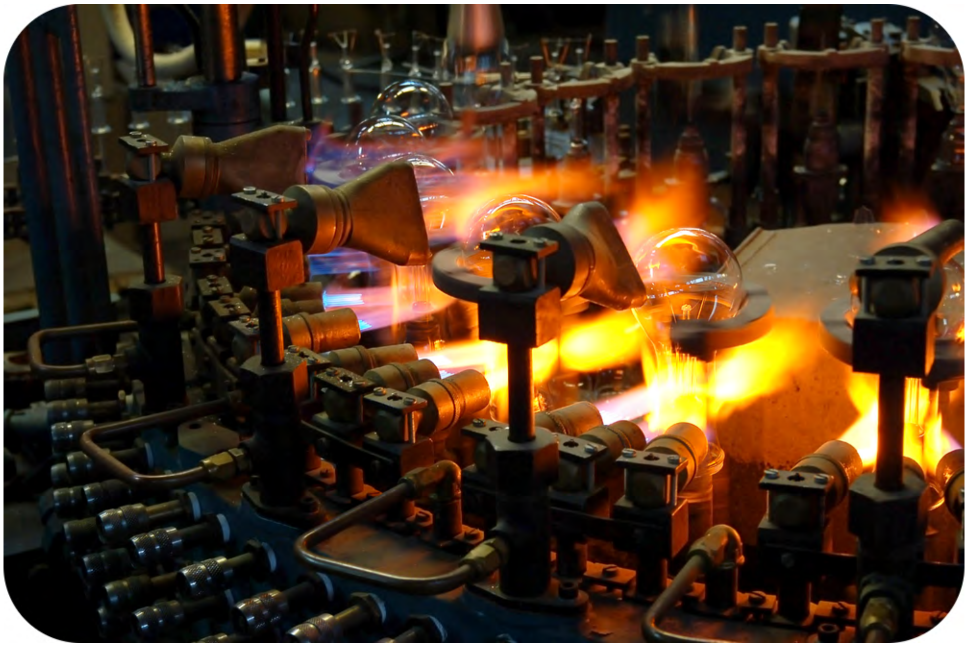
Review

1. What is a gene?
2. What does the genetic code do?
3. What is the nucleotide code for phenylalanine?

- **gene:** A segment of DNA that carries a code for making a specific polypeptide chain.
- **genetic code:** The three-base set of nucleotides that specifies a particular amino acid in a protein sequence.

26.14 Protein Synthesis

- Describe the sequence of processes that take place in protein synthesis.



A very organized process.

The assembly line is an American invention that was developed around 1901 to mass-produce cars. Prior to that time, teams of workers would build a car together. With the advent of the assembly line, cars could be produced much more quickly and at lower cost. The assembly line idea quickly spread to other products, like the light bulbs shown above. Being able to line up parts in order and have a smooth process for putting those parts together means that an item can be produced quickly and reproducibly, coming out the same every time.

Protein Synthesis

The process of protein synthesis is summarized in the diagram below. 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 specific amino acid and brings it to the RNA for incorporation.

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:

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 acid in the proper sequence for the developing protein. After adding the amino acid to the sequence, the tRNA then is cleaved from the amino acid and recycled for further participation in the process.

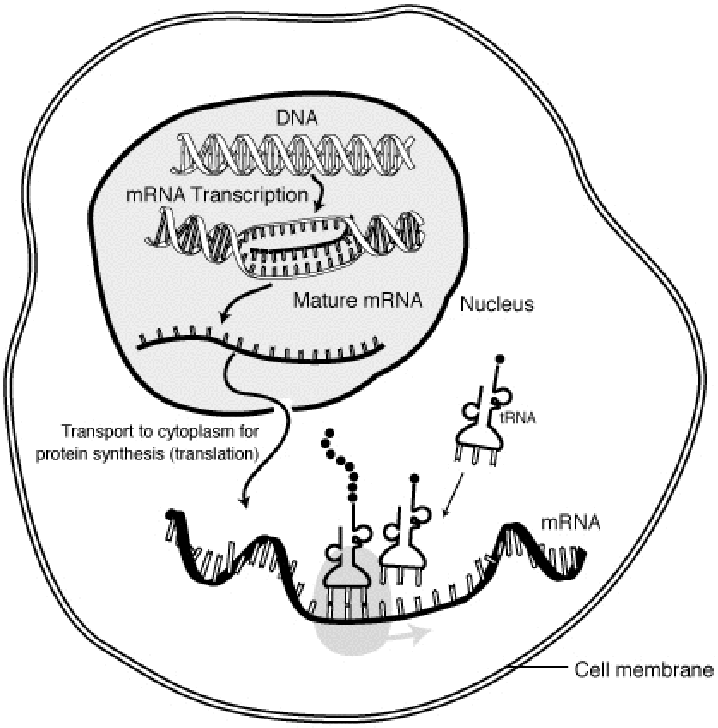


FIGURE 26.32

Overview of protein synthesis

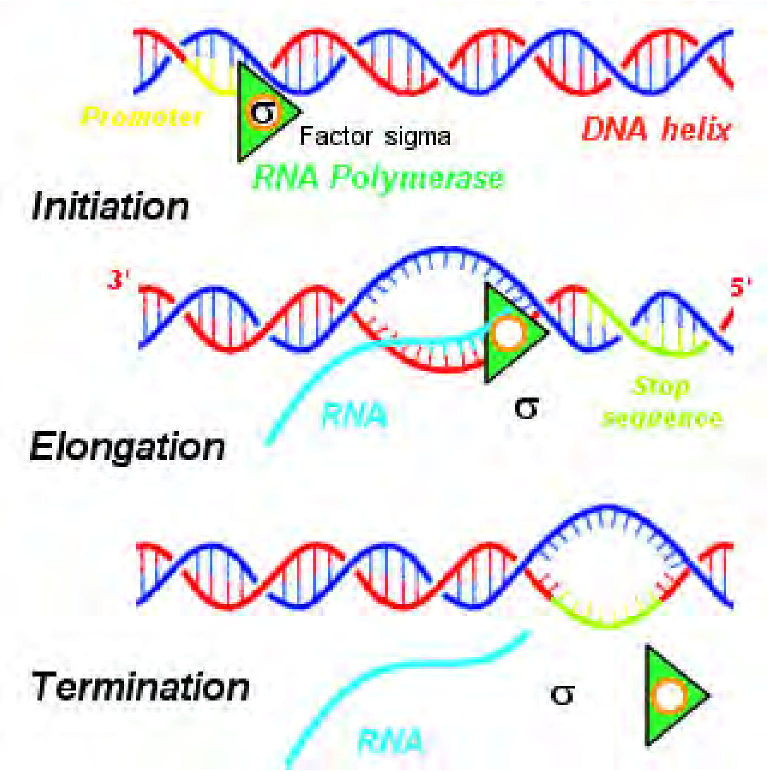


FIGURE 26.33

Formation of RNA from DNA

The process of amino acid assembly takes place in the ribosome. This structure consists of two subunits containing ribosomal RNA that enclose the mRNA and catalyze the formation of the amide linkages in the growing protein in a process known as **translation**. When protein synthesis is complete, the two subunits dissociate and release the completed protein chain.

The process of protein synthesis is fairly fast. Amino acids are added to the growing peptide chain at a rate of about 3-5 amino acids per second. A smaller protein (100-200 amino acids) can be produced in a minute or less.

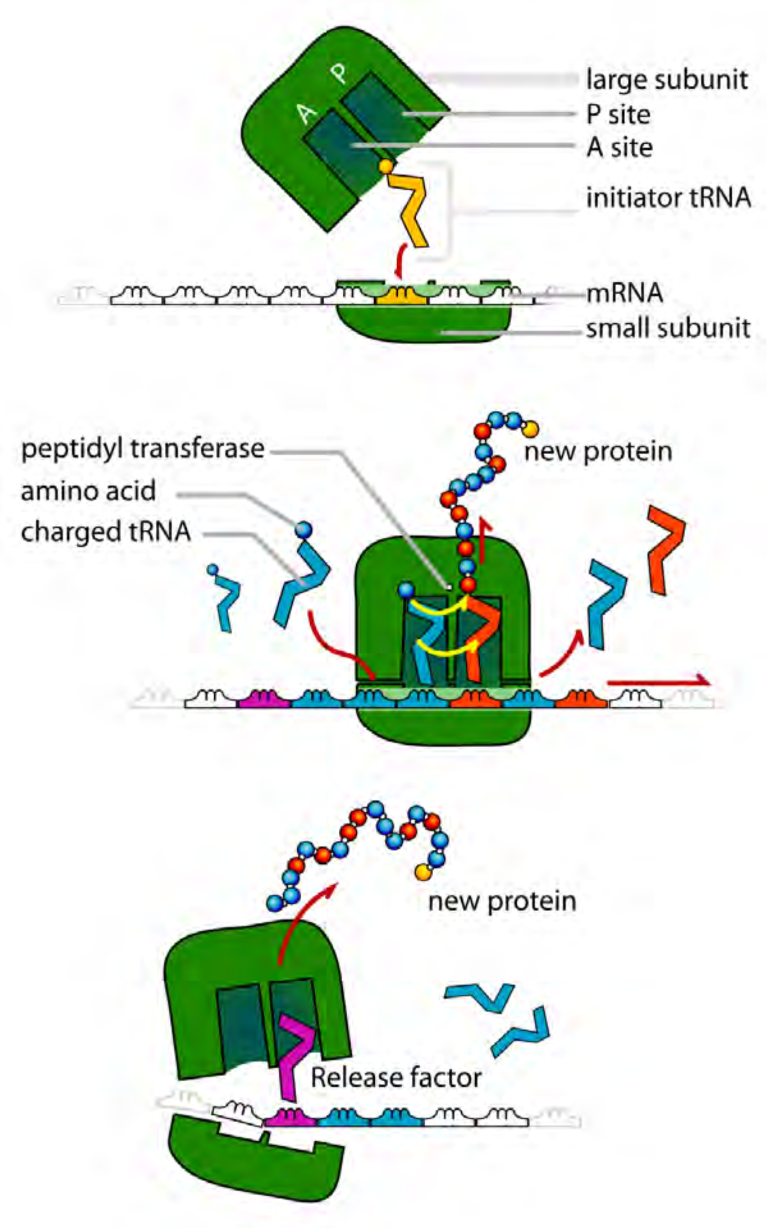


FIGURE 26.34

Role of ribosome in protein synthesis

Summary

- The steps in protein synthesis are described.

Practice

Watch the video at the link below and answer the following questions:

http://www.biostudio.com/demo_freeman_protein_synthesis.htm

1. What is the initiating amino acid?
2. How does the ribosome move when a new amino acid enters?
3. What happens to each tRNA after it delivers its amino acid?

Review

1. What is transcription?
2. What is translation?
3. What molecule gets the amino acid in the sequence at the proper time?

- **transcription:** The production of an mRNA strand from DNA.
- **translation:** Manufacture of proteins by the ribosome.

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