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1. The Science of Chemistry

The Scientific Method

Lesson Objectives

- Describe the steps involved in the scientific method.
- Appreciate the value of the scientific method.
- Recognize that in some cases not all the steps in the scientific method occur, or they do not occur in any specific order.
- Explain the necessity for experimental controls.
- Recognize the components in an experiment that represent experimental controls.

Introduction

"What hopes and fears does this scientific method imply for mankind? I do not think that this is the right way to put the question. Whatever this tool in the hand of man will produce depends entirely on the nature of the goals alive in this mankind. Once the goals exist, scientific method furnishes means to realize them. Yet it cannot furnish the very goals. The scientific method itself would not have led anywhere, it would not even have been born without a passionate striving for clear understanding." - Albert Einstein

Historical Comparisons

Introduction to Science

What is science? Is it a list of marvelous inventions and how they work? Or is it a list of theories about matter and energy and biological systems? Or is science a subject that you learn by carrying out activities in a laboratory? Science is all of these, but it is also something even more basic. Science is a method of thinking that allows us to discover how the world around us works.

To begin this study of one form of science, we will review the last 3,000 years in the history of human transportation, communication, and medicine. The following summary lists humankind's accomplishments in these areas during three periods in the last 3,000 years.

Transportation in 1000 B.C.

In 1000 B.C., people could transport themselves and their goods by walking, riding an animal, or by riding in a cart pulled by an animal. Crossing water, people could paddle a boat or have an animal walk beside the river and pull the boat. These methods of transportation required muscle power, either human muscles or animal muscles.

Figure 1: A horse-drawn Egyptian chariot. Chariots originated in Mesopotamia around 3000 B.C. *(Source:* http://commons.wikimedia.org/wiki/File:Egyptian_chariot, *Created by:* Joseph Bonomi, *License:* Public Domain)

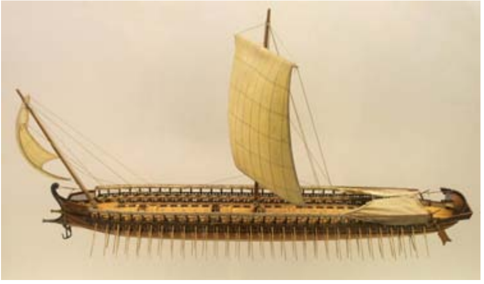


Figure 2: A photo of a wooden model of a Greek ship that has both sails and oars. *(Source:* http://commons.wikimedia.org/wiki/File:Model_of_a_greek_trireme, *License:* GNU Free Documentation)

A few societies had designed rowboats or sailboats, which used muscle power or the force of the wind to move the boat. These early means of transportation were very limited in terms of speed and therefore, also limited in terms of distances traveled. The sail and rowboats were used on rivers and inland seas, but were not ocean-going vessels.

Transportation in 1830

By the year 1830, people were still walking and riding in carts pulled by animals. Iron ore was moved along canals by animals pulling barges. American pioneers crossed the United States in covered wagons pulled by animals. Large cities had streetcars pulled by horses. Ocean crossing was accomplished in sailing ships. The only improvement in transportation was the addition of springs and padded seats to carts and wagons to make the ride less jolting. In the period from 1000 B.C. to 1830, a span of 2,830 years (about 100 generations of people), there were ***no significant changes*** in the mode of human transportation.

Figure 3: A covered wagon of the type used by pioneers to cross the US in the mid-1800s. *(Source:* http://commons.wikimedia.org/wiki/File:Wagon_train, *Created by:* Unknown, *License:* Public Domain)

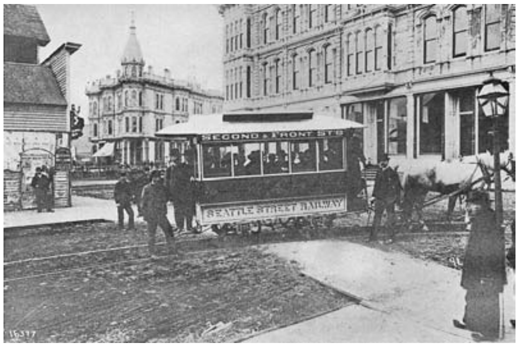


Figure 4: The first horse-drawn street car in Seattle, Washington in 1884. *(Source:* http://commons.wikimedia.org/wiki/File:Seattle_-_occidental_and_Yesler_-_1884, *Photo by:* Unknown, *License:* Public Domain)

Transportation in 1995

By the year 1995, steam engines, gasoline engines, automobiles, propeller-driven and jet engines, locomotives, nuclear-powered ships, and inter-planetary rocket ships were invented. In all industrialized countries, almost anyone could own an automobile and travel great distances in very short times.

In the mid-1800s, several months were required to travel from Missouri to California by covered wagon and the trip was made at considerable risk to the traveler's life. In 1995, an average family could travel this same distance easily in two days and in relative safety. An ordinary person in 1995 probably traveled a greater distance in one year than an ordinary person in 1830 did in an entire lifetime. The significant changes in the means of transportation in the 165 years between 1830 and 1995 (perhaps 5 generations) were phenomenal.

Figure 5: A modern jetliner.

(Source: http://commons.wikimedia.org/wiki/File:Conair, *Created by:* Bryan, *License:* CC-BY-SA)

Communication in 1000 B.C.

Essentially, people's only means of communicating over large distances (more than 15 miles) in 1000 B.C. was to send hand-carried messages. Some societies, for short distances, had developed the use of smoke signals, light signals, or drum signals, but these methods were useless for long distances. Since the means of communicating required hand-carried messages, the speed of communication was limited by the speed of transportation. Sending messages over distances of 1,000 miles could require several weeks and even then delivery was not guaranteed.

Figure 6: Shopping list chiseled on a rock.

(Source: CK-12, *Created by:* Richard Parsons, *License:* CC-BY-SA)

Communication in 1830

By the year 1830, people's means of communication over large distances was still the hand-carried message. While the paper and ink used to write the message had been improved, it still had to be hand-carried. In the United States, communication between New York and San Francisco required more than a month. When a new president was elected, Californians would not know who it was for a couple of months after the election. For a short period of time, the Pony Express was set up and could deliver a letter from St. Louis, Missouri to Sacramento, California in eleven days, which was amazing at the time. The means of communication in 1830 was essentially the same as in 1000 B.C.

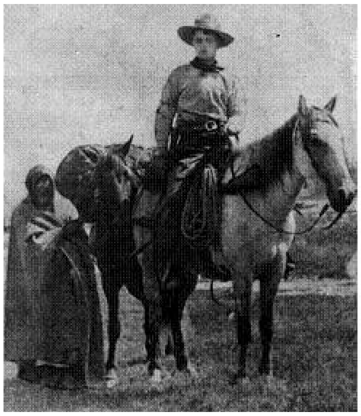


Figure 7: A pony express rider, circa 1861. *(Source:* http://commons.wikimedia.org/wiki/File:Pony_express, *Created by:* US National Archives and Records Administration, *License:* PD-US-Gov)

Communication in 1995

Figure 8: A modern cell phone.

(Source: http://www.pdphoto.org/, *Photo by:* PD-Photo.org, *License:* Public Domain)

By the year 1995, the telegraph, telephone, radio, television, optical fibers, and communication satellites were invented. People could communicate almost anywhere in the industrialized world instantaneously. Now, when a U.S. president is elected, people around the globe know the name of the new president the instant the last vote is counted. Astronauts communicate directly between the earth and the moon. An ordinary person in an industrialized country can speak with people around the world while simultaneously watching events occur in real time globally. There have been truly extraordinary changes in people's ability to communicate in the last 165 years.

Medical Treatment in 1000 B.C.

Medical treatment in 1000 B.C. consisted of a few natural herbs and some superstitious chants and dances. The most advanced societies used both sorcerers and herbalists for medical treatment. Some of the natural herbs helped the patient and some did not. Cleaning and bandaging wounds decreased opportunity for infection while some herbs such as sesame oil demonstrated moderate antiseptic properties. Dances, chants, incense burning, and magic spells were absolutely useless in curing illnesses. At some point in time, bloodletting was added to the physician's repertoire. Bloodletting was accomplished by cutting the patient and allowing the blood to drip out or by applying leeches (which doctors often carried with them). However, bloodletting was not helpful to the patient, and in many cases, it was harmful. Bloodletting was flourishing by 500 B.C. and was carried out by both surgeons and barbers. It wasn't until around 1875 that bloodletting was established as quackery. In those times, for an ordinary person, broken bones went unset and injuries like deep cuts or stab wounds were often fatal due to infection. Infant mortality was high and it was common for at least one child in a family die before adulthood. The death of the mother in childbirth was also quite common.

Figure 9: Physician letting blood from a patient. *(Source:* http://commons.wikimedia.org/wiki/File:Blood_letting, *Created by:* Maggie Black's den medeltida kokboken, *License:* Public Domain)

In the Middle Ages, knowledge of germs, hygiene, and contagion was non-existent. People who were seriously ill might have their disease blamed on the planets going out of line (astrology) or "bad odors," or retribution for sins, or an imbalance in body fluids. Cures could involve anything from magic spells, bleeding, sweating, and vomiting to re-balance bodily fluids. Between 1340 AD and 1348 AD, the Black Death (bubonic plague) was responsible for killing in the vicinity of half the population of Europe. The bacterium causing the disease was carried by fleas, but, of course, none of this was known by the physicians of the time. Efforts to stop the plague included burning incense to eliminate "bad odors," causing loud noises to chase the plague away (the constant ringing of bells or firing of canon), and a number of people used self-flagellation to attempt to cure the disease.

Medical Treatment in 1830

Medical treatment in 1830 remained in the form of natural herbs and bloodletting. During this time, the ability to set broken bones and to amputate limbs was also developed. Amputation saved many lives from infection and gangrene. Gangrene occurs when the blood supply to tissue is interrupted and the tissue dies. The dead tissue remains part of the body, invites infection, and causes death as the poisons from the rotting tissue are carried through the body. Once gangrene afflicted an arm or leg, the poison from the limb would eventually kill the patient. During the American Civil War (1861 - 1863), a common means of treatment for wounds in field hospitals was amputation. Along with amputation was the ability to cauterize wounds to stop bleeding.

Even though bloodletting did not help patients, it continued in use through 1830. There is a tale (which may or may not be true) that George Washington was suffering from pneumonia and his doctors removed so much blood trying to cure him that they actually caused his death.

Medical Treatment in 1995

By 1995, medical science had discovered chemical medicines, antiseptic procedures, surgery, and probably most important of all, vaccination . . . the ability to prevent disease rather than cure it after it had been contracted. Diseases that had killed and crippled hundreds of thousands of people in the past are seldom heard of today (polio, smallpox, cholera, bubonic plague, etc.). These diseases have been controlled by scientific understanding of their causes and carriers and by vaccination. Average life expectancy has nearly doubled in the last 165 years. Both infant mortality and death during childbirth rates have dropped to less than 25% of what they were in 1830.

Figure 10: Receiving a vaccination. (*Source:* http://phil.cdc.gov/phil_images/200301106/1/PHIL_1190_lores, *Created by:* US Dept. of Health and Human Services, *License:* PD-US-Gov)

Methods of Learning About Nature

Opinion, Authority, and Superstition

Why did humans make so little progress in the 2,800 years before 1830 and then such incredible progress in the 160 years after 1830?

Socrates (469 B.C. - 399 B.C.), Plato (427 B.C. - 347 B.C.), and Aristotle (384 B.C. - 322 B.C.) are among the most famous of the Greek philosophers. Plato was a student of Socrates and Aristotle was a student of Plato. These three were probably the greatest thinkers of their time. Aristotle's views on physical science profoundly shaped medieval scholarship and his influence extended into the Renaissance (14th century). Aristotle's opinions were the authority on nature until well into the 1300s.

Unfortunately, many of Aristotle's opinions were wrong. It is not intended here to denigrate Aristotle's intelligence; he was without doubt a brilliant man. It was simply that he was using a method for determining the nature of the physical world that is inadequate for that task. The philosopher's method was logical thinking, not making observations on the natural world. This led to many errors in Aristotle's thinking on nature. Let's consider just two of Aristotle's opinions as examples.

In Aristotle's opinion, men were bigger and stronger than women, and therefore, it was logical that men would have more teeth than women. Therefore, Aristotle concluded it was a true fact that men had more teeth than women. Apparently, it never entered his mind to actually look into the mouths of both genders and count their teeth. Had he done so, he would have found that men and women have exactly the same number of teeth.

In terms of physical science, Aristotle thought about dropping two balls of exactly the same size and shape but of different masses to see which one would strike the ground first. In his mind, it was clear that the heavier ball would fall faster than the lighter one and he concluded that this was a law of nature. Once again, he did not consider doing an experiment to see which ball fell faster. It was logical to him, and in fact, it still seems logical. If someone told you that the heavier ball would fall faster, you would have no reason to disbelieve it. In fact, it is not true and the best way to prove this is to try it. Eighteen centuries later, Galileo decided to actually get two balls of different masses, but with the same size and shape, and drop them off a building (legend says the Leaning Tower of Pisa), and actually see which one hit the ground first. When Galileo actually did the experiment, he discovered, by observation, that the two balls hit the ground at exactly the same time . . . Aristotle's opinion was, once again, wrong. In the 16th and 17th centuries, innovative thinkers were developing a new way to discover the nature of the world around them. They were developing a method that relied upon making observations of phenomena and insisting that their explanations of the nature of the phenomena corresponded to the observations they made. In order to do this, they had to overcome the opinions of the ancient Greeks, the authority of the church, and the superstitions of ordinary people.

Figure 11: Galileo dropping balls off the Leaning Tower of Pisa. (*Source:* http://commons.wikimedia.org/wiki/File:Leaning_tower_of_pisa, *Created by:* Softeis, *Modified by:* Richard Parsons, *License:* GNU Free Documentation)

In the opinion of the ancient Greeks, the earth was the center of the universe and did not move, while the sun, moon, planets, and stars revolved around the earth in orbits. The astronomer Ptolemy (around 150 A.D.) observed the positions of the planets and recognized that the positions where he observed the planets did not match up with the positions predicted by the orbits of the Greeks. Ptolemy designed new orbits that had circles within circles and complicated retrograde motion (planets moving backward in their orbits at certain times). His descriptions came closer but still could not accurately predict where the heavenly orbs would be on a given night. It wasn't until Nicolaus Copernicus (1473 - 1543) suggested a heliocentric (sun-centered) system that the positions of the planets came close to matching predictions. Copernicus was hesitant to publish his ideas - some say because he feared ridicule from his peers and others say because he feared persecution by the church - but eventually, he sent his work for publication just before his death.

The publication of Copernicus' heliocentric theory didn't seem to cause much controversy for the next 50 years until the idea was supported by a scientist named Giordano Bruno who was promptly prosecuted and burned at the stake by Cardinal Bellarmini in 1600. The most famous supporter of the Copernican system was Galileo Galilei (1564 - 1642) who had developed an improved telescope (1610) and turned it toward the sky. Galileo published a small work describing what he saw with his telescope and how his observations supported the Copernican theory. The book was banned by the church in 1616 and Galileo was instructed not to write about the subject any further. In 1632, Galileo published another work, again supporting the Copernican theory and was arrested by the church, prosecuted, and punished by house arrest for the remainder of his life.

But the method of learning by experimenting, observing, and hypothesizing had been launched and many scientists would not turn back. It should be mentioned that the supporters of the methods of opinion, authority, and superstition did not give and have not given up today. We still have "scientists" claiming that unsupported opinions are "facts" and we still have people deciding the "truth" about nature by voting on it. Nor has superstition died. You may remember from your history classes that the pilgrims of Massachusetts were still drowning and hanging women accused of being witches as late as 1693. It is easy to think that the people of those times were not very smart, and nowadays, no one would think that way. However, you should be aware that a student was suspended from school in Tulsa, Oklahoma in 1999 for "casting spells" and a substitute teacher in Florida was fired in 2008 for "wizardry" after performing a magic trick for his students.

The Scientific Method

Scientists frequently list the scientific method as a series of steps. Other scientists oppose this listing of steps because not all steps occur in every case and sometimes the steps are out of order. The scientific method is listed in a series of steps here because it makes it easier to study. You should remember that not all steps occur in every case nor do they always occur in order.

The Steps in the Scientific Method

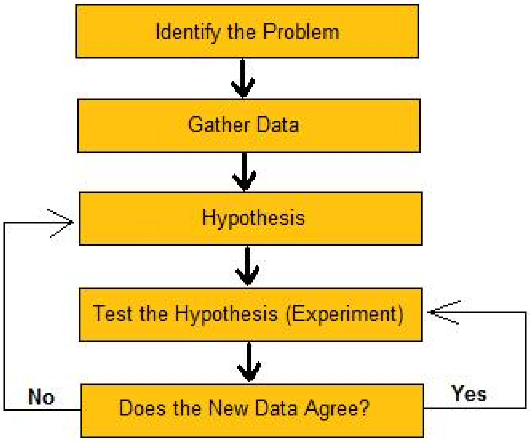
Step 1: Identify the problem or phenomenon that needs explaining. This is sometimes referred to as "defining the problem." This activity helps limit the field of observations.

Step 2: Gather and organize data on the problem. This step is also known as "making observations."

Step 3: Suggest a possible solution or explanation. A suggested solution is called a hypothesis.

Step 4: Test the hypothesis by making new observations.

Step 5: If the new observations support the hypothesis, you accept the hypothesis for further testing. If the new observations do not agree with your hypothesis, you discard the hypothesis, add the new data to your observations list, and return to step 3.



When the results of several experiments support the hypothesis, you might think that the work is finished. However, for a hypothesis to be useful, it must withstand repeated testing. Other scientists must be able to repeat the experiments using the same materials and conditions and get the same results. Scientists submit reports of research to other scientists, usually by publishing an article in a scientific journal, so the work can be verified.

An Example of the Scientific Method

Suppose you are required to maintain a large campfire and you are completely unfamiliar with the property of objects that makes them combustible (able to burn). The first step in the scientific method is to define the problem. ***What property of objects make them combustible?*** The next step is to gather data on the problem. So, you begin to collect objects at random and put them into the fire. You must keep good records of what objects were tried and whether or not they burned. Here's a list of organized data (observations).

Will Burn	**Won't Burn**
tree limbs	rocks
chair legs	bricks
pencils	marbles
baseball bat	hubcaps

The list of organized observations helps because now you can collect only the items on the "will burn" list and not waste the effort of dragging items that won't burn back to the fire. However, you would soon use up all the items on the "will burn" list and it is necessary to guess what property the "will burn" objects have that cause them to burn. If you had that answer, you could bring objects that may not be on the "will burn" list but that have the "will burn" property and keep the fire going.

The third step in the scientific method is to suggest a hypothesis. Your guess about what property the "will burn" objects have that makes them combustible is a hypothesis. Suppose you notice that all the items on the "will burn" list are cylindrical in shape and therefore, you hypothesize that "cylindrical objects burn". The fourth step in the scientific method is to test your hypothesis. To test this hypothesis, you go out and collect a group of objects that are cylindrical including iron pipes, soda bottles, broom handles, and tin cans. When these cylindrical objects are placed in the fire and most of them don't burn, you realize your hypothesis is not supported by these new observations. The new observations are the ***test*** , and your hypothesis has failed the test. When the new observations fail to support your hypothesis, you reject your original hypothesis, add your new data to the table, and make a new hypothesis based on the updated observations list. In the schematic diagram of the scientific method, a failed test returns the scientist to step 3, ***make a new hypothesis*** .

Will Burn	**Won't Burn**
tree limbs	rocks
chair legs	bricks
pencils	marbles
baseball bat	hubcaps
broom handle	iron pipes
	soda bottles
	tin cans

Suppose your new hypothesis is ***"wooden objects burn."*** You will find this hypothesis more satisfactory since all the wooden object you try will burn. Your confidence will grow that you have discovered a "law of nature." Even with your somewhat successful theory, you might be ignoring a large stack of old car tires, objects made of fabric or paper, or perhaps containers of petroleum. You can see that even though you are quite satisfied with your theory because it does the job you want it to do, you actually do not have a complete statement on the property of objects that make them burn. So it is with science.

You can see from this example that the "solution" does not become what we think of as a "fact," but rather becomes ***a tentatively accepted theory which must undergo continuous testing and perhaps adjustment*** . No matter how long a tentative explanation has been accepted, it can be discarded at any time if contradictory observations are found. As long as the theory is consistent with all observations, scientists will continue to use it. When a theory is contradicted by observations, it is discarded and replaced. Even though the terms *hypothesis*, *theory*, and *fact* are used somewhat carelessly at times, a theory will continue to be used while it is useful and will be called into question when contradictory evidence is found. Theories never become facts.

There is a common generalization about theories, which says that "theories are much easier to disprove than to prove." The common example given is a hypothesis that "all swans are white." You may observe a thousand white swans and every observation of a white swan supports your hypothesis, but it only takes a single observation of a black swan to disprove the hypothesis. To be an acceptable scientific hypothesis, observations that disprove the hypothesis must be possible. That is, if every conceivable observation supports the hypothesis, then it is not an acceptable scientific hypothesis. To be a scientific hypothesis, it must be possible to refute the concept.

Some Basic Terminology

- A **hypothesis** is a guess that is made early in the process of trying to explain some set of observations. There are scientists who object to calling a hypothesis a "guess". The primary basis for the objection is that someone who has studied the subject under consideration would make a much better guess than someone who was completely ignorant of the field. Perhaps we should say that a hypothesis is an "educated guess."
- A **theory** is an explanation that stands up to everyday use in explaining a set of observations. A theory is not proven and is not a "fact." A scientific theory must be falsifiable in order to be accepted as a theory.
- A **law** describes an observable relationship, that is, observations that occur with a predictable relationship to each other. It is only after experience shows the law to be valid that it is incorporated into the field of knowledge.

The Scientific Revolution

The explosion of achievement in the last 160 years was produced by using a new method for learning about nature. This sudden and massive achievement in understanding nature is called the **Scientific Revolution** and was produced using the **scientific method**.

The British historian, Herbert Butterfield, wrote a book called *The Origins of Modern Science*. In the preface to the book, Butterfield wrote:

The Revolution in science overturned the authority of not only the Middle Ages but of the ancient world . . . it ended not only in the eclipse of scholastic philosophy but in the destruction of Aristotelian physics. The Scientific Revolution outshines everything since the rise of Christianity and reduces the Renaissance and Reformation to the rank of mere episodes . . .

The beginning of the 17th century is known for the drastic changes that occurred in the European approach to science during that period and is known as the Scientific Revolution. This term refers to a completely new era of academic thought in which medieval philosophy was abandoned in favor of innovative methods offered by Galileo and Newton.

Science is best defined as a careful, disciplined, logical search for knowledge about any and all aspects of the universe, obtained by examination of the best available evidence and always subject to correction and improvement upon discovery of better evidence. What's left is magic. And it doesn't work. - - - James Randi.

What is an Experiment

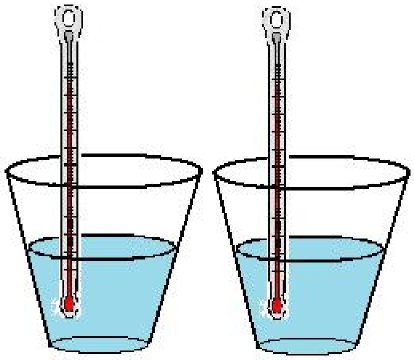
The scientific method requires than observations be made. Sometimes, the phenomenon we wish to observe does not occur in nature or if it does, it is inconvenient for us to observe. Therefore, it is more successful for us to cause the phenomenon to occur at a time and place of our choosing. When we arrange for the phenomenon to occur at our convenience, we can have all our measuring instruments present and handy to help us make observations, and we can control other variables. Causing a phenomenon to occur when and where we want it and under the conditions we want is called an ***experiment*** . When scientists conduct experiments, they are usually seeking new information or trying to verify someone else's data. Classroom experiments often demonstrate and verify information that is already known but new to the student. When doing an experiment, it is important to set up the experiment so that relationships can be seen clearly. This requires what are called **experimental controls**.

Experimental Controls

Suppose a scientist, while walking along the beach on a very cold day following a rainstorm, observed two pools of water in bowl shaped rocks near each other. One of the pools was partially covered with ice while the other pool had no ice on it. The unfrozen pool seemed to be formed from seawater splashing up on the rock from the surf, but the other pool was too high for sea water to splash in, so it was more likely to have been formed from rainwater.

The scientist wondered why one pool was partially frozen and not the other since both pools were at the same temperature. By tasting the water (not a good idea), the scientist determined that the unfrozen pool tasted saltier than the partially frozen one. The scientist thought perhaps salt water had a lower freezing point that fresh water and she decided to go home and try an experiment to see if this were true. So far, the scientist has identified a question, gathered a small amount of data, and suggested a hypothesis. In order to test this hypothesis, the scientist will conduct an experiment during which she can make accurate observations.

For the experiment, the scientist prepared two identical containers of fresh water and added some salt to one of them. A thermometer was placed in each liquid and these were put in a freezer. The scientist then observed the conditions and temperatures of the two liquids at regular intervals.



Data Table 1: The Temperature and Condition of Fresh Water in a Freezer

Time (minutes)	0	5	10	15	20	25	30
Temperature, °C	25	20	15	10	5	0	-5
Condition	Liquid	Liquid	Liquid	Liquid	Liquid	Frozen	Frozen

Data Table 2: The Temperature and Condition of Salt Water in a Freezer

Time (minutes)	0	5	10	15	20	25	30
Temperature, °C	25	20	15	10	5	0	-5
Condition	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Frozen

The scientist found support for the hypothesis from this experiment; fresh water freezes at a higher temperature than salt water. Much more support would be needed before the scientist would be confident of this hypothesis. Perhaps she would ask other scientists to verify the work.

In the scientist's experiment, it was necessary that she freeze the salt water and fresh water under exactly the same conditions. Why? The scientist was testing whether or not the presence of salt in water would alter its freezing point. It is known that changing air pressure will alter the freezing point of water. In order to conclude that the presence of the salt was what caused the change in freezing point, all other conditions had to be identical. The presence of the salt is called the **experimental variable** because it is the only thing allowed to change in the two trials. The fresh water part of the experiment is called the **experimental control**. In an experiment, there may be only one variable and the purpose of the control is to guarantee that there is only one variable. The "control" is identical to the "test" except for the experimental variable. Unless experiments are controlled, the results are not valid.

Suppose you wish to determine which brand of microwave popcorn leaves the fewest unpopped kernels. You will need a supply of various brands of microwave popcorn to test and you will need a microwave oven. If you used different brands of microwave ovens with different brands of popcorn, the percentage of unpopped kernels could be caused by the different brands of popcorn, but it could also be caused by the different brands of ovens. Under such circumstances, the experimenter would not be able to conclude confidently whether the popcorn or the oven caused the difference. To eliminate this problem, you must use the same microwave oven for every test. By using the same microwave oven, you control the number of variables in the experiment.

What if you allowed the different samples of popcorn to be cooked at different temperatures? What if you allowed longer heating periods? In order to reasonably conclude that the change in one variable was caused by the change in another specific variable, there must be no other variables in the experiment. All other variables must be kept constant.

Errors in the Use of the Scientific Method

The scientific method requires the observation of nature and correspondence between the suggested explanation and the observations. That is, the hypothesis must explain ***all*** the observations. Therefore, the scientific method can only work properly when the data (observation list) is not biased. There are several ways in which a biased set of data can be produced. It is always possible for anyone to make an error in observation. A balance can be misread or numbers can be transposed when written down. That is one of the reasons that experiments are run several times and the observations made over and over again. It is also possible that an unrecognized error is present and produces the same error in every experiment. For example, a scientist may be attempting to test normal rainwater, but unknown to him a nearby factory is sending soluble substances out of their smoke stack and the material is contaminating the scientist's samples. In such a case, the scientist's samples would yield false observations for normal rainwater. Other scientists reproducing the experiment would collect uncontaminated samples and find different results. Multiple testing of the experiment would determine which set of data was flawed. Failing to apply appropriate experimental controls would certainly bias data.

There are also dishonest mistakes that occur when the experimenter collects only supporting data and excludes contradictory observations. There have even been scientists who faked observations to provide support for his/her hypothesis. The attractions of fame and fortune can be hard to resist. For all these reasons, the scientific method requires that experimental results be published and the experiment be repeated by other scientists.

Summary

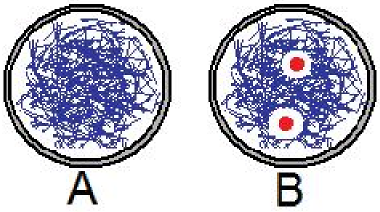
- Before the development of the scientific method, mankind made only slight achievements in the areas of transportation, communication and medicine.
- Use of the scientific method allowed mankind to make significant achievements in transportation, communication, and medicine.
- The scientific method has been much more successful than the methods of superstition, opinion, and authority.
- The steps in the scientific method are:

1. Identify the problem.
2. Gather data (make observations).
3. Suggest a hypothesis.
4. Test the hypothesis (experiment).
5. Continue testing or reject the hypothesis and make a new one.

- Experimental controls are used to make sure that the only variables in an experiment are the ones being tested.

Review Questions

Use the following paragraph to answer questions 1 and 2. In 1928, Sir Alexander Fleming was studying Staphylococcus bacteria growing in culture dishes. He noticed that a mold called Penicillium was also growing in some of the dishes. In the sketch at right, Petri dish A represents a dish containing only Staphylococcus bacteria. The red dots in dish B represent Penicillium colonies. Fleming noticed that a clear area existed around the mold because all the bacteria grown in this area had died. In the culture dishes with the mold, no clear areas were present. Fleming suggested that the mold was producing a chemical that killed the bacteria. He decided to isolate this substance and test it to see if it would kill bacteria. Fleming grew some Penicillium mold in a nutrient broth. After the mold grew in the broth, he removed all the mold from the broth and added the broth to a culture of bacteria. All the bacteria died.



1. Which of the following statements is a reasonable expression of Fleming's hypothesis? **(Beginning)**

A. Nutrient broth kills bacteria.

B. There are clear areas around the Penicillium mold where Staphylococcus doesn't grow.

C. Mold kills bacteria.

D. Penicillium mold produces a substance that kills Staphylococcus.

E. Without mold in the culture dish, there were no clear areas in the bacteria.

2. Fleming grew Penicillium in broth, then removed the Penicillium and poured the broth into culture dishes containing bacteria to see if the broth would kill the bacteria. What step in the scientific method does this represent? **(Beginning)**

A. Collecting and organizing data

B. Making a hypothesis

C. Testing a hypothesis by experiment

D. Rejecting the old hypothesis and making a new one

E. None of these

3. A scientific investigation is NOT valid unless every step in the scientific method is present and carried out in the exact order listed in this chapter. **(Beginning)**

A. True B. False

4. Which of the following words is closest to the same meaning as ***hypothesis*** ? **(Beginning)**

A. fact

B. law

C. formula

D. suggestion

E. conclusion

5. Why do scientists sometimes discard theories? **(Beginning)**

A. the steps in the scientific method were not followed in order

B. public opinion disagrees with the theory

C. the theory is opposed by the church

D. contradictory observations are found

E. congress voted against it

Gary noticed that two plants which his mother planted on the same day that were the same size when planted were different in size after three weeks. Since the larger plant was in the full sun all day and the smaller plant was in the shade of a tree most of the day, Gary believed the sunshine was responsible for the difference in the plant sizes. In order to test this, Gary bought ten small plants of the size and type. He made sure they had the same size and type of pot. He also made sure they have the same amount and type of soil. Then Gary built a frame to hold a canvas roof over five of the plants while the other five were nearby but out in the sun. Gary was careful to make sure that each plant received exactly the same amount of water and plant food every day.

6. Which of the following is a reasonable statement of Gary's hypothesis? **(Beginning)**

A. Different plants have different characteristics.

B. Plants that get more sunshine grow larger than plants that get less sunshine.

C. Plants that grow in the shade grow larger.

D. Plants that don't receive water will die.

E. Plants that receive the same amount of water and plant food will grow the same amount.

7. What scientific reason might Gary have for insisting that the container size for the all plants be the same? **(Intermediate)**

A. Gary wanted to determine if the size of the container would affect the plant growth.

B. Gary wanted to make sure the size of the container did not affect differential plant growth in his experiment.

C. Gary want to control how much plant food his plants received.

D. Gary wanted his garden to look organized.

E. There is no possible scientific reason for having the same size containers.

8. What scientific reason might Gary have for insisting that all plants receive the same amount of water everyday? **(Intermediate)**

A. Gary wanted to test the effect of shade on plant growth and therefore, he wanted to have no variables other than the amount of sunshine on the plants.

B. Gary wanted to test the effect of the amount of water on plant growth.

C. Gary's hypothesis was that water quality was affecting plant growth.

D. Gary was conserving water.

E. There is no possible scientific reason for having the same amount of water for each plant every day.

9. What was the variable being tested in Gary's experiment? **(Intermediate)**

A. the amount of water

B. the amount of plant food

C. the amount of soil

D. the amount of sunshine

E. the type of soil

10. Which of the following factors may be varying in Gary's experimental setup that he did not control? **(Intermediate)**

A. individual plant variation

B. soil temperature due to different colors of containers

C. water loss due to evaporation from the soil

D. the effect of insects which may attack one set of plants but not the other

E. All of the above are possible factors that Gary did not control

11. When a mosquito sucks blood from its host, it penetrates the skin with its sharp beak and injects an anti-coagulant so the blood will not clot. It then sucks some blood and removes its beak. If the mosquito carries disease-causing microorganisms, it injects these into its host along with the anti-coagulant. It was assumed for a long time that the virus of typhus was injected by the louse when sucking blood in a manner similar to the mosquito. But apparently this is not so. The infection is not in the saliva of the louse, but in the feces. The disease is thought to be spread when the louse feces come in contact with scratches or bite wounds in the host's skin. A test of this was carried out in 1922 when two workers fed infected lice on a monkey taking great care that no louse feces came into contact with the monkey. After two weeks, the monkey had NOT become ill with typhus. The workers then injected the monkey with typhus and it became ill within a few days.

Why did the workers inject the monkey with typhus near the end of the experiment? **(Challenging)**

A. to prove that the lice carried the typhus virus

B. to prove the monkey was similar to man

C. to prove that the monkey was not immune to typhus

D. to prove that mosquitoes were not carriers of typhus

E. the workers were mean

12. Eijkman fed a group of chickens exclusively on rice whose seed coat had been removed (polished rice or white rice). The chickens all developed polyneuritis (a disease of chickens) and died. He fed another group of chickens unpolished rice (rice that still had its seed coat). Not a single one of them contracted polyneuritis. He then gathered the polishings from rice (the seed coats that had been removed) and fed the polishings to other chickens that were sick with polyneuritis. In a short time, the birds all recovered. Eijkman had accurately traced the cause of polyneuritis to a faulty diet. For the first time in history, a food deficiency disease had been produced and cured experimentally. Which of the following is a reasonable statement of

Eijkman's hypothesis? **(Intermediate)**

A. Polyneuritis is a fatal disease for chickens.

B. White rice carries a virus for the disease polyneuritis.

C. Unpolished rice does not carry the polyneuritis virus.

D. The rice seed coat contains a nutrient that provides protection for chickens against polyneuritis.

E. None of these is a reasonable statement of Eijkman's hypothesis.

Further Reading / Supplemental Links

http://learner.org/resources/series61.html'''

The ***learner.org*** website allows users to view streaming videos of the Annenberg series of chemistry videos. You are required to register before you can watch the videos but there is no charge. The website has two videos that apply to this lesson. One is a video called ***The World of Chemistry*** that relates chemistry to other sciences and daily life. Another video called ***Thinking Like Scientists*** relates to the scientific method. The audience on the video is young children but the ideas are full grown.

Website with lessons, worksheets, and quizzes on various high school chemistry topics.

- Lesson 1-2 is on the scientific method.

http://www.fordhamprep.org/gcurran/sho/sho/lessons/lesson12.htm

Website of the James Randi Foundation. James Randi is a staunch opponent of fake science.

http://www.randi.org/site/

Websites dealing with the history of the scientific method.

http://www.historyguide.org/earlymod/lecture10c.html

http://www.history.boisestate.edu/WESTCIV/science/

Vocabulary

hypothesis	A proposal intended to explain a set of observations.
theory	A hypothesis that has been supported with repeated testing.
law	A relationship that exists between specific observations.
experiment	The act of conducting a controlled test or observations.
scientific method	A method of investigation involving observation to generate and test hypotheses and theories.
superstition	An irrational belief that an object, action, or circumstance not logically related to an event influences its outcome.

Review Answers

1. D

2. C

3. B

4. D

5. D

6. B

7. B

8. A

9. D

10. E

11. C

12. D

Chemistry in History

Lesson Objectives

- Give a brief history of how chemistry began.
- State the Law of Conservation of Mass.
- Explain the concept of a model, and create simple models from observations.

Introduction

During medieval times, a group of people known as alchemists began looking for ways to transform common metals, such as lead, copper and iron, into gold. Can you imagine how much money you would make if you could go to the store, buy some iron nails, and turn them into gold? You'd be rich in no time!

Alchemists experimented with many different kinds of chemicals, searching for what they termed the "philosopher's stone" – a legendary substance that was necessary for the transformation of common metals into gold. We now know that there is no such thing as a "philosopher's stone," nor is there any chemical reaction that creates gold from another metal. We know this because we now have a much better understanding of the matter in our universe. Nevertheless, it was thanks to those early alchemists that people became interested in chemistry in the first place.

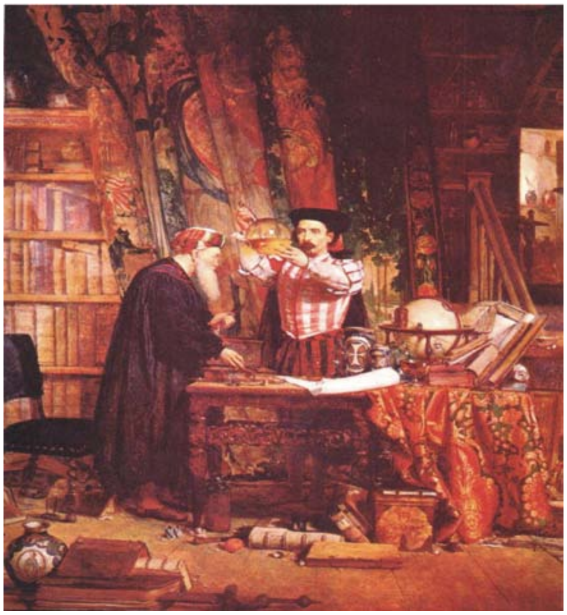


Figure 1: Early alchemists were often regarded as wizards. Their main goal was to discover the "philosopher's stone" – a substance that could turn common metals into gold.

(*Source:* http://upload.wikimedia.org/wikipedia/commons/3/3a/William_Fettes_Douglas_-_The_Alchemist.jpg, *License:* GNU-FDL)

"Chemistry" was Derived from an Arabic Word

When we speak of "chemistry," we refer to the modern, scientific study of matter and the changes that it undergoes. Still, it's no coincidence that the word "chemistry," looks a lot like the word "alchemy." Early **al**chemists were commonly known as 'chemists,' and over time, people started referring to their work, particularly the more legitimate forms of it, as *chemistry.* While it may seem strange, in many ways, it's appropriate that our word for the present-day study of matter comes from the early practice of alchemy. That's because a lot of the techniques and equipment fundamental to modern chemistry were actually developed by early alchemists.

The origin of the word "alchemy" is something of a mystery. Certainly, early Europeans borrowed "alchemy" from the Arabic word *"al-kimia,"* meaning "the art of transformation" (of course, the transformation that alchemists were primarily concerned with involved the creation of gold). Most of what we know today about early alchemy is based on translations of Arabic documents. That's because Muslim alchemists were some of the first to keep careful notes about their experiments.

Even though our earliest records of alchemy come from the Arab Empire, some scholars believe that Arabs adopted alchemy and the word "al-kimia" from the Greeks around 650 AD. The Greeks, in turn, may have learned of alchemy from the Egyptians. *Khem* was an ancient name for Egypt, and Egyptians were known, in early history, as masters of the art of working with gold. It's very likely that "al-kimia" is actually a distorted version of the word "al-kimiya," meaning "the art of the land of Khem," or the art of Egypt.

The Origins of Chemistry was Multi-Cultural

While the word "chemistry" may have its roots in Egypt, chemical experimentation seems to have been prevalent all over the world, even as early as the 5th century BC. In China, the goal of the early alchemists was largely to find "the elixir of life" – a potion that could cure all diseases and prevent death. Ironically, many of these early elixirs involved mixtures of mercury and arsenic salts, both of which are extremely poisonous. In fact, it's rumored that several Chinese emperors actually died after drinking "elixirs of life." Despite never finding a magical potion that could cure all diseases, early Chinese chemists did discover many new chemicals and chemical reactions, including those used in fireworks and gunpowder.

Figure 2: Jiajing Emperor, rumored to have died after drinking poison he believed to be "the elixir of life."

(*Source:* http://upload.wikimedia.org/wikipedia/en/b/b2/Jiajing.jpg, *License:* Public Domain)

Like the Chinese, alchemists from India were interested in some of the medical benefits of different chemicals. In addition to medicine, Indian alchemists were fascinated by metals and metallurgy. Early Indian writings contain methods for extracting and purifying metals like silver, gold and tin from ores that were mined out of the ground. Moreover, it was alchemists from the Indian subcontinent who first realized that by mixing molten metals with other chemicals they could produce materials that had new and beneficial properties. For example, Wootz steel (also known as Damascus steel) was a substance discovered in Sri Lanka around 300 AD. It was made by mixing just the right amounts of molten iron, glass and charcoal, but it became famous because it could be used to produce swords, legendary for their sharpness and strength in battle.

Around the same time that Wootz steel was being developed in Sri Lanka, Egyptian and Greek alchemists were beginning to experiment as well. Much of the alchemy in this part of the world involved work with colors and dyes and, of course, the transformation of common metals into gold and silver. Greek philosophers like Plato and Aristotle, however, were also responsible for the important suggestion that the universe could be explained by unified natural laws. As you will discover in the next section, modern chemistry relies on the study of these universal laws. Of course, modern scientific laws are slightly different than the laws that either Plato or Aristotle had in mind. In general, scientific laws are determined by careful experimentation and observation, whereas the early Greeks believed that their "natural laws" could be deduced through philosophy.

Medieval Europeans were similarly fascinated by alchemy. Unfortunately, many alchemists in Europe borrowed ideas from the more mystical of the Arabian alchemists and, as a result, European alchemy quickly became associated with wizardry, magic, and the search for the "philosopher's stone." It wasn't until the late 17th century that European chemists began applying the scientific method. Robert Boyle (1627 – 1691) was the first European to do so, using quantitative experiments to measure the relationship between the pressure and the volume of a gas. His use of the scientific method paved the way for other European scientists and helped to establish the modern science of chemistry.

About 100 years after Robert Boyle first performed his experiments, a French scientist by the name of Antoine Lavoisier (1743 – 1794) employed the scientific method when he carefully measured the masses of reactants and products before and after chemical reactions. Since the total mass (or quantity of material) never changed, Lavoisier's experiments led him to the conclusion that mass is neither created nor destroyed. This is known as the **Law of Conservation of Mass**. Lavoisier is often called "The Father of Modern Chemistry" because of his important contribution to the study of matter. After the success of Lavoisier's work, experiments involving careful measurement and observation became increasingly popular, leading to a rapid improvement in our understanding of chemicals and chemical changes. In fact, by the end of the 19th century, chemical knowledge had increased so much that practically everyone had stopped searching for the "philosopher's stone"… everyone, that is, except for wizards like Harry Potter!

Figure 6: Antoine Lavoisier, "The Father of Modern Chemistry." (*Source:* http://upload.wikimedia.org/wikipedia/commons/6/6c/Antoine_lavoisier_color.jpg, *License:* Public Domain)

What Chemists Do

You might wonder why the study of chemistry is so important if you can't use it to turn iron into gold or to develop a potion that will make you immortal. Why didn't chemistry die when scientists like Boyle and Lavoisier proved alchemy was nothing but a hoax? Well, even though we can't use chemistry to make gold or to live forever, modern chemistry is still very powerful! There may be no such thing as a potion that cures **all** diseases, but many chemists today are developing cures for *specific* diseases. In fact, chemists are working on everything from treatments for HIV/AIDS to medications for fighting cancer.

Modern chemists study not only chemicals that can help us, but also chemicals that can hurt us. For example, environmental chemists test the air, soil, and water in our neighborhoods to make sure that we aren't exposed to heavy metals (such as mercury or lead) or chemical pesticides. Moreover, when environmental chemists do find dangerous substances, they use their knowledge of chemistry to clean up the contamination. Similarly, every time you buy packaged food from the grocery store, you can be sure that many tests have been done by chemists to make sure that those foods don't contain any toxins or carcinogens (cancer-causing chemicals).

Chemists are also responsible for creating many important materials we use today. Other technologies rely on chemistry as well. In fact, your flat-screen LCD TV, the cubic zirconium ring on your finger, and the energy efficient LED lights in your home are all thanks to our improved understanding of chemistry.

Figure 7: Energy efficient LED lights can be used to brighten your home for a party or a holiday.

(*Source:* http://www.flickr.com/photos/theyoungthousands/1978086180/, *License:* CC-BY)

So, how do chemists accomplish all of these remarkable achievements? Unlike many of the early alchemists that experimented by randomly mixing together anything that they could find, today's chemists use the scientific method. This means that chemists rely on both careful observation and well-known physical laws. By putting observations and laws together, chemists develop what they term *models.* Models are really just ways of predicting what will happen given a certain set of circumstances. Sometimes these models are mathematical, but other times, they are purely descriptive.

A model is any simulation, substitute, or stand-in for what you are actually studying. A good model contains the essential variables that you are concerned with in the real system, explains all the observations on the real system, and is as simple as possible. A model may be as uncomplicated as a sphere representing the earth or billiard balls representing gaseous molecules, or as complex as mathematical equations representing light.

Over time, scientists have used many different models to represent atoms. As our knowledge of the atom changed, so did the models we use for them. Our model of the atom has progressed from an "indestructible sphere," to a dish of "plum pudding," to a "nuclear model."

Hypotheses and theories comprise some ideas that scientists have about how nature works but of which they are not completely sure. These hypothesis and theories are **models** of nature used for explaining and testing scientific ideas.

Chemists make up models about what happens when different chemicals are mixed together, or heated up, or cooled down, or compressed. Chemists invent these models using many observations from experiments in the past, and they use these models to predict what might happen during experiments in the future. Once chemists have models that predict the outcome of experiments reasonably well, those working models can help to tell them what they need to do to achieve a certain desired result. That result might be the production of an especially strong plastic, or it might be the detection of a toxin when it's present in your food.

Science is not the only profession whose members make use of the scientific method. The process of making observations, suggesting hypotheses, and testing the hypotheses by experiment is also a common procedure for detectives and physicians.

Lesson Summary

- The word "chemistry" comes from the Arabic word "al-kimia" meaning "the art of transformation."
- Chemistry began as the study of alchemy. Most alchemists were searching for the "philosopher's stone," a fabled substance that could turn common metals into gold.
- Chinese alchemists were particularly interested in finding "the elixir of life."
- In India, much early chemistry focused on metals.

- The scientific method involves making careful observations and measurements and then using these measurements to propose hypotheses (ideas) that can, in turn, be tested with more experiments.
- Robert Boyle and Antoine Lavoisier employed the “scientific method,” thereby bringing about the rise of modern chemistry.
- The Law of Conservation of Mass states that mass is neither created nor destroyed.
- Modern chemists perform experiments and use their observations to develop models. Models then help chemists to understand and predict the results of future experiments. Models also help chemists to design new materials and cures for diseases.

Review Questions

1. Where does the word “chemistry” come from? **(Beginning)**

2. Consider the following data about John’s study habits, and grades: **(Challenging)**

Hours spent studying	Grade earned on the test
0	20%
5	40%
10	60%
15	80%

a. Propose a qualitative (words, but no math) model that might describe how the length of time John spends studying relates to how well he does on the test?

b. If John wants to earn 92% on his next test, should he study for about 6 hours, 9 hours, 12 hours, or 18 hours? Justify your answer.

c. If John studies for 7 hours, do you think he will score 15%, 97%, 68%, or 48%? Justify your answer.

3. Helen wanted to know if lemon juice chemically reacts with tea to lighten its color. So Helen added 25 drops of lemon juice to 250 mL of tea and observed that the tea colored lightened significantly. Helen wanted to make sure that the color lightening was the result of a chemical reaction and not the result of dilution. Which one of the following activities should Helen carry out to serve as a control for this experiment? **(Challenging)**

A. Helen should add 25 drops of orange juice to another 250 mL sample of tea.

B. Helen should add 25 drops of distilled water to another 250 mL sample of tea.

C. Helen should add 25 drops of lemon juice to a 250 mL sample of distilled water.

D. Helen should add 25 drops of tea to a 250 mL sample of lemon juice.

E. Helen should add 25 drops of tea to a 250 mL sample of tea.

Vocabulary

hypothesis	A proposal intended to explain a set of observations.
theory	A hypothesis that has been supported with repeated testing.
law	A relationship that exists between specific observations.
scientific method	A method of investigation involving observation to generate and test hypotheses and theories.

chemistry	The science of the composition, structure, properties, and reactions of matter.

Review Answers

1. The word chemistry comes from the Arabic word “al-kimia,” meaning “the art of transformation.”

2.

a. The more John studies, the better he does on the test.

b. According to the model in answer (a), the more John studies the better he does. Since John earned an 80% when he studied for 15 hours, he will have to study for *more* than 15 hours in order to score a 92%. Of the possible options, only 18 hours satisfies this criterion, thus John should study for 18 hours.

c. According to the model in answer (a), the more John studies, the better he does on the test. If John studies 7 hours, he will have studied longer than 5 hours, but shorter than 10 hours. Therefore his grade should be higher than 40%, but lower than 60%. Of the possible options, only 48% satisfies this criterion, thus John should expect approximately 48% if he studies for 7 hours.

3. B

Chemistry is a Science of Materials

Lesson Objectives

- Give examples of chemical properties a scientist might measure or observe in a laboratory.
- Explain the difference between a physical change and a chemical change, giving examples of each.
- Identify the situations in which mass can be converted to energy and energy can be converted to mass.

Introduction

In the last chapter we discussed some of the goals of early alchemists and some of the roles of chemists today. What you might have noticed is that while methods of chemical experimentation have improved and while knowledge of chemical properties has increased, chemistry in the 21st century AD and chemistry in the 5th century BC were both concerned with the question: How does matter change from one form to another? Can we predict the properties of matter? And how can we control these properties in order to use them to our advantage? Chemistry is essentially concerned with the science of matter and materials. Therefore, we’ll begin our discussion of chemistry by considering some of the chemical materials that have been important both to early civilizations and to society today.

Ancient Materials Versus Modern Materials

Before humans had any understanding of chemistry, they used whatever they could find in the world around them. One type of material that was easily accessible to early civilizations, at least in small amounts, was metal. Native gold, silver, and copper, and compounds of tin and iron can all be found occurring naturally in cliffs and caves (in fact, the discovery of natural gold in El Dorado County, California is what lead to the great Gold Rush of 1849) and, as a result, these metals became very important to people in early times.

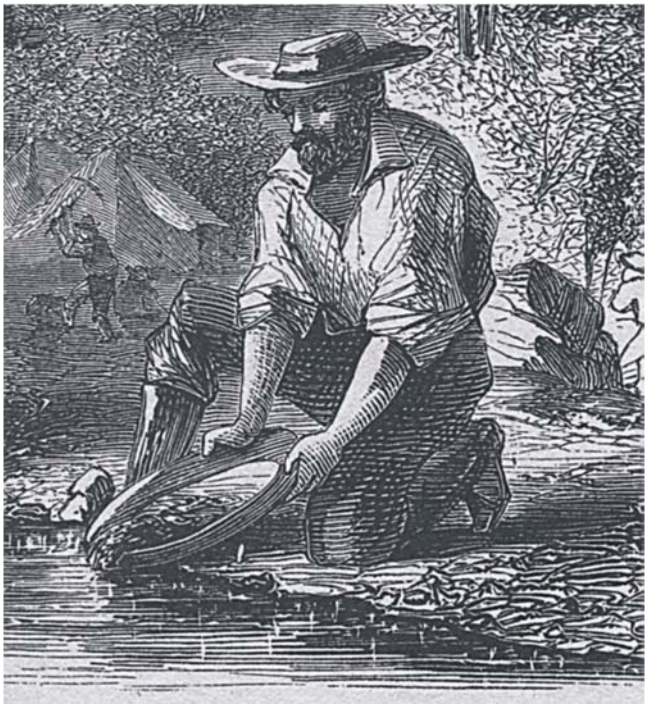


Figure 1: Panning for gold. Gold occurs naturally in some rocks, and as the river wears these rocks away, it picks up the pieces of gold with it.

(*Source:* http://en.wikipedia.org/wiki/Image:Panning_on_the_Mokelumne.jpg, *License:* Public Domain)

Many ancient civilizations fashioned tools, jewelry, and weapons out of metal that they scavenged from rocks around them. After a while, however, people discovered that by mixing naturally occurring metals with other substances, they could create new materials that often had superior properties.

Some of the oldest materials produced by man include mixtures (or more specifically *solutions*) of metals known as *alloys*. One of the earliest alloys ever discovered was bronze. Bronze can be made by heating chunks of tin and copper until they are liquid and then mixing the two pure metals together. Bronze was very important to early civilizations because it was more resistant to rust than iron, harder than copper, and could hold an edge and be sharpened to create tools and weapons. Another alloy, produced early in the history of civilization, is steel. As you learned in an earlier section, steel is an alloy of iron and carbon (or charcoal). Steel, particularly Wootz steel (which required a special technique that involved the addition of glass), was especially strong, and could be fashioned into very sharp edges, perfect for swords. Another old material whose production was known to early civilizations is brass. Again, brass is an alloy, made of two pure metals, copper, and zinc. Early Romans knew that if they melted copper, and a zinc ore known as calamine together, they could produce brass, which was both shiny like gold, and resistant to rust. Brass was a common material used to make coins.

Figure 2: Ancient bronze artifacts (*Source:* http://en.wikipedia.org/wiki/Bronze, *License:* Public Domain)

What you might notice about these “old” materials is that they are mainly alloys. At the time when bronze and brass and steel were discovered, people didn’t know much about the composition of matter or about how matter was assembled on a microscopic scale. As a result, inventing materials was largely a matter of trial and error. Towards the end of the 19th century, however, scientists were beginning to understand the make-up of matter, and this understanding led to new insight into how to develop materials with desirable properties.

One of the huge breakthroughs in recent history has been the discovery of plastic and plastic products. Initially, plastic was made by chemically modifying cellulose, a naturally occurring chemical found in plants. As chemical knowledge developed, however, scientists began to realize that plastics had special properties because, on a microscopic scale, they were composed of thousands of tiny chains of molecules all tangled up together. Scientists reasoned that if they altered the chemicals in these chains, but still managed to keep the chains intact, they could make *new* plastics with *new* properties. Thus began the plastic revolution!

Figure 3: Some common household items made of plastic.

(*Source:* http://upload.wikimedia.org/wikipedia/en/b/b2/Plastic_household_items.jpg, *License:* GNU-FDL)

Semiconductors are another class of “new” materials whose development is largely based on our improved understanding of chemistry. Because scientists know how matter is put together, they can predict how to fine-tune the chemical composition of a semiconductor in order to make it absorb light and act as a solar cell or emit light and act as a light source. We’ve come a long way from our early days of producing bronze and steel. Nevertheless, as our understanding of chemistry improves, we will be able to create even more useful materials than we have today.

Chemists Study the Properties of Matter

Hopefully at this point you are fully convinced of how important and useful the study of chemistry can be. You may, however, still be wondering exactly *what* it is that a chemist does. Chemistry is the study of matter and the changes that matter undergoes. In general, chemists are interested in both characteristics that you can test and observe, like a chemical’s smell or color, and characteristics that are far too small to see, like what the oxygen you breath in or the carbon dioxide you breath out looks like under a microscope 1,000 times more powerful than any existing in the world today.

Wait a minute… how can a chemist *know* what oxygen and carbon dioxide look like under a microscope that doesn't even exist? What happened to the *scientific method?* What happened to relying on *observations* and *careful measurements*? In fact, because chemists *can't* see the underlying structure of different materials, they have to rely on the scientific method even more! Chemists are a lot like detectives. Suppose a detective is trying to solve a murder case – what does she do? Obviously, the detective starts by visiting the site of the crime and looking for evidence. If the murderer has left enough clues behind, the detective can piece together a theory explaining what happened. Even though the detective wasn't at the crime scene when the crime was committed and even though the detective didn't actually see the murderer kill the victim, with the right evidence, the detective can be pretty sure he or she knows how it took place. It's the same with chemistry. When chemists go into the laboratory, they collect evidence by making measurements. Once they've collected enough clues from the properties that they *can* observe, they use that evidence to piece together a theory explaining the properties that they *can't* observe – the properties that are too small to see.

Figure 4: Being a chemist is a lot like being a detective. You have to collect evidence, and then use that evidence to develop theories explaining processes and structures that are too small to see. (*Source:* http://www.chem1.com/acad/webtext/pre/chemsci.html, *License:* CC-BY-SA)

What kinds of properties do chemists actually measure in the laboratory? Well, you can probably guess a few. Imagine that you go to dinner at a friend's house and are served something that you don't recognize – what types of observations might you make to determine exactly *what* you've been given? You might smell the food. You might note the color of the food. You might try to decide whether the food is a liquid or a solid because if it's a liquid, it's probably soup or a drink. The temperature of the food could be useful if you wanted to know whether or not you'd been served ice cream! You could also pick up a small amount of food with your fork and try to figure out how much it weighs – a light dessert might be something like an angel cake, while a heavy dessert is probably a pound cake. The quantity of food you've been given might be a clue too. Finally, you might want to know something about the food's texture – is it hard and granular like sugar cubes, or soft and easy to spread, like butter?

Believe it or not, the observations you are likely to make when trying to identify an unknown food are very similar to the observations that a chemists makes when trying to learn about a new material. Chemists rely on smell, color, state (that is, whether it is a solid, liquid or gas), temperature, volume, mass (which is related to weight, as you'll discover in a later section), and texture. There is, however, one property you might use to learn about a food, but that you should *definitely* not use to learn about a chemical - taste!

In *The Atomic Theory,* you'll see exactly how measurements of certain properties helped early scientists to develop theories about the chemical structure of matter on a scale much smaller than they could ever hope to see. You'll also learn how these theories, in turn, allow us to make predictions about new materials that we haven't even created yet.

Chemists Study of How and Why Matter Changes

In the last section, we discussed the properties of matter and how scientists use these properties to deduce certain facts about the structure of matter. However, if chemists only studied properties such as color and smell, they would only be collecting half of the evidence. While the properties of matter can tell us a lot, so too can the *changes* that matter undergoes. Let's return to our food example. Suppose you've been served a slice of cake that you've noticed is cold to the touch. You might guess that you're dealing with an ice cream cake. But then again, maybe it's just a normal cake that's been kept in the freezer. Can you think of some way to tell between a frozen slice of ice cream cake and a frozen slice of regular cake? Well, one possibility is to wait for a while and see whether your slice melts. If the slice melts, it was an ice cream cake, and if it doesn't, it was just regular cake. In this case, you aren't observing a *property,* but rather a *change in a* *property.* The property being changed in the example is state. Nevertheless, you can learn a lot about the nature of your food by observing the change.

Figure 5: Is this an ice cream cake, or a regular cake? One way to find out would be to wait and see if it melts – although that might make a mess!

(*Source:* http://en.wikipedia.org/wiki/Image:Culinique_Ice_Cream_Cake.jpg, *License:* GNU-FDL)

Similarly, chemists learn a lot about the nature of matter by studying the changes that matter can undergo. Chemists make a distinction between two different *types* of changes that they study – *physical changes* and *chemical changes.* **Physical changes** are changes that *do not* alter the identity of a substance. Some types of physical changes include:

- Changes of state (changes from a solid to a liquid or a gas and vice versa)
- Separation of a mixture
- Physical deformation (cutting, denting, stretching)
- Making solutions (special kinds of mixtures)

When you have a jar containing a mixture of pennies and nickels and you sort the mixture so that you have one pile of pennies and another pile of nickels, you have not altered the identity of either the pennies or the nickels – you've merely separated them into two groups. This would be an example of a physical change. Similarly, if you have a piece of paper, you don't change it into something other than a piece of paper by ripping it up. What was paper before you starting tearing is still paper when you're done. Again, this is an example of a physical change.

You might find it a little harder to understand why changes in state are physical changes. Until we discuss chemicals in terms of the smaller units (atoms and molecules) that make them up, it probably won't be clear to you why freezing a substance or boiling a substance is only a physical change.

Figure 6: When snowmen melt away on a warm day, it's an example of a physical change.

(*Source:* http://www.flickr.com/photos/zanastardust/417759177/, *License:* CC-BY-SA)

For now, though, you just have to trust that changes in state are physical changes. If you're ever in doubt, remember this: when a lake freezes in the winter, the water doesn't disappear or turn into something else – it just takes on a new form. Liquid water and solid water (ice) are just different forms of the substance we know as water. For the most part, physical changes tend to be reversible – in other words, they can occur in both directions. You can turn liquid water into solid water through cooling; you can also turn solid water into liquid water through heating.

The other type of change that chemists are concerned with is **chemical change.** A chemical change occurs when one substance is turned into an entirely new substance as a result of a chemical reaction. Again, as we learn more about chemicals, and what chemicals look like, the meaning of a chemical change and the distinction between a chemical change and a physical change will become more obvious. For now, realize that chemicals are made up of tiny units known as atoms. Some of these atoms are bonded (or "glued") together, but during a chemical change, some of the bonds are broken and new bonds are formed.

You're probably wondering how you know when a chemical change has occurred. Sometimes it can be pretty tricky to tell, but there are several evidences of chemical changes to look for. There has probably been a chemical change if:

- A change in color has occurred
- Light, heat or sound has been given off from the material itself
- A precipitate (a solid formed when two liquids are mixed) has appeared
- A gas has been produced (detected by bubbling or a new odor)

Figure 7: Fireworks are examples of chemical changes. This should be obvious based on all of the light, heat, and sound that they produce.

(*Source:* http://en.wikipedia.org/wiki/Image:Fireworks_in_monterrey.jpg/, *License:* Public Domain)

Chemical changes are frequently harder to reverse than physical changes. One good example of a chemical change is burning paper. In contrast to the act of ripping paper, the act of burning paper actually results in the formation of new chemicals (carbon dioxide and water, to be exact). Notice that whereas ripped paper can be at least partially reassembled, burned paper cannot be "unburned." In other words, burning only goes in one direction. The fact that burning is not reversible is another good indication that it involves a chemical change.

Chemists Study the Interchange of Matter and Energy

Chemists are concerned with the properties of matter, and the changes that matter undergoes. For the most part, though, the changes that chemists are interested in are either physical changes, like changes in state, or chemical changes like chemical reactions. In either case, Lavoisier's Law of Conservation of Mass, applies. In both physical and chemical changes, matter is neither created nor destroyed. There is, however, another type of change that matter can undergo that actually disobeys Lavoisier's Law of Conservation of Mass, and that is the conversion of matter into energy, and vice versa.

Back when Lavoisier was studying chemistry, the technology didn't exist that would allow scientists to turn matter into energy and energy into matter, but it can be done. This is the concept that Einstein proposed in his famous equation $E = mc^2$. (This equation states that the energy in a given amount of matter is equal to the mass of the matter times the speed of light squared.) Chemical reactions don't involve changing measureable amounts of energy to mass or mass to energy. Mass-energy conversion is, however, important in chemistry that deals with radioactivity and particularly in the production of electricity by nuclear power plants.

Lesson Summary

- Some of the earliest materials invented by humans were *alloys* such as bronze, steel, and brass.
- With improved understanding of chemistry comes the ability to design new and useful materials, like plastics and semiconductors.
- Chemists can't actually see the underlying structure of most materials. As a result, they measure properties that they can see or observe and use this evidence to develop theories that explain how chemicals are organized on a sub-microscopic (smaller than you can see with a microscope) scale.
- Some of the physical properties that scientists observe pertain to state (solid, liquid or gas), temperature, volume, mass, and texture.
- Chemists also study the *changes* that different materials undergo; this can give them valuable information about the chemicals involved.
- There are two types of changes that are important in chemistry – physical changes and chemical changes.
- Physical changes are changes that do not alter the identity of a substance; they are usually reversible.
- Chemical changes are changes that occur when one substance is turned into another substance as a result of a chemical reaction. They are usually difficult to reverse.
- It is also possible to change matter into energy and energy into matter.

Review Questions

1. Name the two types of changes that chemists are primarily interested in. **(Beginning)**

2. Decide whether each of the following statements is true or false. **(Beginning)**

a. Plastics were developed in Rome around 300 AD

b. Bronze is an example of an alloy

c. Plastic is an example of an alloy

d. Brass is an example of an alloy

3. Match the following alloys with their common names. **(Beginning)**

1.	Bronze	a. tin and copper
2.	Brass	b. is not an alloy
3.	Plastic	c. iron and carbon
4.	Tin	d. copper and zinc
5.	Steel	e. is not an alloy

4. Decide whether each of the following statements is true or false. **(Intermediate)**

a. Physical changes are typically accompanied by a color change

b. A burning campfire is an example of a chemical change

c. When you heat your house with coal, the coal undergoes a chemical change

d. When you drop a plate, and it breaks, the plate undergoes a physical change

5. In each of the following examples, determine whether the change involved is a physical change or a chemical change. **(Intermediate)**

a. Flattening a ball of silly putty

b. Combining a bowl of cherries and a bowl of blueberries

c. Boiling water

d. Cooking an egg

6. Judy has two beakers filled with clear liquids, and she needs to know whether the liquid in the first beaker is the same as the liquid in the second beaker. In which scenario does Judy use physical properties to answer her question, and in which scenario does Judy use changes in chemical properties to answer her question? **(Intermediate)**

a. Judy smells the two liquids and notices that the liquid in the first beaker has a strong odor, while she can't smell the liquid in the second beaker at all.

b. Judy mixes some table salt into the first beaker and notices that a white precipitate forms. She then mixes some table salt into the second beaker, but nothing happens.

Vocabulary

alloy	A solution (or a special kind of mixture), in which at least one of the components is a metal.
physical change	Changes that do not alter the identity of the substance.

chemical change	A change that occurs when one substance is turned into an entirely new substance as a result of a chemical reaction.

Review Answers

1. Chemical changes and physical changes

2.

a. F b. T c. F d. T

3.

1. a
2. d
3. e
4. e
5. c

4.

a. F b. T c. T d. T

5.

a. physical b. physical c. physical d. chemical

6. Both A and B represent chemical changes.

Matter

Lesson Objectives

- Define matter and explain how it is composed of building blocks known as “atoms.”
- Distinguish between mass and weight.

Introduction

We are all familiar with matter. The definition of matter is anything that has mass and volume (takes up space). For most common objects that we deal with every day, it is fairly simple to demonstrate that they have mass and take up space. You might be able to imagine, however, the difficulty for people several hundred years ago to demonstrate that air has mass and volume. Air (and all other gases) are invisible to the eye, have very small masses compared to equal amounts of solids and liquids, and are quite easy to compress (change volume). Without sensitive equipment, it would have been difficult to convince people that gases are matter. Today, we can measure the mass of a small balloon when it is deflated and then blow it up, tie it off, and measure its mass again to detect the additional mass due to the air inside. The mass of air, under room conditions, that occupies a one quart jar is approximately 0.0002 pounds. This small amount of mass would have been difficult to measure in times before balances were designed to accurately measure very small masses. Later, scientists were able to compress gases into such a small volume that the gases turned into liquids, which made it clear that gases are matter.

On the other hand, when you add heat to an object, the temperature of the object increases, but even the most sensitive balance cannot detect any difference in mass between an object when cold and when hot. Heat does not qualify as matter.

The Material in the Universe

Knowing that planets, solar systems, and even galaxies are made out of matter doesn't bring us any closer to understanding what matter is. Up until the early 1800s, people didn't really understand matter at all. They knew that there were "things" in the world that they could pick up and use, and that some of these "things" could be turned into other "things." For example, someone who found a piece of copper could shape it into a necklace or melt it together with zinc to make brass. What people didn't know, though, was how all of these "things" were related. If they had, the alchemists probably wouldn't have wasted so much time trying to convert common metals into gold. You'll understand why by the time you're finished with this section. Even though the universe consists of "things" as wildly different as ants and galaxies, the matter that makes up all of these "things" is composed of a very limited number of building blocks.

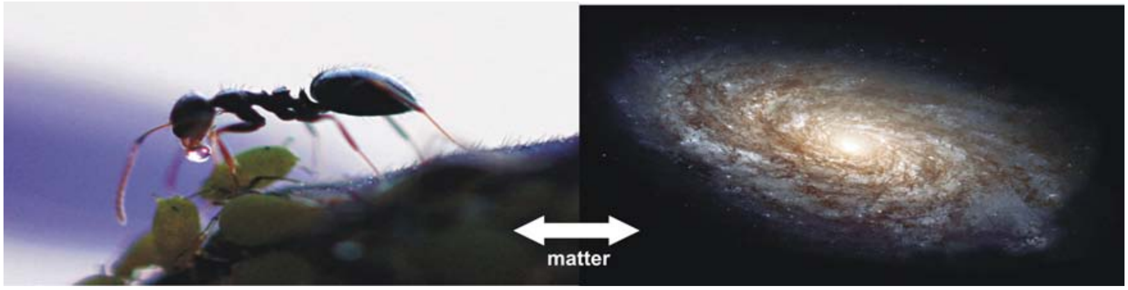


Figure 1: Everything from an ant to an entire galaxy is composed of matter.

(*Sources:* http://en.wikipedia.org/wiki/Image:Ant_Receives_Honeydew_from_Aphid.jpg, *License:* GNU-FDL; http://en.wikipedia.org/wiki/Image:NGC_4414_%28NASA-med%29.jpg, *License:* Public Domain)

These building blocks are known as atoms, and so far, scientists have discovered or created a grand total of 117 different types of atoms. Scientists have given a name to each different type of atom. A substance that is composed of only one type of atom is called an element. Each element, therefore, has its own name; it also has its own symbol. The "periodic table" is a way of summarizing all of the different atoms that scientists have discovered. Each square in the periodic table contains the symbol (a capital letter or a capital letter followed by a lower case letter) for one of the elements.

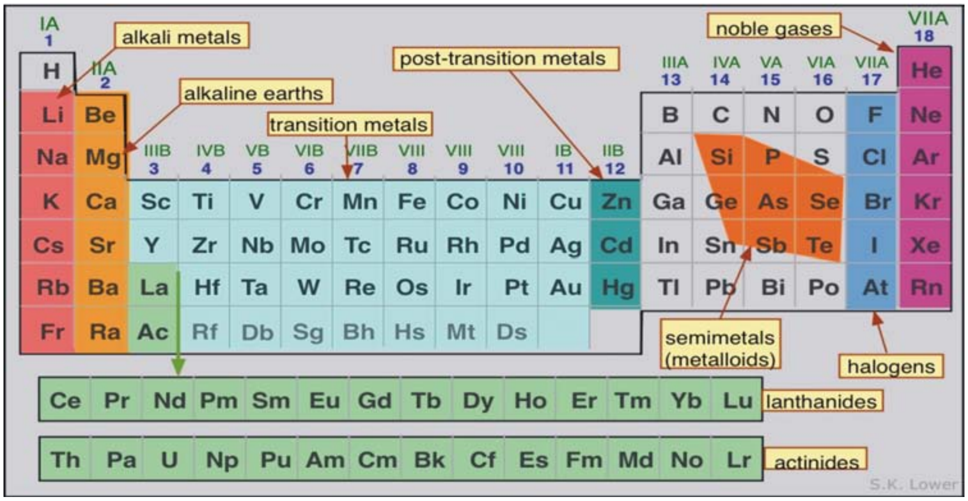


Figure 2: The Periodic Table.

(*Source:* http://www.chem1.com/acad/webtext/intro/AT.html, *License:* CC-SA)

At this point, what should amaze you is that all forms of matter in our universe are made with only 117 different building blocks. In some ways, it's sort of like cooking a gourmet, five-course meal using only three ingredients! How is it possible? To answer that question, you have to understand the ways in which different elements are put together to form matter. The most important method that nature uses to organize atoms into matter is the formation of molecules. Molecules are groups of two or more atoms that have been bonded together. There are millions of different ways to bond atoms together, which means that there are millions of different possible molecules. Each of these molecules has its own set of chemical properties, and it's these properties with which chemists are most concerned. You will learn a lot more about atoms and molecules, including how they were discovered, in a later part of the textbook. Figure 3, however, gives you a preview of some of the common molecules that you might come in contact with on a daily basis.

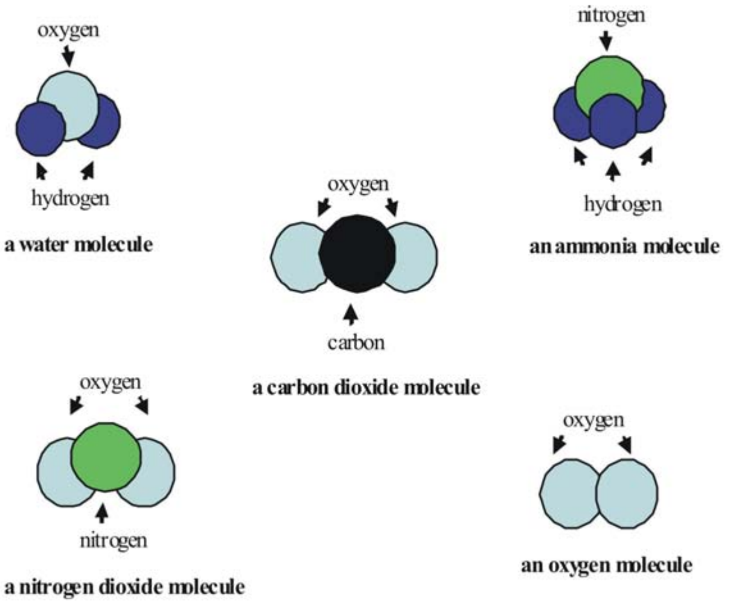


Figure 3: Some common molecules and the atoms that they are made from.

(*Source: Created by:* Sharon Bewick, *License:* CC-BY-SA)

Now back to the question of why alchemists had trouble making gold out of other common metals. Most naturally occurring metals, including gold, iron, copper, and silver are *elements.* Look carefully at the periodic table in Figure 3. Do you see the symbol Au? Au is the symbol for gold. Gold is one of the 117 different types of atoms – it's one of nature's building blocks. Take another look at the periodic table. Do you see the symbol Fe? Fe is the symbol for iron. Again, that means that iron is an element, or a type of atom. In fact, copper (Cu), tin (Sn), and silver (Ag) are all elements. In other words, alchemists were trying to convert one type of element, or building block, into another type of element, and that just can't be done by chemical means.

Chemical reactions can turn elements into molecules, molecules into other molecules, and molecules back into elements. Chemical reactions **cannot,** however, turn one type of element into another type of element. The only way to do that is through what are known as *nuclear* reactions, and nuclear reactions require advanced technical equipment that wasn't around in the days of the alchemists. It's like building a house. You can make a house by cementing together bricks, stones, and wood, just like you can make a molecule by bonding together different types of atoms. You can also get your bricks, stones, and wood back by taking the house apart just like you can get your atoms back by breaking the molecule down. No matter how hard you try, though, you can't turn bricks into stones, or bricks into wood. Converting common metals like copper into gold or iron into gold would be like turning bricks into stones or bricks into wood – it's simply not possible.

Matter Has Mass and Occupies Space

So far we've decided that the entire universe is composed of matter, which is in turn composed of atoms. Frequently, though, chemists want to know *how much* matter they actually have. To figure this out they rely on two fundamental properties of matter. All matter in the universe, from a teaspoon of salt to the Pacific Ocean, has mass and occupies space. When scientists measure how much space is taken up by a certain quantity of matter, they are measuring the objects *volume.* Obviously, the volume of the Pacific Ocean is a lot larger than the volume of a teaspoon of salt. Unfortunately, while volume is an important property, and plays an important role in a lot of different chemical experiments, volume is not the best way to determine how much matter you have.

Typically we think that the bigger something is, the more there is in it. That's certainly true a lot of the time in our everyday lives. If you pour yourself two cups of coffee in the morning, you'll be drinking twice as much coffee as you would have if you'd only poured yourself a single cup. Unfortunately, any time that we compare volumes in this way, we are making two assumptions that aren't always true in chemical experiments. First, we are assuming constant temperature. That's important, because the amount of space taken up by a certain quantity of matter depends on the temperature of that matter. In general, heating something up causes it to expand, and cooling something down causes it to contract. Secondly, when you compare volumes in everyday life, you are almost always comparing volumes of the same material. You can compare two cups of coffee to one cup of coffee, but how do you compare two cups of coffee to one cup of ice cream? It really doesn't make sense. Volume is not a good way to determine the quantity of matter that you have.

If you can't use volume to figure out how much matter you've got, what can you use? It turns out that the best way to determine quantities of matter is to use a measure known as *mass.* The mass of an object doesn't change with temperature, which makes it a lot easier to determine how much stuff you're dealing with, especially when you don't know what the temperature is or when the temperature keeps changing. Another good thing about mass is that an atom of a particular element always has the same mass (Strictly speaking that's not entirely true because of what are known as isotopes, but you won't need to worry about that now). For example, an atom of gold always has a mass of about 197 *atomic mass units or daltons.* Atomic mass units are units that we use to measure mass, just like a mile is a unit that we use to measure distance, and an hour is a unit that we use to measure speed. Even when atoms are bonded together into molecules, the individual atoms have the same mass, meaning that by adding up all of the masses of the atoms in a molecule, it's fairly easy to figure out the mass of the molecule itself. You'll eventually learn how to do this.

The Difference Between Mass and Weight

One typical mistake that students make when learning about mass for the first time is confusing mass with weight. Again, this confusion is largely due to the fact that, in everyday English, we frequently use the word "weight" when we actually *mean* "mass." For example, when you say "I want to lose weight," what you really *mean* is, "I want to lose mass." In science, the word "weight" has a very specific definition that is different from what you might expect. Do not confuse the everyday meaning of the word "weight" with the scientific meanings of the word "weight."

Figure 4: The type of balance a chemist might use to measure the mass of an object.

(*Source:* http://upload.wikimedia.org/wikipedia/commons/5/59/Analytical_balance_mettler_ae-260.jpg, *License:* Public Domain)

In science, **mass** is an intrinsic ("built-in") property of matter. The mass of an atom is the same regardless of the temperature or the other atoms that are bonded to it.

Similarly, the mass of an atom doesn't change depending on where it is. The mass of an atom is the same on Earth as it would be on the moon, or on Jupiter, or in the middle of space. Weight, on the other hand, does change with location. An object that weighs 240 pounds on earth would weigh about 40 pounds on the moon and that same object in a spaceship far away from any large mass would weigh zero. In all three cases, however, the object would have exactly the same mass.

Figure 5: With no large mass nearby, this spaceship is weightless. (*Source:* CK-12 Foundation, *License:* SA-BY-CC)

In science, **weight** is a measurement of how strongly gravity pulls on an object. Weight depends on both the mass of the object and the force of gravity the object is experiencing. That's why your weight changes depending on where you're standing. In each case, your mass will be the same, but the force of gravity on Earth is different than the force of gravity on the moon, or on Jupiter and, as a result, your weight is different too. The force of gravity, however, doesn't change significantly on the surface of Earth. In other words, the force of gravity in California is approximately the same as the force of gravity in Australia. As a result, as long as you stick to the surface of the Earth, the more massive an object is, the more it weighs.

Lesson Summary

- All physical objects are made of matter.

- Matter itself is composed of tiny building blocks known as “atoms.” There are only 117 different types of atoms known to man.
- Frequently, atoms are bonded together to form “molecules.”
- All matter has mass and occupies space.
- Volume is a measure of how much space an object occupies. Volume is not a good measure of how much matter makes up any given object.
- Mass is an intrinsic property of matter that does not depend on temperature, location, or the way in which the matter is organized (how the atoms are bonded) As a result, mass is an excellent measure of how much matter is in any given object.
- “Mass” and “weight” have two very different scientific meanings.
- “Mass” only depends on how much matter is in an object. “Weight,” on the other hand, depends on how strongly gravity pulls on an object.

Review Questions

1. What is matter? **(Beginning)**

2. In this chapter, we’ll learn about atoms, which are the building blocks of all matter in the universe. As of 2007, scientists only know of 117 different types of atoms. How do you think it’s possible to generate so many different forms of matter using only 117 types of building blocks? **(Beginning)**

3. Which do you think has more matter, a cup of water or a cup of mercury? Explain. **(Beginning)**

4. Decide whether each of the following statements is true or false. **(Beginning)**

a. Mass and weight are two words for the same concept.

b. Molecules are bonded together to form atoms.

c. Alchemists couldn’t make gold out of common metals because gold is an element.

d. The symbol for Gold in the periodic table is Gd.

5. Would you have more mass on the moon or on Earth? **(Challenging)**

6. Would you have more weight on the moon or on Earth? The force of gravity is stronger on the Earth than it is on the moon. **(Intermediate)**

7. Match the following terms with their meaning. **(Beginning)**

1 Mass	a. a measure of the total quantity of matter in an object
2 Volume	b. a measure of how strongly gravity pulls on an object
3 Weight	c. a measure of the space occupied by an object

8. For the following statements, circle all of the options that apply: **(Intermediate)**

Mass depends on…

a. the total quantity of matter

b. the temperature

c. the location

d. the force of gravity

Volume depends on…

a. the total quantity of matter

b. the temperature

c. the object's shape (independent of size)

d. the object's size (independent of shape)

Weight depends on…

a. the total quantity of matter

b. the temperature

c. the location

d. the force of gravity

Further Reading / Supplemental Links

Website with lessons, worksheets, and quizzes on various high school chemistry topics.

- Lesson 1-4 is on the Classification of Matter.
- Lesson 1-5 is on Physical and Chemical Properties and Changes.

http://www.fordhamprep.org/gcurran/sho/sho/lessons/lesson14.htm

Vocabulary

matter	Anything of substance that has mass and occupies space.
atom	The basic building block of all matter. There are 117 known types of atoms. While atoms can be broken down into particles known as electrons, protons and neutrons, this is very difficult to do.
element:	A type of atom. There are 117 known elements.
molecule	Two or more atoms bonded together. Specific molecules, like water, have distinct characteristics.
Periodic Table	A way of summarizing all the different atoms that scientists have discovered. Each square in the periodic table contains the symbol for one of the elements.
mass	An intrinsic property of matter that can be used to measure the quantity of matter present in a sample.
weight	A measurement of how strongly gravity pulls on an object.
volume	A measurement of how much space a substance occupies.

Review Answers

1. Matter is anything of substance that has mass and occupies space.

2. You can combine them in millions of different ways, etc.

3. Mercury is much more dense than water, so a cup of mercury has a lot more mass, which translates to a lot more matter.

4.

a. F b. F c. T d. F

5. You would have the *same* mass on both the moon and Earth.

6. You would have *more* weight on Earth.

7.

1. a

2. c

3. b

8.

Mass depends on…

a. only

Volume depends on…

a., b., and d.

Weight depends on…

a., c., and d

Energy

Lesson Objectives

- Define heat and work.
- Distinguish between kinetic energy and potential energy.
- State the law of conservation of matter and energy.

Introduction

Just like matter, energy is something that we are all familiar with and use on a daily basis. Before you go on a long hike, you eat an *energy* bar; every month, the *energy* bill is paid; on TV, politicians argue about the *energy* crisis. But have you ever wondered what energy really is? When you plug a lamp into an electric socket, you see energy in the form of light, but when you plug a heating pad into that same socket, you only feel warmth. When you eat a bowl of spaghetti, the energy it provides helps you to function throughout the day, but when you eat five bowls of spaghetti, some of that energy is turned into body fat.

If you stop to think about it, energy is very complicated. Still, we use energy for every single thing that we do, from the moment we wake up to the moment we go to sleep. Without energy, we couldn't turn on lights, we couldn't brush our teeth, we couldn't make our lunch, and we couldn't travel to school. In fact, without energy, we couldn't even wake up, because the moment our bodies stop processing energy, we die! Although we all use energy, very few of us understand how we use it.

Ability to Do Work or Produce Heat

When we speak of *using* energy, we are really referring to *transferring* energy from one place to another. When you use energy to throw a ball, you transfer energy from your body to the ball, and this causes the ball to fly through the air. When you use energy to warm your house, you transfer energy from the furnace to the air in your home, and this causes the temperature in your house to rise. Although energy is used in many kinds of different situations, all of these uses rely on energy being transferred in one of two ways. Energy can be *transferred* as *heat* or as *work*. Unfortunately, both "heat" and "work" are common words, so you might think that you already know their meanings. In science, the words "heat" and "work" have very specific definitions that are different from what you might expect. Do not confuse the everyday meanings of the words "heat" and "work" with the scientific meanings.

When scientists speak of *heat*, they are referring to energy that is transferred from an object with a higher temperature to an object with a lower temperature as a result of the temperature difference. Heat will "flow" from the hot object to the cold object until both end up at the same temperature. When you cook with a metal pot, you witness energy being transferred in the form of heat. Initially, only the stove element is hot – the pot and the food inside the pot are cold. As a result, heat moves from the hot element to the cold pot. After a while, enough heat is transferred from the element to the pot, raising the temperature of the pot and all of its contents.

Figure 1: Energy is transferred as heat from the hot stove element to the cooler pot until the pot and its contents become just as hot as the element. The energy that is transferred into the pot as heat is then used to cook the food.

We've all observed heat moving from a hot object to a cold object, but you might wonder how the energy actually travels. Whenever an object is hot, the molecules within the object are shaking and vibrating vigorously. The hotter an object is, the more the molecules jiggle around. As you'll learn in the next section, anything that is moving has energy, and the more it's moving, the more energy it has. Hot objects have a lot of energy, and it's this energy that is transferred to the colder objects when the two come in contact. The easiest way to visualize heat transfer is to imagine a domino effect.

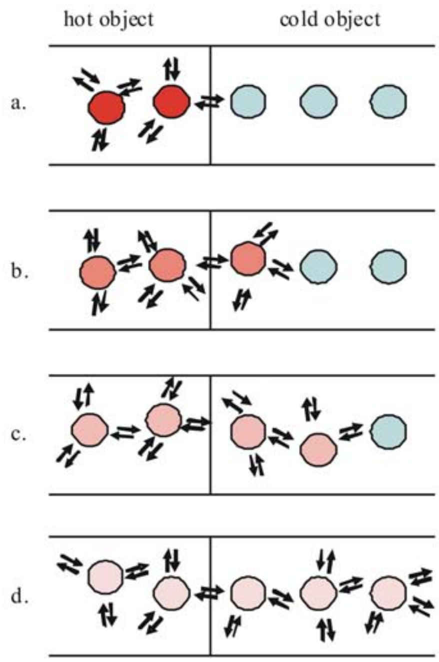


Figure 2: Heat is being transferred from a hot object to a colder object. a. As the **red** molecules in the hot object jiggle and vibrate, they hit some of the **blue** molecules in the colder object. This transfers energy from the hot molecules to the colder molecules, causing these molecules to vibrate faster. b. - d. Just like dominoes, heat passes along the chain until the energy is spread equally between all of the molecules.

(*Source: Created by:* Sharon Bewick, *License:* CC-BY-SA)

Take a close look at Figure 2. When the vibrating molecules of the hot object bump into the molecules of the colder object, they transfer some of their energy, causing the molecules in the colder object to start vibrating vigorously as well. As these molecules vibrate, they bump into their neighbors and transfer some of their energy on down the chain. In this way, energy passes through the whole system until all of the molecules have about the same amount, and the initial objects are at the same temperature.

Heat is only one way in which energy can be transferred. Energy can also be transferred as **work**. The scientific definition of work is *force (any push or pull) applied over a distance*. Whenever you push an object and cause it to move, you've done work, and you've transferred some of *your* energy to the object. At this point, it's important to warn you of a common misconception. Sometimes we think that the amount of work done can be measured by the amount of effort put in. This may be true in everyday life, but it isn't true in science. By definition, scientific work requires that force be applied **over a distance**. It doesn't matter how hard you push or how hard you pull. If you haven't moved the object, you haven't done any work.

So far, we've talked about the two ways in which energy can be transferred from one place, or object, to another. Energy can be transferred as heat, and energy can be transferred as work. But the question still remains – *what IS energy?* We'll try to at least partially tackle that question in the next section.

Types of Energy: Kinetic and Potential

Machines use energy, our bodies use energy, energy comes from the sun, energy comes from volcanoes, energy causes forest fires, and energy helps us to grow food. With all these seemingly different types of energy, it's hard to believe that there are really only two different *forms* of energy – *kinetic energy* and *potential energy.* **Kinetic energy** is energy associated with motion. When an object is moving, it has kinetic energy. When the object stops moving, it has no kinetic energy. While all moving objects have kinetic energy, not all moving objects have the same amount of kinetic energy. The amount of kinetic energy possessed by an object is determined by its mass, and its speed. The heavier an object is and the faster it is moving, the more kinetic energy it has.

Kinetic energy is very common, and it’s easy to spot examples of it in the world around you. Sometimes we even try to capture kinetic energy and use it to power things like our home appliances. If you’re from California, you might have driven through the Tehachapi Pass near Mojave or the Montezuma Hills in Solano County and seen the windmills lining the slopes of the mountains. These are two of the larger wind farms in North America. As wind rushes along the hills, the kinetic energy of the blowing air particles turns the windmills, trapping the wind’s kinetic energy so that people can use it in their houses and offices.

Figure 3: A wind farm in the Tehachapi Mountains of Southern California. Kinetic energy from the rushing air particles turns the windmills, allowing us to capture the wind’s kinetic energy and use it.

(*Source:* http://en.wikipedia.org/wiki/Image:Tehachapi_wind_farm_2.jpg, *License:* GNU-FDL)

Capturing kinetic energy can be very effective, but if you think carefully, you’ll realize that there’s a small problem. Kinetic energy is *only* available when something is moving. When the wind is blowing, we can use its kinetic energy, but when the wind stops blowing, there’s no kinetic energy available. Imagine what it would be like trying to power your television set using the wind’s kinetic energy. You could turn on the TV and watch your favorite program on a windy day, but every time the wind stopped blowing, your TV screen would flicker off because it would run out of energy. You’d probably only be able to watch about half of the episodes, and you’d *never* know what was going on!

Of course, when you turn on the TV, or flip on the lights, you can usually count on them having a constant supply of energy. This is largely because we don’t rely on kinetic energy alone for power. Instead, we use energy in its other form – we use potential energy. **Potential energy** is *stored* energy. It’s energy that remains available until we choose to use it. Think of a battery in a flashlight. If you leave a flashlight on, the battery will run out of energy within a couple of hours, and your flashlight will die. If, however, you only use the flashlight when you need it, and you turn it off when you don’t, the battery will last for days or even months. The battery contains a certain amount of energy, and it will power the flashlight for a certain amount of time, but because the battery stores *potential* energy, you can choose to use the energy all at once, or you can save it and only use a small amount at a time.

Any stored energy is potential energy. Unfortunately, there are a lot of different ways in which energy can be stored, and that can make potential energy very difficult to recognize. In general, an object has potential energy because of its *position relative to another object.* For example when you hold a rock above the earth, it has potential energy because of its position relative to the ground. You can tell that this is *potential energy* because the energy is *stored* for as long as you hold the rock in the air. Once you drop the rock, though, the stored energy is released.

There are other common examples of potential energy. A ball at the top of a hill stores potential energy until it is allowed to roll to the bottom. When you hold two magnets next to each other, they store potential energy too. For some examples of potential energy, though, it’s harder to see how “position” is involved. In chemistry, we are often interested in what is called **chemical potential energy.** Chemical potential energy is energy stored in the atoms, molecules, and chemical bonds that make up matter. How does this depend on position?

As you learned earlier, the world, and all of the chemicals in it are made up of atoms and molecules. These store potential energy that is dependent on their positions relative to one another. Of course, you can't see atoms and molecules. Nevertheless, scientists do know a lot about the ways in which atoms and molecules interact, and this allows them to figure out how much potential energy is stored in a specific quantity (like a cup or a gallon) of a particular chemical. *Different chemicals have different amounts of potential energy* because they are made up of different atoms, and those atoms have different positions relative to one another.

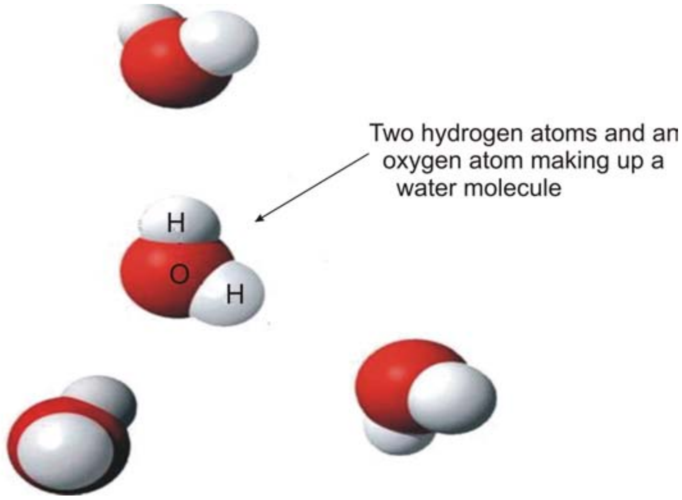


Figure 4: Scientists use their knowledge of what the atoms and molecules look like and how they interact to determine the potential energy that can be stored in any particular chemical substance.

(*Source:*http://en.wikipedia.org/wiki/Image:3D_model_hydrogen_bonds_in_water.jpg, *License:* GNU-FDL)

Since different chemicals have different amounts of potential energy, scientists will sometimes say potential energy depends not only on ***position*** , but also on ***composition.*** Composition affects potential energy because it determines which molecules and atoms end up next to each other. For example, the total potential energy in a cup of pure water is different than the total potential energy in a cup of apple juice, because the cup of water and the cup of apple juice are *composed* of different amounts of different chemicals.

At this point, you might be wondering just how useful chemical potential energy is. If you want to release the potential energy stored in an object held above the ground, you just drop it. But how do you get potential energy out of chemicals? It's actually not that difficult. You use the fact that *different chemicals have different amounts of potential energy.* If you start with chemicals that have a lot of potential energy and allow them to react and form chemicals with less potential energy, all the extra energy that was in the chemicals at the beginning but not at the end is released.

Law of Conservation of Matter and Energy

So far we've talked about how energy exists as either *kinetic energy* or *potential energy* and how energy can be transferred as either *heat* or *work*. While it's important to understand the difference between kinetic energy and potential energy and the difference between heat and work, the truth is, energy is constantly changing. Kinetic energy is constantly being turned into potential energy, and potential energy is constantly being turned into kinetic energy. Likewise, energy that is transferred as work might later end up transferred as heat, while energy that is transferred as heat might later end up being used to do work.

Even though energy can change form, it must still follow one fundamental law – *Energy cannot be created or destroyed, it can only be changed from one form to another*. This law is known as the **Law of Conservation of Energy**. In a lot of ways, energy is like money. You can exchange quarters for dollar bills and dollar bills for quarters, but no matter how often you convert between the two, you won't end up with any more or any less money than you started with. Similarly, you can transfer (or spend) money using cash, or transfer money using a credit card, but you still spend the same amount of money, and the store still makes the same amount of money.

As it turns out, the law of conservation of energy isn't exactly the whole truth. If you think back, you'll remember that energy and matter are actually interchangeable. In other words, energy can be created (made out of matter) and destroyed (turned into matter). As a result, the law of conservation of energy has been changed into the **Law of Conservation of Matter and Energy**. This law states that

The total amount of mass and energy in the universe is conserved (does not change).

This is one of the most important laws you will ever learn. Nevertheless, in chemistry we are rarely concerned with converting matter to energy or energy to matter. Instead, chemists deal primarily with converting one form of matter into another form of matter (through chemical reactions) and converting one form of energy into another form of energy.

Let's take a look at several examples, where kinetic energy is switched to potential energy and vice versa. Remember Wile E. Coyote with his anvil poised at the top of the cliff? As long as Wile E. Coyote holds the anvil and waits for Road Runner, the anvil stores potential energy. However, when Wile E. Coyote drops the anvil, the original potential energy stored in the anvil is converted to kinetic energy. The further the anvil falls, the faster it falls, and more and more of the anvil's potential energy is converted to kinetic energy.

The opposite, of course, happens when you throw a ball into the air. When the ball leaves your hand, it has a lot of kinetic energy, but as it moves higher and higher into the sky, the kinetic energy is converted to potential energy. Eventually, when all of the kinetic energy has been converted to potential energy, the ball stops moving entirely and hangs in the air for a moment. Then the ball starts to fall back down, and the potential energy is turned into kinetic energy again. Just as kinetic energy and potential energy are interchangeable, work and heat are interchangeable too. Think of a hot-air balloon. To operate a hot-air balloon, a flame at the base of the balloon is used to transfer energy in the form of heat from the flame to the air molecules inside the balloon. The whole point of this heat transfer, though, is to capture the heat and turn it into work that causes the balloon to rise into the sky. The clever design of the hot-air balloon makes the conversion of heat to work possible.

Figure 5: A hot air balloon transfers energy in the form of heat from the flame to the air particles in the balloon. The design of the hot air balloon takes this energy and changes it from heat to work. (*Source:* http://en.wikipedia.org/wiki/Image:Virgin_Hot_Air_Balloon.jpg, *License:* Public Domain)

Lesson Summary

- Any time we use energy, we transfer energy from one object to another. Energy can be transferred in one of two ways – as heat, or as work.
- Heat is the term given to energy that is transferred from a hot object to a cooler object due to the difference in their temperatures.
- Work is the term given to energy that is transferred as a result of a force applied over a distance.
- Energy comes in two fundamentally different forms – kinetic energy and potential energy.
- Kinetic energy is the energy of motion.
- Potential energy is stored energy that depends on the position of an object relative to another object.

- Chemical potential energy is a special type of potential energy that depends on the positions of different atoms and molecules relative to one another. Chemical potential energy can also be thought of as depending on chemical composition.
- Energy can be converted from one form to another.
- The total amount of mass and energy in the universe is conserved.

Review Questions

1. Classify each of the following as energy primarily transferred as heat or energy primarily transferred as work: **(Beginning)**

a. The energy transferred from your body to a shopping cart as you push the shopping cart down the aisle.

b. The energy transferred from a wave to your board when you go surfing.

c. The energy transferred from the flames to your hotdog when you cook your hotdog over a campfire.

2. Decide whether each of the following statements is true or false: **(Beginning)**

a. When heat is transferred to an object, the object cools down.

b. Any time you raise the temperature of an object, you have done work.

c. Any time you move an object by applying force, you have done work.

d. Any time you apply force to an object, you have done work.

3. Rank the following scenarios in order of *increasing* work: **(Intermediate)**

a. You apply 100 N of force to a boulder and successfully move it by 2 m.

b. You apply 100 N of force to a boulder and successfully move it by 1 m.

c. You apply 200 N of force to a boulder and successfully move it by 2 m.

d. You apply 200 N of force to a boulder but cannot move the boulder.

4. In science, a vacuum is defined as space that contains absolutely no matter (no molecules, no atoms, etc.) Can energy be transferred as heat through a vacuum? Why or why not? **(Challenging)**

5. Classify each of the following energies as kinetic energy or potential energy: **(Intermediate)**

a. The energy in a chocolate bar.

b. The energy of rushing water used to turn a turbine or a water wheel.

c. The energy of a skater gliding on the ice.

d. The energy in a stretched rubber band.

6. Decide which of the following objects has more kinetic energy: **(Intermediate)**

a. A 200 lb. man running at 6 mph or a 200 lb. man running at 3 mph.

b. A 200 lb. man running at 7 mph or a 150 lb. man running at 7 mph.

c. A 400 lb. man running at 5 mph or a 150 lb. man running at 3 mph.

7. A car and a truck are traveling along the highway at the same speed. **(Intermediate)**

a. If the car weighs 1500 kg and the truck weighs 2500 kg, which has more kinetic energy, the car or the truck?

b. Both the car and the truck convert the potential energy stored in gasoline into the kinetic energy of motion. Which do you think uses more gas to travel the same distance, the car or the truck?

8. You mix two chemicals in a beaker and notice that as the chemicals react, the beaker becomes noticeably colder. Which chemicals have more chemical potential energy, those present at the start of the reaction or those present at the end of the reaction? **(Challenging)**

Vocabulary

heat	Energy that is transferred from one object to another object due to a difference in temperature. Heat naturally flows *from* a hot object *to* a cooler object.
force	Any push or pull.
work	A force applied over a distance.
kinetic energy	Energy associated with motion.
potential energy	Stored energy. Potential energy depends on an object's position (or mixture's composition).
chemical potential energy	Potential energy stored in the atoms, molecules, and bonds of matter.
Law of Conservation of Energy	Energy cannot be created or destroyed; it can only be changed from one form to another.
Law of Conservation of Mass and Energy	The total amount of mass and energy in the universe is conserved.

Review Answers

1.

a. work b. work c. heat

2.

a. false

b. false

c. true

d. false - The force only does work if the object moves.

3. d.,b., a., c

4. No, heat cannot be transferred through a vacuum. Heat transfers from a hot object to a cold object, because the molecules in the hot object *collide* with the molecules in the cold object, passing some of their kinetic energy to the cold molecules in the process. Since there are no molecules in the vacuum, there can be no collisions between molecules. As a result, there can be no transfer of heat through the vacuum

5.

a. potential energy

b. kinetic energy

c. kinetic energy

d. potential energy

6.

a. A 200 lb. man running at 6 mph

b. A 200 lb man running at 7 mph

c. A 400 lb. man running at 5 mph

7.

a. the truck

b. the truck

8. chemicals present at the end of the reaction

2. Chemistry - A Physical Science

Measurements in Chemistry

Lesson Objectives

- State the different measurement systems used in chemistry.
- State the different prefixes used in the metric system.
- Do unit conversions.
- Use scientific notation and significant figures.
- Use basic calculations and dimensional analysis.
- Use mathematical equations in chemistry.

Introduction

When you read an advertisement for a new car, the manufacturer often writes about the engine size. Terms such as “4.6 liter engine” are used to describe the car’s engine.

Figure 1: Cubic centimeters are often used to measure the size of car engines.

(*Source:* http://www.flickr.com/photos/daveseven/1068440286/, *License:* CC-BY-SA)

Also, when you go shopping for potatoes, you will probably want to know the cost per pound. In other words, you will adjust your choice of measurement to the object that you are interested in; you aren’t going to buy diet soda in inches!

In science as well as everyday life, we need to work with measurements for length, mass, and volume.

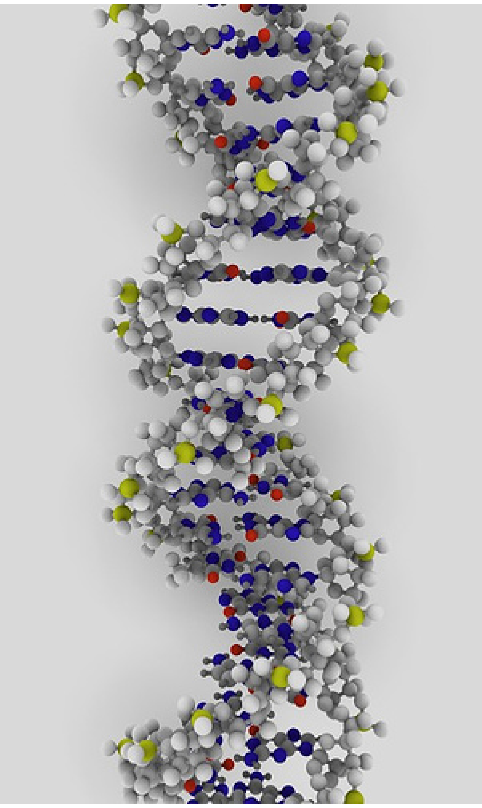


Figure 2: What is the most appropriate metric system unit for measuring the size of this molecule?.

(*Source:* http://www.flickr.com/photos/ynse/542370154/, *License:* CC-BY-SA)

Mass and Its SI Unit

When you step on a bathroom scale, you are most likely thinking that about determining your *weight*, right? You probably aren't wondering if you have gained mass. Is it okay then to use either term?

Although we often use mass and weight interchangeably, each one has a specific definition and usage. The *mass* of an object does not change; whether the object is on the earth's equator, on top of Mt. Everest, or in outer space, the mass will always be the same. Because mass measures how much matter the object contains, it has to be a constant value.

Weight, on the other hand, is a measure of the *force* with which an object is attracted to the earth or body upon which it is situated. Since the force of gravity is not the same at every point on the earth's surface, the weight of an object is not constant. For example, an object weighing 1.00000 lb in Panama weighs 1.00412 lb in Iceland. For large objects this difference may not be significant. However, since we will often be working with extremely tiny pieces of matter – atoms, molecules, etc. – we need to use mass and not weight.

The basic unit of mass in the International System of Units (SI comes from the French name, *Systeme Internationale*) is the gram. A gram is a relatively small measurement compared to, for instance, one pound. 454 grams equals one pound. While pounds are helpful in measuring the mass of a package that needs to be mailed, grams are much more useful in science.

One gram is equal to 1,000 milligrams or 0.001 kilogram; there are numerous intermediate measurements between each of these mass units as well as ones that are even larger and smaller that may be appropriate to the application at hand. These will be discussed in more detail in a later section.

Length and its SI Unit

When the four minute mile was achieved on May 6, 1954 by Roger Bannister, it was an international sensation. Today, many runners have broken that record. Only a few countries measure length or distance using miles, feet or inches. For instance, if you live in the US, you probably know your height in feet and inches, right? Or, if there is a mountain or even a hill near where you live, you probably know its height in feet. And when you discuss how far school is from your home, you probably try to figure out the distance in miles.

However, most of the world measures distances in meters and kilometers; for shorter lengths, millimeters and centimeters will be used. For a student in Germany, she will state how many kilometers her school is from home, and the height of the mountain she is thinking of climbing will be given in meters.

Figure 3: Using a laser to make a precise distance measurement.

(*Source:* http://www.flickr.com/photos/criminalintent/100786858/, *License:* CC-BY-SA)

Because the metric system is a decimal system, changing between the various measurements simply becomes a matter of moving a decimal point to the right or left. We will discuss this in greater depth later on.

While a gram is a relatively small measurement, a meter is quite similar in length to a measurement with which we are familiar, a yard. Specifically 1 meter is equal to 1.1 yards or 39.4 inches; one kilometer is equal to 0.621 miles; and one inch is equal to 2.54 centimeters.

Volume: A Derived Unit

Volume is used to measure how much space an object takes up. It is a derived unit, meaning it is based on another basic SI unit- in this case, the meter (length) was used to measure the sides of a cube, designating a certain volume. This volume was determined to be a cubic meter, m^3, which is used as the standard SI unit of volume. This is a very large unit, and it is not very useful for most measurements in chemistry. A more common unit is the liter (L), which is equal to 1/1000 of a cubic meter. Another commonly used volume measurement is the milliliter; 1000 mL = 1 L.

One liter is the volume of the soda bottle that you might have recently purchased and have sitting in the refrigerator at home. You might also have a quart of milk in your refrigerator. Even though the size of the liter container and the milk carton may not appear to be the same, they are, in fact, almost exactly the same volume. A quart is just slightly smaller in volume than a liter (1 L = 1.057 quarts). It's only the packaging that is different!

Measuring Temperature

In order to discuss temperature scales, let's briefly compare the concepts of *heat* and *temperature.* Heat is a measurement of the total amount of kinetic energy while temperature describes the intensity of the heat, or what is often referred to as the average kinetic energy of the material. When we are measuring the temperature of an object we are measuring its average kinetic energy. For that, we use the Celsius and kelvin scales. Scientists do not usually use the Fahrenheit scale. The size of a degree in kelvin is the same as 1 degree Celsius. The difference is that the kelvin scale begins with an absolute zero, the temperature at which all motion stops. To convert between the two scales you can use: $K = {}^{o}C + 273$. Therefore, on the kelvin scale, water freezes at 273 K and boils at 373 K.

You might want to make note of the following: while most mathematical calculations in chemistry require you to convert Celsius temperatures into kelvin, when you are given a *difference in temperature*, ΔT, you do ***not*** need to convert it to kelvin! A difference in temperature is the same whether it is in Celsius or kelvin.

Lesson Summary

- The International System unit for mass if the gram.
- The International System unit for length is the meter.
- The unit for volume is derived from a cube that is 1.00 meter on each side; therefore the volume unit is cubic meters. A more common unit is the liter which is $\frac{1}{1000}$ of a cubic meter.
- The SI uses both ^{o}C and absolute temperature in Kelvin (K) for temperature units. $K = {}^{o}C + 273$.

Review Questions

1. What are the basic units of measurement in the metric system for length and mass? **(Beginning)**

2. What unit is used to measure volume? How is this unit related to the measurement of length? **(Beginning)**

3. Explain the difference between *weight* and *mass.* **(Intermediate)**

4. Give both the Celsius and Kelvin values for the boiling and freezing points of water. **(Beginning)**

5. How do you convert from Celsius to Kelvin? How does one degree Celsius compare with one Kelvin? **(Beginning)**

6. If someone told you that a swimming pool's temperature was 275 K, would it be safe for you to go for a swim? **(Intermediate)**

7. Determine which metric measurement you would use for each of the following: **(Intermediate)**

A) The distance to the moon.

B) The mass of an donut.

C) The volume of a drinking glass.

D) The length of your little finger.

Further Reading / Supplemental Links

Website with lessons, worksheets, and quizzes on various high school chemistry topics. Lesson 1-3 is on Measuring Matter.

http://www.fordhamprep.org/gcurran/sho/sho/lessons/lesson13.htm

Vocabulary

International System of Units, SI	The SI system of units is the modern form of the metric system and is generally a system devised around the convenience of multiples of 10.
Kelvin temperature scale	The kelvin is unit of increment of temperature and is one of the seven SI basic units. The Kelvin scale is thermodynamic absolute temperature scale where absolute zero is the absence of all thermal zero. At K = 0, there is no molecular motion. The kelvin is not referred to as a "degree", it is written simply as K, not °K.

Review Answers

1. Length: meter; mass: gram

2. Volume: liter; it is a derived measure determined from m^3.

3. Mass is an intrinsic characteristic while weight depends on the force of gravity.

4. 100°C , 0.0°C; 273 K, 373K

5. °C + 273 = K The size of a Celsius degree and a Kelvin degree are the same.

6. It would be too cold.

7.

A) km B) g C) mL D) cm

Using Measurements

Lesson Objectives

- Understand the metric system and its units.
- Convert between units.
- Use scientific notation in writing measurements and in calculations.
- Use significant figures in measurements.

Introduction

The metric system is a decimal system. This means that making conversions between different units of the metric system are always done with factors of ten. Let's consider the English system – that is, the one that is in everyday use in the US as well as England – to explain why the metric system is so much easier to manipulate. For instance, if you need to know how many inches are in a foot, you only need to remember what you at one time memorized: 12 inches = 1 foot. But now you need to know how many feet are in a mile. What happens if you never memorized this fact? Of course you can look it up online or elsewhere, but the point is that this fact must be given to you as there is no way for you to derive it out yourself. This is true about all parts of the English system: you have to memorize all the facts that are needed for different measurements.

The Metric System

In the metric system, you need to know (or yes, memorize) one set of prefixes and then apply them to each type of measurement. Then if a larger measurement is needed, such as kilometers, but you have used a meter stick, you only need to move the decimal to convert the units.

Example: If you have measured the distance as 60.7 meters, what is the length in kilometers?

Solution: 60.7 meters = 0.0607 kilometers since there are 1,000 meters in 1 kilometer.

Not only can you easily convert from kilometers to meters, but conversions, such as liters to cubic meters, are also easy. Try converting from cubic feet to gallons! All metric system conversions simply require the moving of the decimal and/or adding zeros. You don't even need a calculator. On the other hand, if you had to convert from miles to inches, not only would you have to remember all of the conversion factors, but you would probably also need a calculator to make the conversion.

Metric Prefixes

The metric system uses a number of prefixes along with the base unit. To review: the basic unit of mass is a gram (g), that of length is meter (m), and that of volume is liter (L). When the prefix *centi* is place in front of gram, as in centigram, the measure is now 1/100 of a gram. When *milli* is placed in front of meter, as in millimeter, the measure is now 1/1000 of a meter. Common prefixes are in the chart below:

Prefix	Meaning	Symbol
pico-	10^{-12}	p
nano-	10^{-9}	n
micro-	10^{-6}	μ
milli-	10^{-3}	m
centi-	10^{-2}	c
deci-	10^{-1}	d
kilo-	10^{3}	k

Unit Conversions

Making conversions in the metric system is relatively easy: you just need to remember that everything is based on factors of ten. For example, let's say you want to convert 0.0856 meters into millimeters. Looking at the chart above, you can see that 1 millimeter is 10^{-3} meters; another way to say this is that there are 1000 millimeters in one meter. You can set up a mathematical expression as follows

(0.0856 m) x (1000 mm /1 m) = ? mm

When you solve this equation, you first want to see which units to divide out. In this case, you notice *meters* appear in both the numerator and denominator, so you will be able to cancel them.

(0.0856 m) x (1000 mm / 1 m) = ? mm

Now all that is left to do is multiply 0.0856 by 1000. To do this, you are just going to move the decimal point three places to the right:

(0.0856 m) x (1000 mm / 1 m) = 85.6 mm

Example: Convert 153 grams to centigrams.

Solution:

$$153 \text{ grams} \times \frac{100 \text{ centigrams}}{\text{gram}} = 15300 \text{ centigrams}$$

Scientific Notation

Scientific notation is a way to write very large or very small numbers; the decimal point is moved so that there is one digit in the unit's position and all of the decimal places are held as a power of ten. This is important in chemistry because many of the measurements we make either involve very large numbers of atoms/molecules or very tiny measurements, such as masses of electrons or protons. For example, consider a number such as 839,000,000. While this number is not too difficult to write out, it is more conveniently written in scientific notation. Written in scientific notation, this number becomes: 8.39×10^8. The "10^8" means that ten is multiplied by itself eight times: 10 x 10 x 10 x 10 x 10 x 10 x 10 x 10. As you can see, writing 10^8 is much easier!

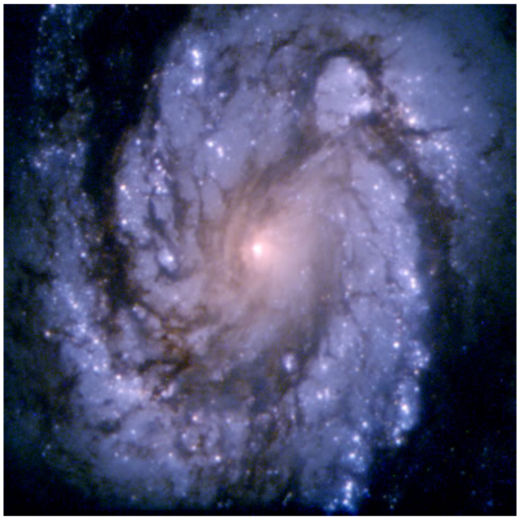


Figure 4: Even using large distance units such as kilometers, you would still need to use scientific notation to measure the size of this galaxy.

(*Source:* http://www.flickr.com/photos/pingnews/474783096/, *License:* CC-BY-SA)

We can also use scientific notation to write very small numbers. Take a number such as 0.00000481. It is easy to make mistakes in counting the number of zeros in this number. Also, many calculators only let you enter in a certain number of digits. When we write this in scientific notation, it is important to notice that the measurement is less than one, therefore, the exponent on 10 will be negative: this number becomes 4.81×10^{-6}. In this case, the decimal point was moved six places to the right.

It is important that you know how to perform calculations using numbers written in scientific notation. For example, the following problem shows two numbers with exponents being multiplied together:

$(2.90 \times 10^3)(1.60 \times 10^6) = ?$

To solve this problem, you would multiply the terms (2.90 and 1.60) like you normally would; then you would *add* the exponents:

$2.90 \times 1.60 = 4.64$

$10^3 \times 10^6 = 10^9$

Therefore, combining these values gives the answer 4.64×10^9.

Significant Figures

The tool that you use determines the number of digits that will be in a measurement. For example, if you say an object has a mass of “5 kg”, that is not the same as saying it has a mass of “5.00 kg” since you must have measured the masses with two different tools – the two zeros in “5.00 kg” would not be written if the tool that was used could not measure to two decimal places. Even though the mass seems to be the same, the uncertainty of the measurement is not. When you say “5 kg”, that means you have measured the mass to within +/-1 kg. The actual mass could be 4 or 6 kg. For the 5.00 kg measurement, you have measured the mass to within +/-0.01 kg, so the actual mass is between 4.99 and 5.01 kg.

Using Significant Figures in Measurements

How do you know how many significant figures are in a measurement? General guidelines are as follows:

- Any nonzero digit is significant [4.33 has three significant figures].
- A zero that is between two nonzero digits is significant [4.03 has three significant figures].
- All zeros to the left of the first nonzero digit are not significant [0.00433 has three significant figures].
- Zeros that occur after the decimal are significant. [40.0 has three significant figures. The zero after the decimal point tells us that the value was measured to the tenths place].
- Zeros that occur without a decimal are not significant [4000 has one significant figure since the zeros are holding the 4 in the thousands position].

Examples:

1) How many significant figures are in the number 1.680?

Solution: There are three nonzero digits and one zero appears after the decimal point. Therefore, there are four significant figures.

2) How many significant figures are in the number 0.0058201?

Solution: There are 4 nonzero digits and 1 zero between two numbers. Therefore, there are 5 significant figures. The first three zeros are not significant since they are simply holding the number away from the decimal point.

Lesson Summary

- The metric system is a decimal system; all magnitude differences in units are multiples of 10.
- Unit conversions involve creating a conversion factor.
- Very large and very small numbers are expressed in exponential notation.
- Significant figures are used to express uncertainty in measurements.

Review Questions

1. Convert the following linear measurements: **(Beginning)**

A) 0.01866 m = _______________ cm

B) 2156 mm = ______________m

C) 15.38 km = ________________ m

D) 1250.2 m = ________________ km

2. Convert the following mass measurements: **(Beginning)**

A) 155.13 mg = ________________kg

B) 0.233 g = _________________mg

C) 1.669 kg = ________________g

D) 0.2885 g = ________________mg

3. Write the following numbers in scientific notation: **(Beginning)**

A) 0.0000479

B) 251,000,000

C) 4260

D) 0.00206

4. How many significant figures are in the following numbers? **(Beginning)**

A) 0.006258

B) 1.00

C) 1.01005

D) 12500

Further Reading / Supplemental Links

The website listed below offers lessons, worksheets, and quizzes on many topics in high school chemistry.

- Lesson 1-7 is on Temperature Conversion.
- Lesson 2-1 is on the International System of Measurements.
- Lesson 2-3 is on Significant Figures.
- Lesson 2-5 is on Scientific Notation.

http://www.fordhamprep.org/gcurran/sho/sho/lessons/lesson12.htm

Vocabulary

scientific notation	A shorthand way of writing very large or very small numbers. The notation consists of a decimal number between 1 and 10 multiplied by an integral power of 10. It is also known as exponential notation.

significant figures Any digit of a number that is known with certainty plus one uncertain digit. Beginning zeros and placeholder zeros are not significant figures.

Review Answers

1.

A) 1.866 cm B) 2.156 m C) 15380 m D) 1.2502 km

2.

A) 0.00015513 kg B) 233 mg C) 1669 g D) 288.5 mg

3.

A) 4.79×10^{-5}

B) 2.51×10^{8}

C) 4.26×10^{3}

D) 2.06×10^{-3}

4.

A) 4 sig figs B) 3 sig figs C) 6 sig figs D) 3 sig figs

Using Mathematics in Chemistry

Lesson Objectives

- Use units in problem solving.
- Do problem solving using dimensional analysis.
- Use significant figures in calculations.

Introduction

Unit terms are the words following a measurement that tell you on which standard the measurement is based. Every measurement must have a unit term. The unit terms also follow the algebraic rules of exponents and cancellation. Carrying the unit terms through mathematical operations provide an indication as to whether the mathematical operation was carried out correctly. If the unit term of the answer is not correct, it is an indication that the mathematical operation was not done correctly.

Using Units in Problem Solving

Anytime we have to do a calculation, it is important to include the units along with the actual numbers. One reason is that you can often decide how to solve the problem simply by looking at the units. For example, let’s say you are trying to calculate solubility. One of the units used for solubility is grams/liter (g/L). Imagine that you have forgotten how to do the mathematical calculation for this problem, but you have measured how many grams of a solid dissolved into a certain number of liters. Looking at the units of the values that you have (g and L) and at the units of the answer you want to get (g/L), you can figure out the mathematical set-up. The g/L unit allows you to know it needs to be “grams divided by liters.”

You will also note that as you do a calculation, you will be working with units in a similar manner as you would a number. Just as with numbers, units can be divided out when that specific unit appears in the numerator as well as the denominator.

As a final note on units, think of them in an "apples and oranges" context. You can't subtract meters from kilometers without first converting the measurements into common units. Always check a measurement's units to make sure that they are appropriate for a given calculation.

Using Conversion Factors

Conversion factors are used to convert one unit of measurement into another. A simple conversion factor can be used to convert meters into centimeters, or a more complex one can be used to convert miles per hour into meters per second. Since most calculations require measurements to be in certain units, you will find many uses for conversion factors. What always must be remembered is that a conversion factor has to represent a fact; this fact can either be simple or much more complex. For instance, you already know that 12 eggs equal 1 dozen. A more complex fact is that the speed of light is 1.86×10^5 miles/sec. Either one of these can be used as a conversion factor depending on what type of calculation you might be working with. The following section provides you with more examples of this.

Dimensional Analysis

When using conversion factors (and for that matter, a lot of other calculations), a process called dimensional analysis is extremely useful. Dimensional analysis allows you to make a number of unit conversions in a single calculation. It will also help you keep the units straight.

Example: A car travels 58.5 miles, using 1.5 gallons of gasoline. How do you express this in kilometers/liter? You know that there are 3.78 liters in a gallon, and a kilometer is 0.62 miles. How would you make this conversion?

Solution:

You first need to write out a mathematical expression showing all your conversion factors and units:

$$\left(\frac{58.5\ \textit{miles}}{1.5\ \textit{gallons}}\right) \times \left(\frac{1\ \textit{gallon}}{3.78\ \textit{liters}}\right) \times \left(\frac{1\ \textit{kilometer}}{0.62\ \textit{miles}}\right)$$

Next, you need to check for units to divide out:

$$\left(\frac{58.5\ \textit{miles}}{1.5\ \textit{gallons}}\right) \times \left(\frac{1\ \textit{gallon}}{3.78\ \textit{liters}}\right) \times \left(\frac{1\ \textit{kilometer}}{0.62\ \textit{miles}}\right)$$

Notice that at this point you are left with *kilometers* in the numerator and *liters* in the denominator. Your last step is to multiply your numbers, and your answer will be in kilometers/liter:

$$\left(\frac{58.5}{1.5}\right) \times \left(\frac{1}{3.78\ \textit{liters}}\right) \times \left(\frac{1\ \textit{kilometer}}{0.62}\right) = \left(\frac{16.64106503\ \textit{kilometers}}{\textit{liter}}\right)$$

This is the answer that your calculator will give to you. However it is not the correct answer. For that we have to proceed to the next section:

Using Significant Figures in Multiplication and Division

Whenever we do a calculation, we need to pay attention to the significant figures. The rule is that your final answer can only be as precise as your least precise measurement. This means that the least precise tool used for any measurement in the calculation will determine how precise the *answer* will be.

For multiplication and division, first determine the number of significant figures in each of the measurements; the number of significant figures in your answer will be the same as the *least* number in the calculation. For example, if you multiplied the number 1.02584 by 2.1, your answer can only have two significant figures. The same rule applies for division.

Example: Divide the number 125.688 by 14.01. Express your answer using correct significant figures.

Solution: 125.688 has 6 significant figures, and 14.01 has 4. Therefore, your answer can only have 4 significant figures.

$\frac{125.688}{14.01} = 8.971$

An important point to remember is that if you are multiplying or dividing by an exact number, then you treat that number as having an infinite number of significant figures. An exact number is a number that is written without all of its known significant figures. For instance, one meter or one dozen have many significant figures but we just don't write all of them, so these kind of measurements never determine the number of significant figures in a calculation. There is another type of exact number and that is using a measurement such as five people, ten dogs, or one cat. Again, these do not determine the number of significant figures in an answer.

Example: You have one dozen identical objects, with a total mass of 46.011 grams. What is their average mass?

Solution:

$\frac{46.011}{12}$ = 3.83425, which rounds off to 3.8342 (5 significant figures, the same as 46.011)

Using Significant Figures in Addition and Subtraction

There is a different rule for determining significant figures when adding or subtracting measurements. Now, you will need to look for the measurement with the least number of significant figures to the right of the decimal place; this number of decimal places will determine the number of significant figures to be used in the answer.

Example: What is the sum of 14.3 and 12.887?

Solution:

14.3 + 12.887 = 27.187

The number 14.3 only has 1 digit to the right of the decimal point, so our answer is rounded off to 27.2.

Lesson Summary

- Dimensional analysis aids in problem solving.
- Conversion factors are created by unit analysis.
- Significant figures must be carried through mathematical operations.
- The answer for an addition or subtraction problem must have digits no further to the right than the shortest addend.

- The answer for a multiplication or division problem must have the same number of significant figures as the factor with the fewest significant figures.

Review Questions

1. Perform the following calculations and give your answer with the correct number of significant figures: **(Intermediate)**

A) 0.1886 x 12

B) $\frac{2.995}{0.16685}$

C) $\frac{1210}{0.1223}$

D) 910 x 0.18945

2. Perform the following calculations and give your answer with the correct number of significant figures: **(Beginning)**

A) 10.5 + 11.62

B) 0.01223 + 1.01

C) 19.85 – 0.0113

3. Do the following calculations *without a calculator:* **(Intermediate)**

A) $(2.0 \times 10^{3})(3.0 \times 10^{4})$

B) $(5.0 \times 10^{-5})(5.0 \times 10^{8})$

C) $(6.0 \times 10^{-1})(7.0 \times 10^{-4})$

D) $\frac{(3.0 \times 10^{-4})(2.0 \times 10^{-4})}{2.0 \times 10^{-6}}$

Further Reading / Supplemental Links

The website listed below offers lessons, worksheets, and quizzes on many topics in high school chemistry.

- Lesson 2-4 is on the Factor-Label Method of Unit Conversion.

http://www.fordhamprep.org/gcurran/sho/sho/lessons/lesson12.htm

Vocabulary

dimensional analysis	A technique that involves the study of the dimensions (units) of physical quantities. It affords a convenient means of checking mathematical equations.

Review Answers

1.

A) 2.3 B) 17.95 C) 9.89×10^{3} D) 170

2.

A) 22.1 B) 1.02 C) 19.84

3.

A) 6.0×10^7

B) 2.5×10^4

C) 4.2×10^{-4}

D) 3.0×10^{-2}

Using Algebra in Chemistry

Lesson Objectives

- Be able to rearrange mathematical formulas for a specific variable.
- Have an understanding of how to use units in formulas.
- Be able to express answers in significant figures and with units.

Introduction

During your studies of chemistry (and physics also), you will note that mathematical equations are used in a number of different applications. Many of these equations have a number of different variables with which you will need to work. You should also note that these equations will often require you to use measurements with their units. Algebra skills become very important here!

Solving Formulas with Algebra

Sometimes, you will have to rearrange an equation to get it in the form that you need. When you are working with an equation such as $D = \frac{M}{V}$ (density = mass/volume) and asked to solve for density, it is relatively easy; all you have to do is substitute the measurements and solve – of course, keeping in mind significant figures!

If you are asked to solve the above equation for M, then you will need to manipulate the equation to isolate the desired variable, in this case in the form of "M =." To do this, you will need to move the V from the right side to the left side of the equation. As the V is in the denominator, you will need to multiply both sides of the equation by V:

$$V \times D = (V)\left(\frac{M}{V}\right)$$

Multiplying this out:

$V \times D = M$

A similar process is used if you need to solve for V:

Take the previous equation ($V \times D = M$) and divide both sides by D:

$$\left(\frac{V \times D}{D}\right) = \left(\frac{M}{D}\right)$$

Solving, this becomes:

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

What if you are given a more complex equation, like PV =nRT, and asked to solve for “n”? You need to follow the same steps as you did in the above examples. The only difference is that there are more symbols to rearrange.

Solution:

Look at the original equation: PV = nRT. Our goal is to get “n” on one side of the equation by itself.

To remove the RT from the right side, we will divide both sides by RT:

$$\frac{PV}{RT} = \frac{nRT}{RT}$$

After solving, we are left with:

$$n = \frac{PV}{RT}$$

Algebra with Units and Significant Figures

So far, you’ve learned about units, significant figures, and algebraic manipulation of equations. Now it’s time to put all three of these together. We’ll start with a simple example: density. Density is a measure of the amount of mass per unit of volume, and a common unit used is g/mL. In the first example, we’re going to do a straightforward calculation of density from a given mass and volume.

Example 1

What is the density of an object that has a mass of 13.5 g and a volume of 7.2 mL?

Solution:

The equation is as follows:

$D = \frac{mass}{volume}$

Substituting in the known values (with units): $D = \frac{13.5\ g}{7.2\ mL}$

Finally, solving the equation and rounding off the answer based in significant figures:

$D = \frac{13.5\ g}{7.2\ mL}$ = 1.9 g/mL (2 significant figures)

This calculation was easy to do because there was no rearranging of the equation and no cancellation of units.

For the next example, let’s look at a more complex calculation.

Example 2:

A sample of an ideal gas has a volume of 14.2 L at a pressure of 1.2 atm. If the gas pressure is increased to 1.8 atm, what is the new volume?

Solution:

This problem uses Boyle's law:

$P_1 V_1 = P_2 V_2$

All the variables are known except for V_2, so the equation needs to be rearranged to solve for the one unknown. We can do this by dividing both sides by P_2:

$\frac{P_1 V_1}{P_2} = V_2$

Now we substitute in the known values and their units:

$\frac{(1.2\ atm)(14.2\ L)}{(1.8\ atm)} = V_2$

Next, we cancel out units:

$\frac{(1.2)(14.2\ L)}{(1.8)} = V_2$

Finally, we calculate our answer and round off to the appropriate number of significant figures:

$V_2 = 9.5\ L$

Lesson Summary

- Students of chemistry need to be able to use algebra in their calculations.

Review Questions

1. For the equation PV = nRT, re-write it so that it is in the form of "T =." **(Intermediate)**

2. The equation for density is D = M/V. If D is 12.8 g/cm^3, and M is 46.1 g, solve for V, keeping significant figures in mind. **(Intermediate)**

3. The equation $P_1 V_1 = P_2 V_2$, known as Boyle's law, shows that gas pressure is inversely proportional to its volume. Re-write Boyle's law so it is in the form of $V_1 = ?$. **(Intermediate)**

4. The density of a certain solid is measured and found to be 12.68 g/mL. Convert this measurement into kg/L. **(Intermediate)**

5. In a nuclear chemistry experiment, an alpha particle is found to have a velocity of 14,285 m/s. Convert this measurement into miles/hour. **(Challenging)**

Further Reading / Supplemental Links

College Chemistry- Schaum's Outlines. Jerome Rosenberg and Lawrence Epstein, McGraw-Hill, 1997.

Chemistry, 7th Edition, Raymond Chang, McGraw-Hill, 2002.

Chemistry, J. Dudley Herron, Jerry L. Sarquis, Clifford L. Schrader, David V. Frank, Mickey Sarquis, David A. Kukla. D.C. Heath and Co., 1993.

World of Chemistry, Steven S. Zumdahl, Susan L. Zumdahl, and Donald J. DeCoste. McDougal Littell, 2007.

Review Answers

1. $T = \frac{PV}{nR}$

2. $V = 3.60\ \text{cm}^3$

3. $V_1 = \frac{P_2V_2}{P_1}$

4. 12.68 kg/L

5. 8.2796×10^{10} miles/hour

3. Chemistry in the Laboratory

Making Observations

Lesson Objectives

- Define qualitative and quantitative observations.
- Distinguish between qualitative and quantitative observations.
- Use Quantitative observations in measurements.

Introduction

Take out a piece of paper and record a chart similar to the one below. Look up from this text and scan the room. Write down what you see around you in as much detail as you feel necessary to remember it after you walk away. Better still, you want to be able to show your chart to someone who can then be able to picture where in the room you were sitting. A chart is usually necessary to record these observations simply for organization.

Item	**Observation**
1.	
2.	
3.	
4.	
5.	

Science depends on keeping records of observations for later interpretations. These interpretations may lead to the development of theories or laws. Without accurate observations, scientists cannot make any interpretations and therefore cannot draw conclusions.

Here is a simple test for you. Pretend we're visiting a forensic scientist, hired to investigate the scene of a crime. You are only asked to analyze the observations gathered by the other scientists at the scene. You must try not to make too many assumptions yet try and make your decision based on the data at hand. One summer evening, Scott and Brenda came home from work to find their house in shambles. Neighbors, friends, and colleagues are baffled by the strange occurrence. The television was found on in the house. Food was on the table ready to be eaten. All of Scott's coin collections, his precious metals, and Brenda's prized possession – her statue of Galileo – were gone. Foul play is suspected. The lead investigator gives you the following observations gathered from the scene and suspects:

Observations at Scene	**Suspect 1: 180 lb male**	**Suspect 2: 220 lb male**	**Suspect 3: 120 lb female**
Blood type = B	Blood type = B	Blood type = B	Would not comply
Fiber sample = polyester	Sweater = polyester	Blazer = wool knit	Pants = polyester
Powder found = white	Works in sugar factory	Pastry chef	Car sales woman
Shoe Print found = work boot			

From the table, can you deduce who might have been involved in the alleged crime? Do you need more information? How good are the observations in order for you, the scientist, to make accurate conclusions? What will you base your decision on? What other information do you need? Remember someone will be charged for this crime. Observations are the key to science all around us and in our everyday lives.

Qualitative Observations

Science is full of observations but of two different types. What we see, smell, feel, and hear are observations that scientists depend on to determine whether chemical reactions have been occurring or have come to completion. This is one type of observation known as a ***qualitative*** observation. Qualitative observations give the descriptive properties of a substance or being and therefore are without numbers.

When you made your table above, what kind of observations did you make? Take a look at the table. Did you note any colors from the surroundings? Was there a window nearby? If so, was it open? Did you happen to hear any sounds from outside the window? Did you see a vehicle drive by? If so, what color was it? Take a look at the sample question below and see if you can determine the qualitative observations from each of the figures in the question.

Sample Problem: List the qualitative observations for each of the figures below.

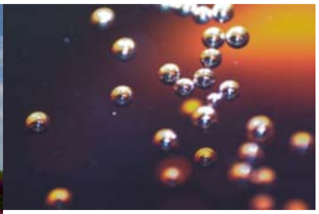


Figure 1: Fog caused by dry ice.

(*Source:* http://commons.wikimedia.org/wiki/File:DryIceSublimation.jpg, *Photo by:* sarathtly, *License:* Public Domain)

Figure 2: Tulips

(*Source:* http://commons.wikimedia.org/wiki/File:Violett_tulips.jpg, *Photo by:* Gayer Inge Close, *License:* Public Domain)

Figure 3: Soda

Source: ; *License:* Public Domain)

(*Source*: http://en.wikipedia.org/wiki/Image:Soda_bubbles_macro.jpg: *License:* Public Domain)

Solution:

Figure 1: fog or smoke coming from top of the cup pouring over onto the tabletop

Figure 2: purple tulips, sky with clouds in the background

Figure 3: bubbles, almost looks like effervescence from soda pop when you pour a glass of cola

Quantitative Observations

Sometimes qualitative measurements are enough to give an accurate representation of the events occurring. In other cases, scientists need more information than what the senses offer in order to make correct interpretations and then conclusions. Say, for example, there was a window in your classroom and outside the window you see a battleship gray car zoom by, speeding you suspect because behind him you hear the sirens of a police car. You make the interpretation that the car is speeding because of the police sirens. The police could, in fact, be on another call. The only real accurate qualitative observations you can make here are that you see a battleship gray car drive by, you hear the sirens of the police car, and you see the police car drive by with sirens on. Now if you say, happen to have a hand held radar gun, and could then measure that the car was travelling 50 mph in a 35 mph zone, then you could conclude the police were chasing the car.

Quantities are a useful strand of observations. When you have observations that involve the use of numbers, we refer to these as ***quantitative*** observations because they have amounts. In our car chase example above, the measurement of 50 mph and 35 mph are both quantitative measurements. If we said that it is 85°F outside in British Columbia, the temperature of 85°F is a quantitative observation. Now, if we said that it is 85°F outside in sunny British Columbia, the temperature of 85°F is a quantitative observation, and the "sunny" is a qualitative observation. See how it works? Now you try.

Sample Question:

Pick out the quantitative and qualitative observations from each phrase:

1. 3 g of NaCl dissolves in 10 mL of H_2O to make a clear solution.

2. The spider on the wall only has seven legs remaining but is still big and hairy.

3. When 0.5 mL of a solution is put into a flame, the flame turns a brilliant green.

Solution:

1.Quantitative: 3 g 10 mL; qualitative: clear.

2.Quantitative: seven; qualitative: big, hairy.

3.Quantitative: 0.5 mL; qualitative: brilliant green.

Lesson Summary

- Qualitative observations describe the qualities of a substance or event.
- Qualitative observations are made using the senses (except taste – used only when appropriate).
- Qualitative observations do not involve numbers.
- Quantitative observations describe the quantities of a substance or event.
- Quantitative observations use numbers in the descriptions for the substance or event.
- Observations, either qualitative or quantitative, or both, are used as tools by scientists to make representations and then interpretations about the surroundings.

Review Questions

Indicate in the following chart whether the observation is qualitative or quantitative. **(Beginning)**

Number	Observation	Qualitative or Quantitative
1.	The temperature of this room is 25°C.	
2.	It is comfortably warm in this room.	
3.	Most people have removed their coats.	
4.	The building is 25 stories high.	
5.	It is a very tall building.	

6.	The building is taller than any nearby trees.	
7.	The bottle is green.	
8.	The bottle contains 250 mL of liquid.	
9.	Robert bought his son a small car.	
10.	The car is smaller than his hand.	
11.	The car is about three inches long.	
12.	The race is about 27 miles long.	

Vocabulary

qualitative observations	Describe the qualities of something and are described without numbers.
quantitative observations	Observations that involve the use of numbers (quantities).

Further Reading / Supplemental Links

http://en.wikipedia.org/wiki

Review Answers

Number	Observation	Qualitative or Quantitative
1.	The temperature of this room is 25°C.	quantitative
2.	It is comfortably warm in this room.	qualitative
3.	Most people have removed their coats.	qualitative
4.	The building is 25 stories high.	quantitative
5.	It is a very tall building.	qualitative
6.	The building is taller than any nearby trees.	qualitative
7.	The bottle is green.	qualitative
8.	The bottle contains 250 mL of liquid.	quantitative
9.	Robert bought his son a small car.	qualitative
10.	The car is smaller than his hand.	qualitative
11.	The car is about three inches long.	quantitative
12.	The race is about 27 miles long.	quantitative

Making Measurements

Lesson Objectives

- Match equipment type based on the units of measurements desired.
- Determine significant figures of the equipment pieces chosen.
- Define accuracy and precision.

- Distinguish between accuracy and precision.

Introduction

As we learned in the previous section, qualitative observations require the use of the senses to gather data in order to interpret what is happening in our surroundings and then make conclusions based on these interpretations. Quantitative observations gather data by using measurements. From these measurements we can interpret the data and draw conclusions. How exactly do scientists gather all of this numerical data? What kind of equipment is necessary and for what purposes? How accurate is it? Let's take a look, first at some of the typical equipment used in chemistry and then at the skills necessary to determine accuracy and precision. Let's explore the quantitative side of chemistry.

Equipment Determines the Unit of the Measurement

Think of the last laboratory experiment that you did. What kind of equipment did you use? If you were measuring out a volume of a liquid, did you use a beaker or a graduated cylinder?

Figure 1: Beakers used in experiments. (*Source:* http://en.wikipedia.org/Image:Beakers.jpg, *License* CC-BY-SA)

Figure 2: 100 mL graduated cylinder. (*Source:* http://en.wikipedia.org/wiki/Image:Graduated_cylinder.jpg, *License:* Public Domain)

Look at the two figures; if you were required to measure out 65 mL, what instrument would you most likely want to use? The graduated cylinder has graduations every 10 mL and then further graduations every 5 mL. The beakers could have graduations every 10 mL, 50 mL, or 100 mL depending on which type you use. It would be easier to measure out the volume in a graduated cylinder. What if, in this same lab, you needed to mass out 3.25 g of sodium chloride, NaCl. Look at the two figures below and determine which piece of equipment you would use.

Figure 3: A pan Balance. (*Source:* http://en.wikipedia.org/wiki/Image:Balance_à_tabac_1850.jpg, *License:* GNU-FDL)

Figure 4: A digital balance. (*Source:* http://en.wikipedia.org/wiki/Image:Digi-keukenweegschaal1284.jpg, *License:* GNU-FDL)

The pan balance measures only to +/- 0.1g. Therefore, you would have to mass out 3.3 g of NaCl rather than 3.25 g. The digital balance can measure to +/- 0.01g. With this instrument you could measure exactly what you need, depending on your skill of course!

The equipment you choose also determines the units in your measurement and vice versa. For example, if you are given graduated cylinders, beakers, pipettes, burettes, flasks, or bottles, you are being asked to measure volume. Volume measurements in the International System of Units use the metric system rather than the imperial system in order to standardize these measurements around the globe. Thus, for volume measurements, we use liters (L) for large volumes and milliliters (mL) for smaller volumes measured in the lab. Look at the figure below and determine what volumes are present in each piece of equipment.

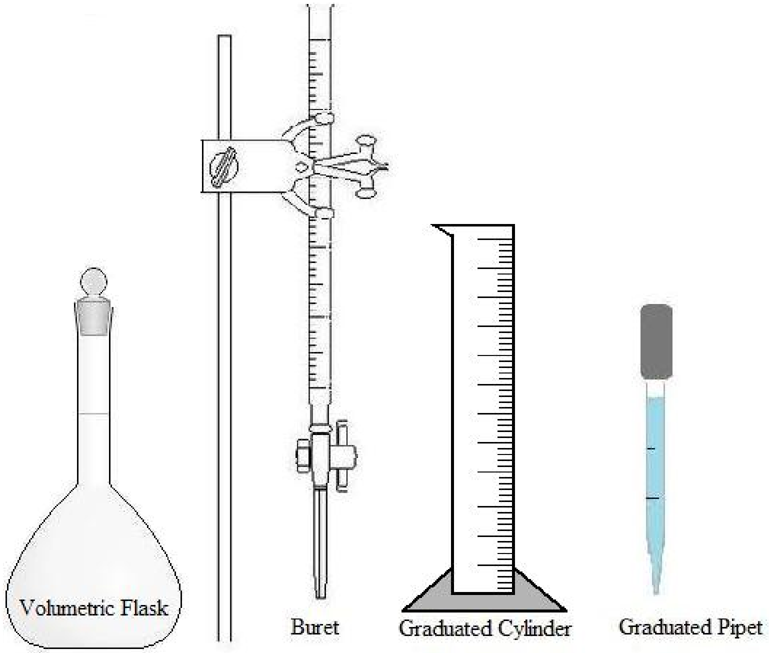


Figure 5: Volume equipment pieces.

(*Source:* Richard Parsons, *License:* CC-BY-SA)

The contrary is also true. What if you were to measure out 5 g of a solid, or 3 cm of wire, or the temperature of a solution; would any of the objects in Figure 5 be helpful? Why not? These objects are not helpful because these units of measurement are not volumes and all of these pieces of equipment measure volume. For the measurements you need to take, you would need different pieces of equipment. Look at Figure 5 and match the three required measurements with the pieces of equipment shown.

a) 5 g of a solid

b) 3cm of wire

c) temperature of a solution

Figure 5: Examples of measuring devices.

(*Sources:* http://en.wikipedia.org/wiki/Image:Steel_ruler_closeup.jpg, *License:* GNU-FDL; http://en.wikipedia.org/wiki/Image:Clinical_thermometer_38.7.jpg, *License:* GNU-FDL; http://en.wikipedia.org/wiki/Image:Digi-keukenweegschaal1284.jpg, *License:* GNU-FDL)

Equipment Determines the Significant Figures

In the previous section, we looked at a lot of equipment that is used for measuring specific units. The graduated cylinder that measures volume, the balance that measures mass, and the thermometer that measures temperature are a few that we looked at before. We also saw that of two types of balances, one type of balance can more precisely measure mass than the other. The difference between these two balances has to do with the number of significant digits that the balances are able to measure. Remember the pan balance could measure to +/- 0.1 g and the digital balance can measure to +/- 0.01 g.

Before going any further, what do we recall about significant digits? A measurement can only be as accurate as the instrument that produced it. A scientist must be able to express the accuracy of a number, not just its numerical value.

The instruments that we choose for the laboratory experiments depend on the required amount of accuracy. For example, if you were to make a cup of hot chocolate at home using powdered cocoa, you would probably use a measuring spoon or a teaspoon. Compare this to the requirement of massing out 4.025 g of sodium bicarbonate for a reaction sequence you are doing in the lab. Would the teaspoon do? Probably not! You would need to have what is known as an analytical balance that measures to +/- 0.001 g.

Accuracy and Precision

Accuracy and precision are two words that we hear a lot in science, in math, and in other everyday events. They are also, surprisingly, two words that are often misused. How often have you heard these terms? For example, you often hear car advertisements that talk about their precision driving ability. But what do these two words mean. Accuracy is how close a number is to the actual or predicted value. If the weatherperson predicts that the temperature on July 1st will be 30°C and it is actually 29°C, she is likely to be considered pretty accurate for that day.

Once you have gone into the lab and made measurements, whether they are mass, volume, or length, how do you know if they are correct? **Accuracy** is the difference between a measured value and the accepted - or what we call the correct - value for that quantity. To improve accuracy, scientists will repeat the measurement as many times as is possible. **Precision** is a measure of how close all of these measurements are to each other. Therefore, measurements can have precision but not very close accuracy. An example of accuracy of measurements is having the following data: 26 mL, 26.1 mL, and 25.9 mL when the accepted value is 26.0 mL. This data also shows precision. However, if the data had been 25.2 mL, 25.0 mL, and 25.2 mL, they would show precision without accuracy.

Sample question: Jack collected the following volumes when doing a titration experiment: 34.25 mL, 34.30 mL, 34.60 mL, 34.00 mL, and 34.50 mL. The actual volume for the titration required to neutralize the acid was 34.50 mL. Would you say that Jack's data was accurate? Precise? Both accurate and precise? Neither accurate nor precise? Explain.

Solution: All of Jack's data would be accurate because they are close to the true value of 34.50 mL. The data would also be precise having only 2% variance between the highest number and the lowest number.

Lesson Summary

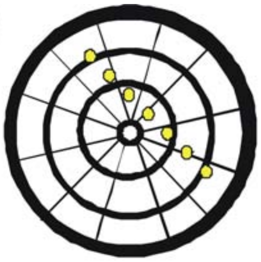
- The task in the experiment determines the unit of measurement; this then determines the piece of equipment. Example: If mass is to be measured, a balance will be chosen as the piece of equipment.
- Conversely, the piece of equipment chosen will determine the unit of measurement. Example: If a graduated cylinder is chosen, the unit of measurement will be volume (mL or L).

- Each piece of equipment has a specified number of significant digits to which it is able to measure. Example: A household thermometer may measure to ±1°C or ±1°F, where as an ordinary high school alcohol thermometer measures to ± 0.1° C.
- Significant digits are used in all parts of quantitative measurements in science. Five main rules are provided to read the significant digits of numbers and two main rules for solving algebraic equations maintaining proper significant digits.
- Accuracy is how close the value is to the actual value (remember A and a).
- Precision is how close values are in an experiment to each other. Precision is dependent on the significant digits of the instrument or measurement.

Review Questions

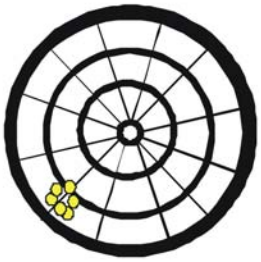
1. Suppose you want to hit the center of this circle with a paint ball gun. Which of the following are considered accurate? Precise? Both? Neither? **(Beginning)**

(a)



(b)

(C)



2. Four students take measurements to determine the volume of a cube. Their results are 15.32 cm^3, 15.33 cm^3, 15.33 cm^3, and 15.31 cm^3. The actual volume of the cube is 16.12 cm^3. What statement(s) can you make about the accuracy and precision in their measurements?

3. Find the value of each of the following to the correct number of significant digits. **(Beginning)**

(a) 1.25 + 11

(b) 2.308 – 1.9

(c) 498 – 97.6

(d) 101.3 ÷ 12

(e) 25.69 x 0.51

4. Why is the metric system used in chemistry? **(Beginning)**

5. Distinguish between accuracy and precision. **(Intermediate)**

6. How many significant digits are present in each of the following numbers: **(Beginning)**

a. 0.002340 b. 2.0×10^{-2} c. 8.3190 d. 3.00×10^{8}

7. Nisi was asked the following question on her lab exam. When doing an experiment, what term best describes the reproducibility in your results? What should she answer? **(Beginning)**

a. accuracy

b. care

c. precision

d. significance

e. uncertainty

8. Karen was working in the lab doing reactions involving mass. She needed to weigh our 1.50 g of each reactant and put them together in her flask. She recorded her data in her data table and began to look at it. What can you conclude by looking at Karen's data? **(Beginning)**

	Mass of Reactant 1	**Mass of Reactant 2**
Trial 1	1.45 ± 0.02 g	1.46 ± 0.02 g
Trial 2	1.43 ± 0.02 g	1.46 ± 0.02 g
Trial 3	1.46 ± 0.02 g	1.50 ± 0.02 g

a. The data is accurate but not precise.

b. The data is precise but not accurate.

c. The data is neither precise nor accurate.

d. The data is precise and accurate.

e. You really need to see the balance Karen used.

9. Find the value of each of the following to the correct number of significant digits. **(Challenging)**

a. 3.567 + 3.45

b. 298.968 + 101.03

c. 1.25 × 11

d. 27 ÷ 5.67

e. 423 × 0.1

Further Reading / Supplemental Links

The website listed below offers lessons, worksheets, and quizzes on many topics in high school chemistry.

- Lesson 2-2 is on Accuracy and Precision.

http://www.fordhamprep.org/gcurran/sho/sho/lessons/lesson12.htm

http://learner.org/resources/series61.html"

The ***learner.org*** website allows users to view streaming videos of the Annenberg series of chemistry videos. You are required to register before you can watch the videos but there is no charge. The website has two videos that apply to this lesson. One is a video called ***Measurement, The Foundation of Chemistry*** that details the value of accuracy and precision. Another video called ***Modeling the Unseen*** relates to the scientific method and the use of models.

Vocabulary

significant digits	A way to describe the accuracy or precision of an instrument or measurement.
accuracy	How close a number is to the actual or predicted value.
precision	How close values are in an experiment to each other.

Review Answers

1. A is neither accurate nor precise, B is both accurate and precise, C is precise but not accurate.

2. Their work is precise but not accurate.

3. a) 12 b) 0.4 c) 400. d) 8.4 e) 13

4) Answers may vary, but primarily because the units in the metric system are multiples of 10.

5) Accuracy deals with how close your values are to the true values, precision is how close the values are to each other.

6) a) 4 b) 2 c) 5 d) 3

7) c

8) d

9)

a) 7.02

b) 400.00

c) 14

d) 4.8

e) 40 or 4×10^1

Using Data

Lesson Objectives

- Recognize patterns in data from a table of values, pictures, charts and graphs.
- Make calculations using formulae for slope and other formulae from prior knowledge.
- Construct graphs for straight lines.

- Construct graphs for curves.
- Read graphs using the slope of the line or the tangent of the line.

Introduction

Earlier, we learned about qualitative and quantitative observations, and that with quantitative observations, we need measurements. In science, measurements mean data. In this upcoming section, we will delve deeper with data to look at patterns and to graph data. Sometimes we can graph the data, make calculations, sketch the line, and calculate the slope. All of these quantitative observations help us to formulate a conclusion that will be based on evidence.

Recognizing Patterns in the Data

As stated earlier, data can provide enormous information to scientists for making interpretations and drawing conclusions. In order for scientists to do this, they have to be able to look at a set of data and recognize patterns. Data can be in the form of pictures, charts, or graphs. Take for example, the picture found in Figure 1. This, although not particularly chemistry related, has much to do with the concept of pattern recognition and the data gathered from these patterns. What do you believe scientists determined when first viewing this image prior to August 23, 2005?

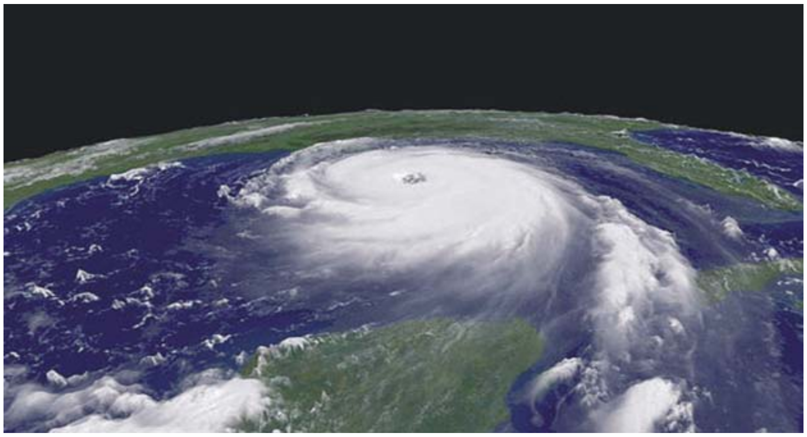


Figure 1: Hurricane Katrina taken on Aug. 28, 2005, at 11:45 a.m. EDT by NOAA when the storm was a Category Five hurricane.

(*Source*: www.gisuser.com)

Now, let us look at a common chemistry example. We all know that metals are supposed to be chemically reactive. How do we know that? Well, that is a property of metals. But how reactive are they? How can you tell? What do you know about the periodic table that would help you determine this right now? Look at the table below and see if you can gather a little evidence that can solidify your conclusions about the chemical reactivity of metals and the periodic table.

Table 1: Information about Metals and Reactivity

Metal	**Chemical Reactivity in Atmosphere**
Sodium	Stored in toluene, extremely reactive
Potassium	Burns in O_2 in seconds
Calcium	Slower to react with O_2 than its neighbors to the right
Titanium	Resists corrosion after forming an oxide barrier
Aluminum	Resists corrosion after forming an oxide barrier
Gold	Does not react with oxygen

Platinum	Does not react with oxygen
Copper	Does not react with H_2O, will react slowly with O_2
Iron	Rusts in O_2

What kinds of conclusions can you make from reading this table? Can you determine that the reactions between the metals and the oxygen in the air decrease going across a row on the periodic table? Did you notice that the alkali (group one) metals (sodium and potassium) are the most reactive of all the metals with oxygen and the alkaline earth (group two) metals (calcium) are the second most reactive? Yes, they are. Aluminum as well as titanium will actually become coated with an oxide of their metals, which acts like a protective shield against further reaction. Look at the figure below. The copper has turned green as a result of this protective coating that formed on the copper rooftop. Have you ever seen this before?

Figure 2: The current Hotel Vancouver took over a decade to build during the 1930s as the Great Depression put a temporary halt to construction. It was Vancouver's tallest building from 1939 to 1972.

(*Source:* http://upload.wikimedia.org/wikipedia/commons/1/10/HotelVancouver.jpg)

What kind of observations are these? Are they quantitative? No, of course not because they have no measurements attached; they are qualitative observations.

What about other types of data that involve quantitative observations? Can we look at measurements and determine patterns? Yes we can. Statisticians, weather persons, stock market workers, sports analysts, and chemists (to name a few occupations) do this on a daily basis for their regular jobs. What if you were trying to identify an unknown substance based on a volume displacement experiment. You were given a series of known substances of known masses, and you then determined how much volume they displaced in a cylinder of water. Through your experiment, the following data was recorded.

Table 2: Volume Displacement Data

Substance	**Mass**	**Volume of Water Displaced**
Aluminum	2.7g	1.0 mL
Iron	7.86g	1.0 mL
Copper	8.92g	1.0 mL

Silver	10.5g	1.0 mL
Zinc	7.14g	1.0 mL
Lead	11.34g	1.0 mL

First, which metal do you think is the densest, just looking at the data table? Do you think it would be lead or aluminum? How can you tell? Lead is the right answer because there is a heavier mass of lead displacing the same volume of water. Did you notice that copper is heavier than iron, and iron is heavier than zinc? Now what kind of data do you think this is? Is it qualitative or quantitative? Quantitative is the right answer because we are dealing with measurements.

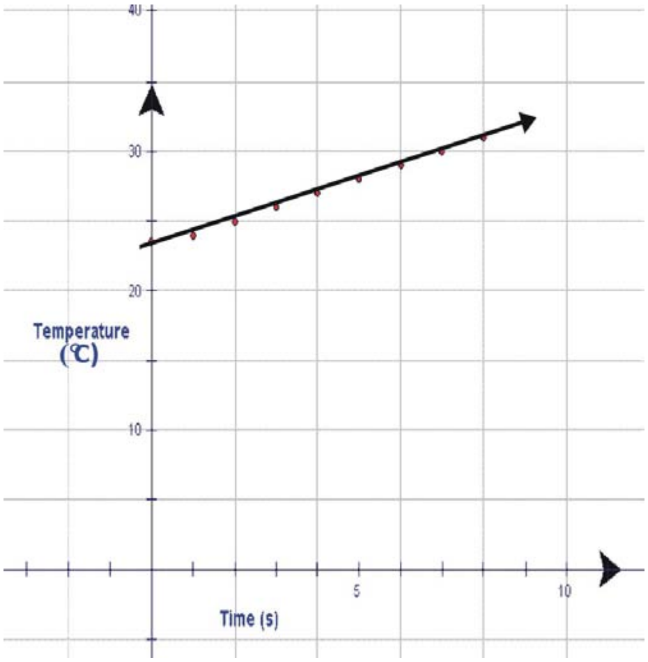
An interesting note is that 19.3 g of gold would have displaced the same volume of water. Would it be the densest? Yes it would. It also means that this same amount of gold converts to approximately 212.5 lb/gal. Remember seeing in television or movies where the villain is running off with a bag full of gold bars? This would be rather difficult knowing the density of the metal from this table. Being able to read tables and data gives us the power to understand the world around us.

Another way to generalize trends in data and to make interpretations based on these trends is to plot a graph. Graphs are like numerical pictures that provide an image of the data collected in an experiment. Suppose you were asked to record the temperature of a mixture as it was slowly heated in a hot water bath. You record the following data as you watch your experiment. You then plot the data on a graph to see what the numbers tell you.

Table 3: Time vs. Temperature

Time (s)	**Temperature (°C)**
0	23.5
1	24
2	25
3	26
4	27
5	28
6	29
7	30
8	31
9	32

Graph 1: Time vs. Temperature



Looking at the graph, what do you notice about the temperature of the mixture as it is heated in the hot water bath? It is constantly increasing. What does the initial point, or the *y-intercept* represent? It is the value of the initial temperature, most likely room temperature. Using a graph, it is clear to see that the *y-axis,* in this case temperature, is dependent on the *x-axis*. For our example, the independent variable is time. What does this mean? It means that for a change to be made in temperature, time must pass.

Being able to plot tables of values and read the corresponding graphs is an important skill, not only for mathematics but also for science. Interpretations can be made by using either of these representations; one may be more visual and thus sometimes easier to interpret than the other. Now try one example where you have to plot a graph and make some interpretations.

Sample Question: The following data represents the marks of 12 students in a Math Test and in a Chemistry Test. All Marks are out of 50.

Table 4: Math Marks vs. Chemistry Marks

Math	17	38	40	17	28	30	45	24	48	42	32	36
Chemistry	8	32	36	17	19	20	43	16	48	40	22	29

a. Plot this data on an x-y axis, with Math marks on the x-axis.

b. Draw the line of best fit. A line of best fit is drawn on a scatter plot so that it joins as many points as possible and shows the general direction of the data. When constructing the line of best fit, it is also important to keep, approximately, an equal number of points above and below the line.

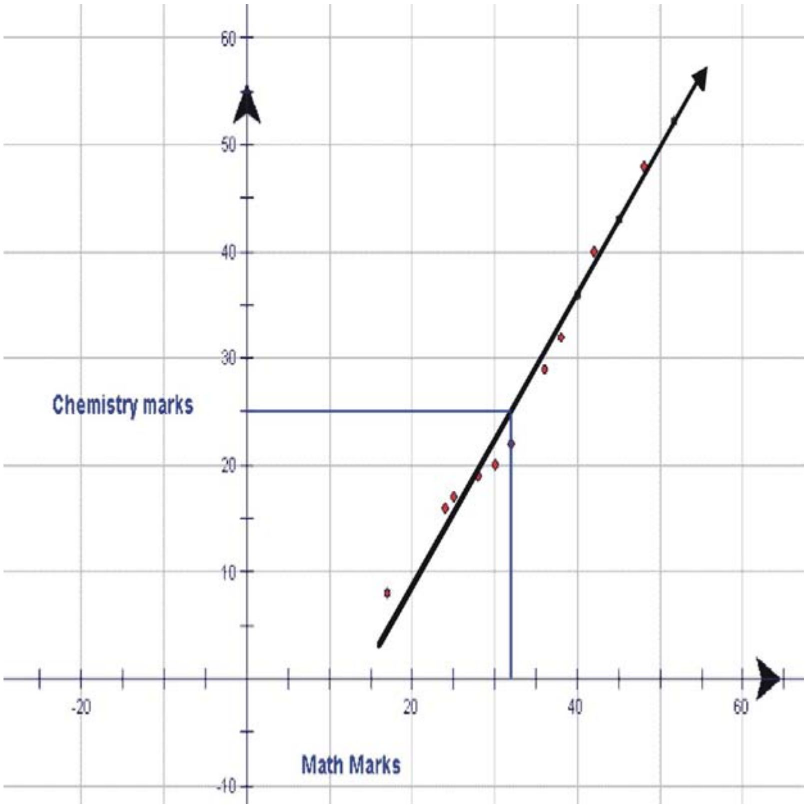
c. Estimate the chemistry mark of a student who scored 32 on a math test.

d. Estimate the math mark of a student who scored 45 on a chemistry test.

e. Based on the trend found in the data, what can you say about the relationship between math and chemistry marks?

Solution: a) and b)

Graph 2: Math Marks vs. Chemistry Marks



c) The chemistry mark when a student makes 32 in math is approximately 25. We can see this by the blue line. By interpolating the data, we can draw a line up from the 32 mark on the x-axis to where the line of best fit runs through the data points. Here, we cut across to the y-axis to find the corresponding chemistry mark.

d) The math mark when a student makes 45 in chemistry is approximately 47. We can see this by the green line. By interpolating the data, we can draw a line across from the 45 mark on the y-axis to where the line of best fit runs through the data points. Here, we draw a line down to the x-axis to find the corresponding math mark.

e) The trend shows that as math marks increase, so do chemistry marks. The dependent variable in this graph is the chemistry mark.

Making Calculations With Data

Being able to recognize patterns from tables, charts, pictures, and graphs is a worthy skill for any scientist and science student. By having charts, pictures, tables, and graphs, you can also perform a large variety of calculations depending on the independent and dependent variables. From here we can accomplish such things as making further predictions, drawing more conclusions, or identifying unknowns. Let's say, for example, in the density experiment from earlier, we were given an unknown for our experiment. Now, take the same chart but add a fourth column representing the density of the metal. Recall the formula for density:

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

Now, filling in the fourth column, using the density formula for our experimental data, we see the following information. Remember density = mass / volume or, in the table below, column 4 = column 2 / column 3.

Substance	**Mass**	**Volume of Water Displaced**	**Density**
Aluminum	2.7g	1.0 mL	2.7 g/ mL
Iron	7.86g	1.0 mL	7.86 g/ mL

Copper	8.92 g	1.0 mL	8.92 g/ mL
Silver	10.5 g	1.0 mL	10.5 g/ mL
Zinc	7.14 g	1.0 mL	7.14 g/ mL
Lead	11.34 g	1.0 mL	11.34 g/ mL
Unknown	1.78 g	0.2 mL	8.9 g/ mL

Just by doing this calculation, we can identify our unknown in the experiment? Sure, it is copper. Calculations are frequent in chemistry, as you will learn. Most times you will see we will use a variety of formulae to solve problems similar to those you would solve in any course. The relationship from comparing sets of answers give us the interesting parts of these types of calculations.

Sample Question: How long does it take you to run 3.5 miles at 7 mph?

Solution: We know that: *speed* = $\frac{\text{distance}}{\text{time}}$

Therefore: *time* = $\frac{\text{distance}}{\text{speed}}$

time = $\frac{3.5\ \text{mi}}{7\ \text{mi/h}}$

time = 0.5 h

Another important skill with calculations is converting from one unit to another. Frequently in chemistry, data will appear in problems that require us to use conversion factors before completing the problem. Some conversion factors include 100 cm = 1m, 1000 mL = 1L, and 1 km = 1000 m.

Sample Question: The speed of light is 3.00×10^8 m/s. The speed of sound is 1230 km/h. How much faster is the speed of light than the speed of sound.

Solution: Speed of Sound = 1230 km/h x $\frac{1000\ m}{1\ km} \times \frac{1\ h}{60\ min} \times \frac{1\ min}{60\ sec}$

Speed of Sound = 342 m/s

$$\frac{\text{speed of light}}{\text{speed of sound}} = \frac{3.00 \times 10^8\ m/s}{342\ m/s}$$

$$\frac{\text{speed of light}}{\text{speed of sound}} = 8.77 \times 10^5$$

In other words, the speed of light is almost 900,000 times faster than the speed of sound. Amazing isn't it!

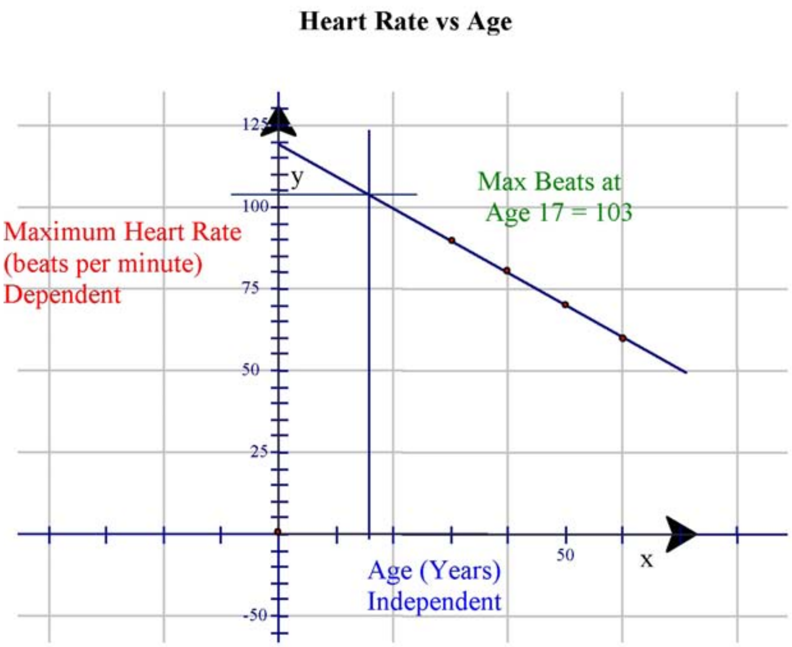
Preparing Graphs From Data

Most times in the laboratory, we collect data of some sort and then carry it back to our desk to analyze. We want to determine the melting point of an unknown solid, so we take the melting points of various knowns and then that of our unknown; following this, we make a table, finally writing the data gathered from our experiment into the table. Some laboratory experiments that we, as scientists, do require us to draw graphs in order to interpret the results and make any conclusions. Drawing a graph that anyone can understand is a useful skill to any scientist. Graphs have to be properly labeled on the x-axis (the horizontal) and the y-axis (the vertical). The graphs should indicate a straight line or smooth curve indicating that the data is continuous. A straight line represents a linear relationship; a curved line does not.

Sample Question: Medical practitioners have been studying the heart for a long time. As a result, we can now calculate your heart rate based on a formula derived from your age. Plot the table of values given below. Properly label the graph include the independent and dependent variable. Draw the line all the way to the y-axis so that you can find the y-intercept. Finally, find your age on the x-axis and then find your maximum heart rate by drawing a vertical line up to the graph.

Age in Years (x)	30	40	50	60
Beats Per Minute (y) (maximum heart rate)	90	80	70	60

Solution: At the age of 17, the maximum heart rate (beats per minute) read from the graph is 103.



Reading Results From the Graph

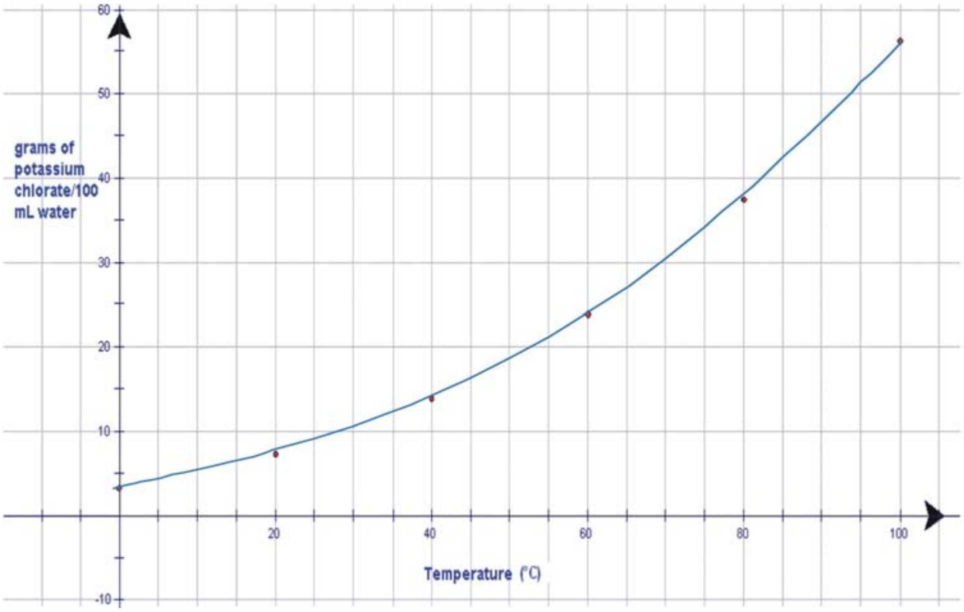
Many properties in chemistry lead to linear relationships when plotted. We saw this with the temperature/time relationship. Other properties in chemistry do not form this linear relationship. Take for example the relationship between concentration and temperature. Remember the last time you made a cup of instant coffee or hot chocolate? Why did you boil the water? What would have happened if you used warm tap water or even cold water from the refrigerator? Putting aside the anticipated taste difference, what would have happened to the solid you were trying to dissolve? The amount of instant coffee or hot chocolate powder in your cup that actually dissolves in warm or cold water would be small compared to when you use boiling water. This property is known as solubility. The solubility of a substance is the amount that can dissolve in a given amount of solution. Solubility is affected by the temperature but rarely linearly. Look at the data table below. This data is for the solubility of $KClO_3$ (potassium chlorate) in water.

Temperature(°C)	**Solubility (g/100 mL H_2O)**
0	3.3
20	7.3
40	13.9
60	23.8
80	37.5

100	56.3

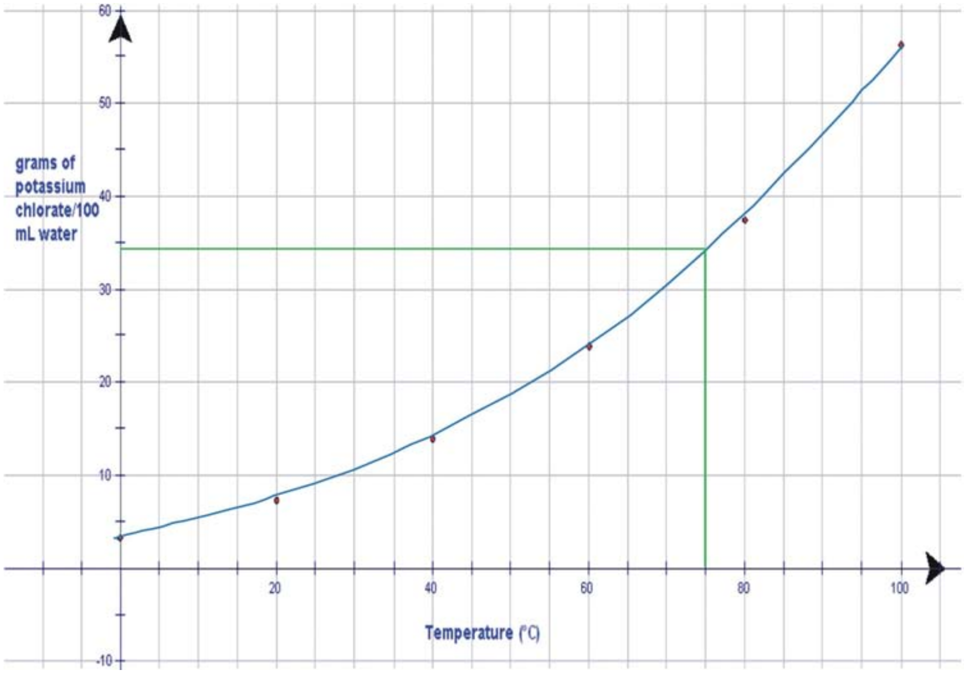
Now graph the data and see what kind of curve we get.

Solubility of Potassium Chlorate



Notice how when the line is drawn, the relationship between grams of potassium chlorate that dissolve in 100 mL of water and temperature is not linear but curved. We can still interpret the data as we did earlier. For example, what is the solubility of $KClO_3$ (how much $KClO_3$) when the temperature is 75°C or at room temperature.

Solubility of Potassium Chlorate



Using the same procedure, we draw a line up from 75°C and then over to the y-axis. It reads 34.5 g/100 mL. Therefore, 34.5g of $KClO_3$ can dissolve in 100 mL of H_2O at 75°C.

Now you try one:

Sample Question:

Ammonia, NH_3, and sodium chloride, NaCl, are known to have the following solubility data.

Temperature ($^{\circ}$C)	**NH_3 Solubility (g/100 mL H_2O)**	**NaCl Solubility (g/100 mL H_2O)**
0	88.5	35.7
20	56.0	35.9
40	34.0	36.4
60	20.0	37.1
80	11.0	38.0
100	7.0	39.2

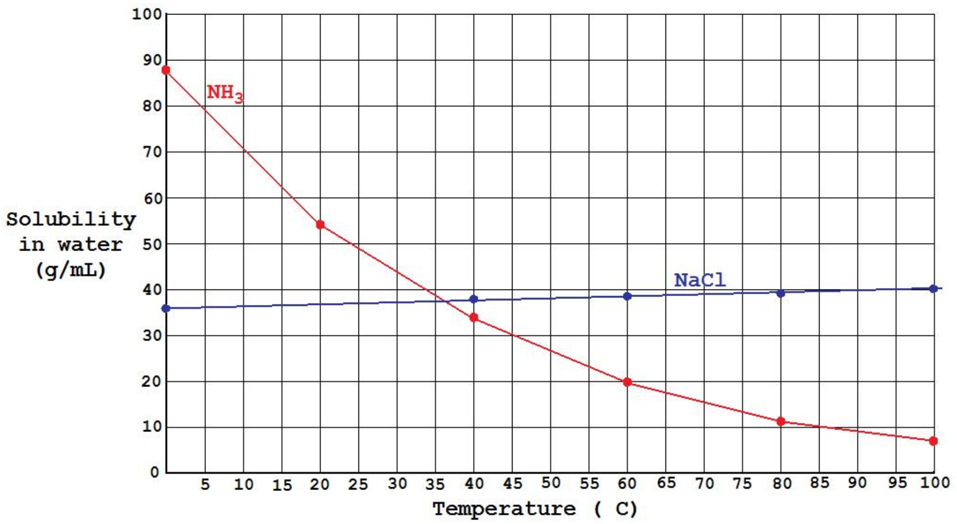
a) Properly graph the data for each substance.

b) Are either of these linear? Explain.

c) What would be the solubility of each of the substances at 50^{0}C?

Solution:

Solubility of NH_3 and NaCl



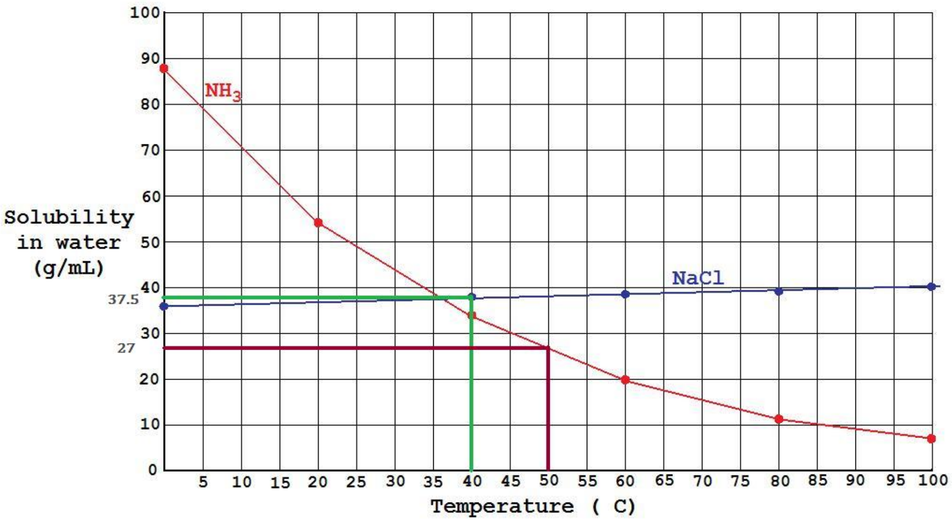
a)

b) The Solubility data for NaCl represents a linear relationship when graphed. You can see this with the blue line in the graph above. The NH_3 line (in red) is curved; therefore it is non-linear.

c) The solubility of NH_3 at 50 $^{\circ}$C is 27 g/100 mL H_2O. The solubility for NaCl at 50 $^{\circ}$C is 37.5 g/100 mL H_2O.

The graph below is marked to show the line travelling up from 50 $^{\circ}$C and over to the y-axis (solubility) to find the answer for both of these parts.

Solubility of NH_3 and NaCl



We can do more than just graph and read graphs of linear and non-linear data in order to make conclusions. For this, we use formulas like the slope of a line. Remember slope from math class? It is a formula used to find the rate at which one factor is affecting the other, either positively or negatively. Remember the formula for slope from math class?

$$\text{slope} = \frac{\text{rise}}{\text{run}} \quad \text{or} \quad m = \frac{y_2 - y_1}{x_2 - x_1}$$

Let's look at how the slope formula can be used on a graph to see how one factor is affecting another in an experiment.

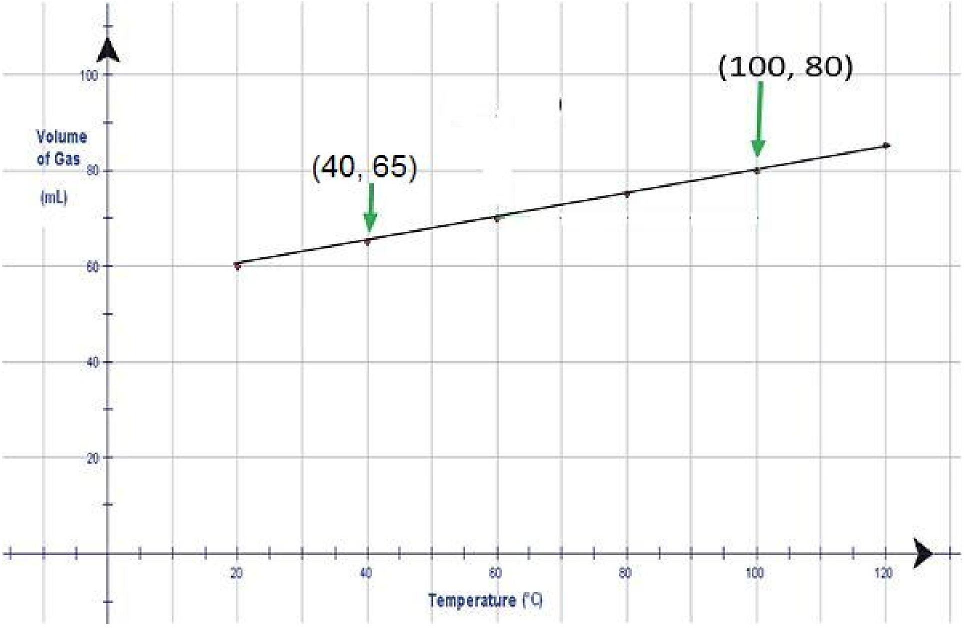
Figure 3: A modern hot air balloon.

(*Source:* http://en.wikipedia.org/wiki/Image:2006_Ojiya_balloon_festival_011.jpg, *License:* CC-BY-SA)

In the 1800s, the use of the hot air balloons was extremely popular as a sport as well as an extracurricular activity for those who could afford the luxury. Up to this point, the study of the relationship of gases and the factors of temperature, pressure, and volume was limited to Robert Boyle's experiments with pressure and volume. Jacques Charles came along with his experiments on the relationship between volume and temperature. Here is some typical data from a volume/temperature experiment with gases.

Temperature (C^0)	Volume of Gas (cm^3)
20	60
40	65
60	70
80	75
100	80
120	85

Volume of a Gas vs. Temperature



Now, find out what affect the temperature has on the volume of the gas. In other words, find the slope. Pick two points that are on the line and use the equation above to find the value of *m*.

$$m = \frac{y_2 - y_1}{x_2 - x_1}$$

$$m = \frac{80 - 65}{100 - 40}$$

$$m = \frac{15}{60}$$

$m = 0.25\ cm^3/^oC$

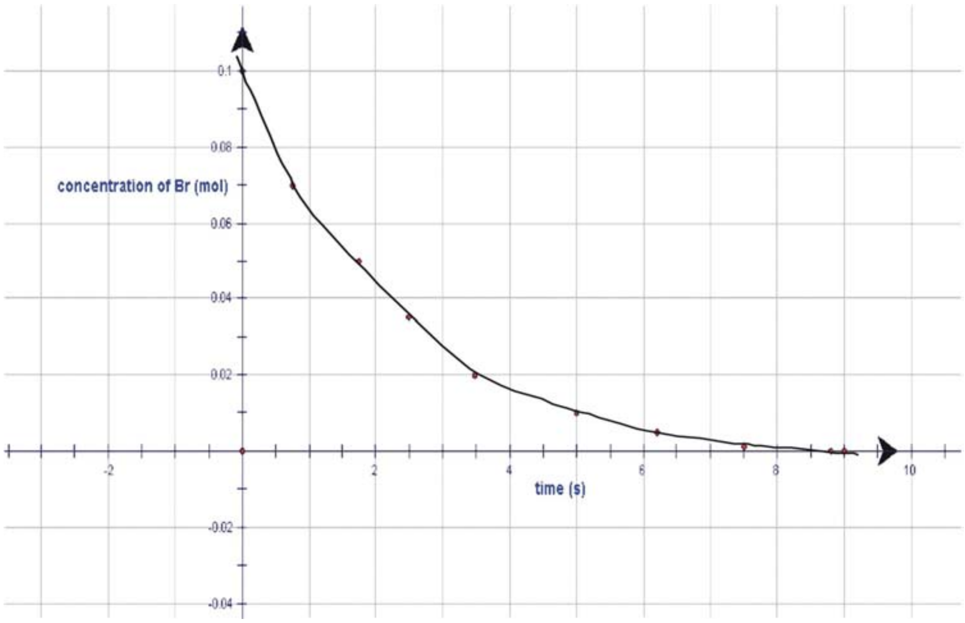
What does this mean? It means that for each increase in temperature of 1^oC, the volume increased by 0.25 cm^3 (or 0.25 mL). This translates to approximately 1 mL increase every 4^oC. This is a positive increase (notice the slope is increasing or going up). Now let's try another one.

Look at the table below for a set of data from an experiment performed between bromine and formic acid in a laboratory setting. The reaction was performed to see if the decrease in bromine concentration could cause the reaction to subsequently slow down. In other words, if they took some of the bromine out of the reaction, would the reaction start to slow down? Look at the data and see what happened.

Reading	Concentration of Bromine (mol/L)	Time
1	0.1	0
2	0.07	0.75
3	0.05	1.75
4	0.035	2.49
5	0.02	3.48
6	0.01	5
7	0.005	6.2
8	0.001	7.5
9	0.0	8.8
10	0.0	9

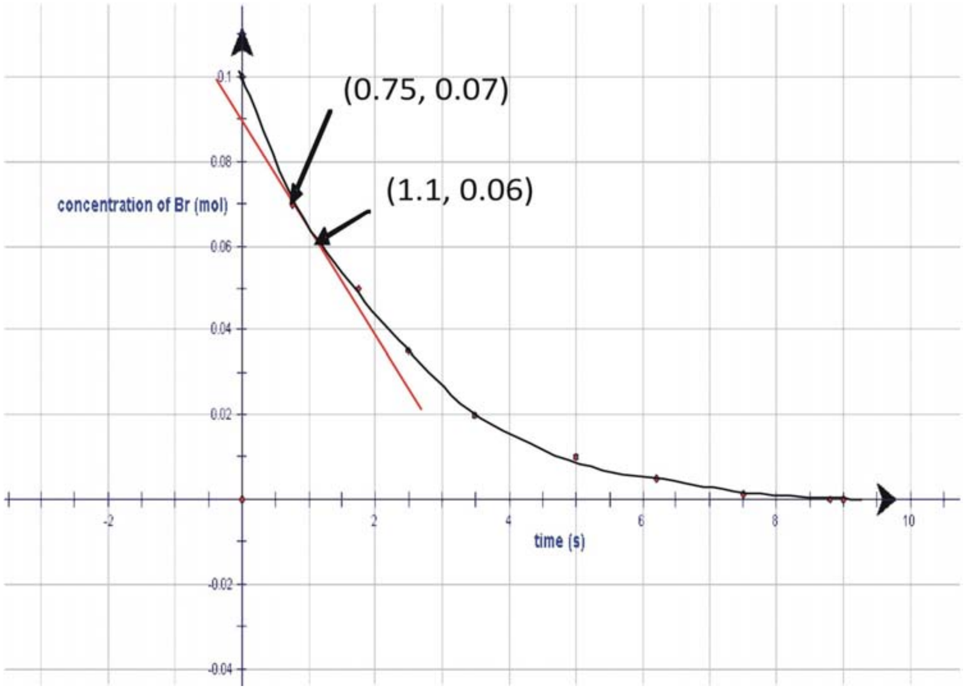
Look at the data table, can you tell if an increase in bromine concentration had an effect on the rate of a reaction? Did it make it go faster or slower. Let's take a look. From T_1 to T_7 the bromine concentration decreased from 0.1 mol/L to 0.005 mol/L, a decrease of 0.095 mol/L. The time it took for this decrease was 6.2 seconds. What does this tell us about the rate? A preliminary conclusion would be that a decrease in bromine concentration causes the rate of the reaction to also decrease. A graph might make it a little easier to make conclusions based on the data.

Concentration of Bromine vs. Time



Using slope to calculate the effect here is not as easy because we have a curve. We can easily see that as the concentration increases, so does the rate, but by how much? The slope would actually tell us that. In order to determine the slope of a curve, you need to draw in a tangent to the curve. A tangent is just a straight line drawn to the curve; from this you would calculate the slope. Look at the graph below, the tangents are drawn in using a red pen.

Concentration of Bromine vs. Time



If we draw a tangent, look, we have a straight line. We can now, find two points.

$$m = \frac{y_2 - y_1}{x_2 - x_1}$$

$$m = \frac{0.06 - 0.07}{1.1 - 0.75}$$

m = -0.028 mol/L·s

This means that as the concentration of bromine decreases, so does the rate of the reaction. Look at the units for the slope. The units are mol/L ·s. These are the units for rate. This means, interestingly enough, that as the concentration goes down, the reaction slows down.

Lesson Summary

- Patterns can be found in data sets, pictures, charts, and graphs. From here scientists can make interpretations of the data and draw conclusions.
- When drawing graphs of tables of values, a straight line or a smooth curves can be drawn. Some data sets do require a line of best fit.
- A line of best fit is drawn on a scatter plot so that it joins as many points as possible and shows the general direction of the data. When constructing the line of best fit, it is also important to keep, approximately, an equal number of points above and below the line.
- Conversion factors are necessary for calculations where the units do not match. For example, km and m.
- Recall the slope formula: $m = \frac{y_2 - y_1}{x_2 - x_1}$
- For curved lines, remember to draw the tangent first and then find the slope of the tangent line.

Review Questions

1. Why is the slope of a graph so important to chemistry? **(Intermediate)**

2. What would you do to find the slope of a curved line? **(Intermediate)**

3. What is a conversion factor used for? **(Intermediate)**

4. Of the following professions, choose the one that uses data to find the identity of unknown fingerprints? **(Beginning)**

a. analytical chemist

b. archaeological chemist

c. inorganic scientist

d. forensic scientist

e. quality control chemist

5. Which speed is the slowest? **(Intermediate)**

a. 200 m/min (200 m/min × 1 km/1000 m = 0.2 km/min)

b. 0.2 km/min

c. 10 km/h (10 km/h × 1 h/60 min = 0.17 km/min)

d. 1.0×10^5 mm/min (1.0×10^5 mm/min × 1 m/1000 mm × 1 km/1000 m = 0.1 km/min)

e. 10 mi/h (10 mi/h × 1.603 km/mi × 1 h/60min = 0.267 km/min or 0.27 km/min)

6. Andrew was completing his density lab for his chemistry lab exam. He collected the following data in his data table. **(Intermediate)**

Mass of Solid (g)	Volume of Solution (mL)
3.4	0.3
6.8	0.6
10.2	0.9
21.55	1.9
32.89	2.9
44.23	3.9
55.57	4.9

(a) Draw a graph to represent the data.

(b) Calculate the slope.

(c) What does the slope of the line represent?

(d) Can you help Andrew determine what his unknown is by looking in a standards table?

7. Donna is completing the last step in her experiment to find the effect of the concentration of ammonia on the reaction. She has collected the following data from her time trials and is ready for the analysis. Donna is now required to graph the data, describe the relationship, find the slope and then discuss the meaning of the slope. Help Donna with the interpretation of her data. **(Challenging)**

Time (s)	Concentration (mol/L)

0.20	49.92
0.40	39.80
0.60	29.67
0.81	20.43
1.08	14.39
1.30	10.84
1.53	5.86
2.00	1.95
2.21	1.07
2.40	0.71
2.60	0.71

Further Reading / Supplemental Links

http://en.wikipedia.org/wiki/Metal

http://en.wikipedia.org/wiki/Hurricane_Katrina

http://en.wikipedia.org/wiki/Solubility_table

Vocabulary

chemical reactivity	An observation of the behavior of the element of compound based on its position in a reactivity (or activity) series.
periodic table	An arrangement of elements in order of increasing atomic number.
alkali metals	Group 1 metals of the periodic table (H, Li, Na, K, Rb, Cs, Fr).
alkaline earth metals	Group 2 metals of the periodic table (Be, Mg, Ca, Sr, Ba, Ra).
density	Measurement of a mass per unit volume. *Density* = $\frac{\text{mass}}{\text{volume}}$.
graphs	Pictorial representation of patterns using a coordinate system (x-y axis).
dependent variable	The variable that changes depending on another variable (y-axis variable).
independent variable	The variable that changes to cause another variable to change (x-axis variable).
y-intercept	Where the line crosses the y-axis.
conversion factor	A ratio used to convert one unit to another.
linear relationship	A relationship where the x-values change proportionally with the y-values leading to a straight line.
non-Linear relationship	A relationship where the x-values do not change proportionally with the y-values leading to a curved line.
a line of best fit	A line drawn on a scatter plot so that it joins as many points as possible and shows the general direction of the data. When constructing the line of best fit, it is also important to keep, approxi-

	mately, an equal number of points above and below the line.
slope	A formula to find the rate at which one factor is affecting the other. $m = \frac{y_2 - y_1}{x_2 - x_1}$
tangent	A straight line drawn to the curve.
solubility	The amount of a substance that can dissolve in a given amount of solution.

Review Answers

1) the slope tells us the rate at which one factor is affecting the other

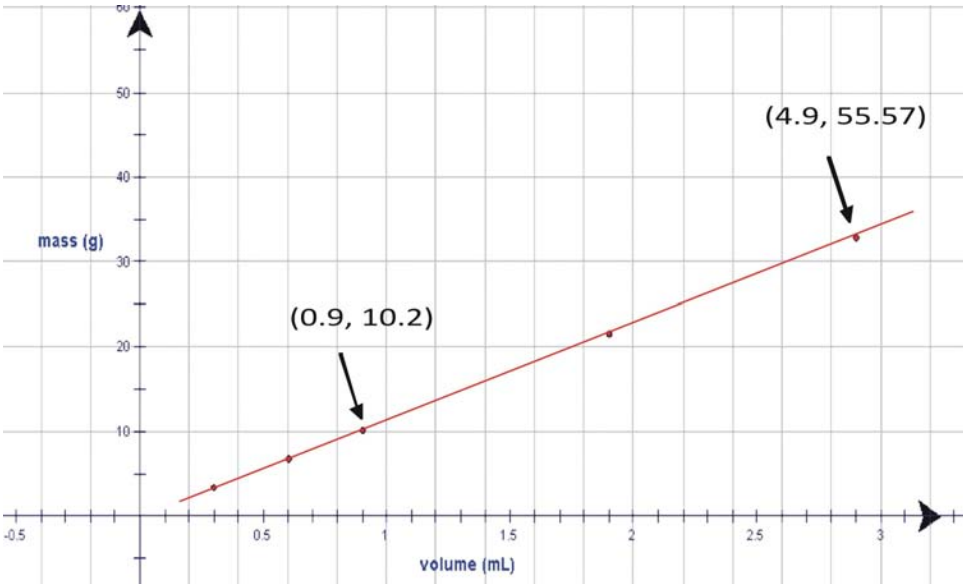
2) draw a tangent to the curve and find the slope of the tangent line

3) to change one unit into another

4) d

5) d

6) a



b) $m = \frac{y_2 - y_1}{x_2 - x_1}$

$m = \frac{55.57 - 10.2}{4.9 - 0.9}$

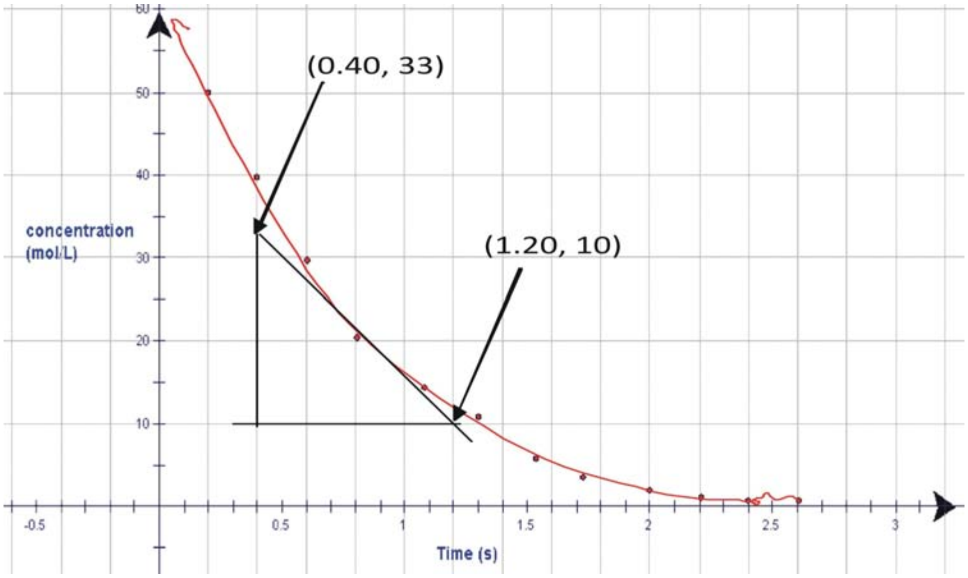
m = 11.3 g/mL

c) The slope represents the density of the unknown.

d) The unknown is lead.

7)

a)



b) The graph is a curve so draw the tangent and take the slope of the tangent:

$$m = \frac{y_2 - y_1}{x_2 - x_1}$$

$$m = \frac{10 - 33}{1.20 - 0.40}$$

m = -28.75 mol/L·s

c) The slope represents the rate of the reaction or the rate at which the concentration of ammonia changes with time (in this case decreases).

How Scientists Use Data

Lesson Objectives

- Define the terms law, hypothesis, and theory.
- Explain why scientists use models.

Introduction

In the last section, we learned a little more about making quantitative and qualitative observations. A set of observations about a particular phenomenon is called data. Scientist use many techniques to analyze and interpret data. Data analysis produces organized data that is more conducive to seeing regularities and drawing conclusions. Making tables and graphs of data are two of the most useful techniques in data analysis.

Natural Laws are Statements of Repeated Data Patterns

Around the year 1800, Jacque Charles and other scientists were working with gases to, among other reasons, improve the design of the hot air balloon. These scientists found, after many, many tests, that patterns and regularities existed in the observations on gas behavior. If the temperature of the gas increased, the volume of the gas increased. This is known as a natural law. A natural law is a relationship that exists between variables in a group of data. Natural laws describe the patterns we see in large amounts of data. These laws have withstood the test of time because they have been based on repeated observation with no known exceptions.

Figure 1: Scuba Divers.

Around the same time as Charles was working with hot air balloons, another scientist, names J.W. Henry was doing experiments trying to find a pattern between the pressure of a gas and the amount of the gas that dissolved in water. Henry found that when one of these variables increased, the other variable increased in the same proportion. Have you ever gone scuba diving? Scuba Divers learn about a problem known as “the Bends” when they are being trained. As scuba divers dive deeper, the increased pressure of the breathing air causes more nitrogen to be dissolved in the diver's blood. Coming up too quickly from a dive causes the pressure to decrease rapidly and therefore, the nitrogen to leave the blood quickly which leads to "the bends." Henry's Law is called a natural law because it indicates a relationship (regularity) between gas pressure and the amount of dissolved nitrogen.

A Hypothesis is a Tentative Explanation

When scientists develop a description of the nature of matter to explain observations (including natural laws), the first attempt at an explanation is often referred to as a hypothesis. A hypothesis is your educated or best guess as to the nature of matter that causes those observations. The requirements for a hypothesis are only that the hypothesis explains ALL the observations and that it is possible to make an observation that will refute the hypothesis.

The hypothesis must be testable. The test of a hypothesis is called an experiment. If the results of the experiment contradict the hypothesis, the hypothesis is rejected and a new hypothesis is formulated. The results of the experiment are now included in the observations list and the new hypothesis must explain this new observation as well as all the previous observations. If the result of the experiment supports the hypothesis, more tests are still required. Hypotheses are not proven by testing . . . they are merely supported or contradicted.

A Theory is an Explanation of a Law

As stated earlier in this section, a law describes a pattern of data that is observed with no known exception. A theory is a possible explanation for a law. In science, theories can either be descriptive (qualitative) or mathematical (quantitative), but because they explain the patterns described in the law, theory can be used to predict future events. On a popular television show, mathematical theories are used to analyze and describe behavior in order to predict future events. Hypotheses that have survived many supportive tests are often called theories. Theories have a great deal more supportive testing behind them than do hypotheses.

Let’s put it together. The Law of Conservation of Mass that you learned earlier stated that matter cannot be created nor destroyed. For example, in the reaction below, you will see that there are 28 g + 6 g = 34 g of reactants (before the arrow) and 34 g of products (after the arrow).

$$N_{2(g)} + 3\ H_{2(g)} \longrightarrow 2\ NH_{3(g)}$$

28 g   6 g   34 g

Mass must remain constant from the start of a reaction to completion. This law was the result of many quantitative experiments done by John Dalton and others in the early part of the 1800s. Dalton had formulated many hypotheses surrounding his vision of how the elements worked together, how compounds formed, and how chemical reactions would take place maintaining this mass from beginning to end. Eventually, in 1803, Dalton was able to propose the atomic theory which was an explanation for this law.

Sample Question: What distinguishes a law from a theory?

Solution: A law is an observation of nature; a theory is a possible explanation of the law.

Models Developed to Aid in Understanding

Scientists often use models when they need a way to communicate their understanding of what might be very small (such as an atom or molecule) or very large (such as the universe). A model is another way to express a theory.

If you were asked to determine the contents of a box that cannot be opened, you would do a variety of experiments in order to develop an idea (or a model) of what the box contains. You would probably shake the box, perhaps put magnets near it and/or determine its mass. When you completed your experiments, you would develop an idea of what is inside; that is, you would make a model of what is inside a box that cannot be opened.

A good example of how a model is useful to scientists is the kinetic molecular theory. The theory can be defined in statements, but it becomes much more easily understood if representations of the particles in their three phases are drawn.

Another example is how models were used to explain the development of the atomic theory. As you will learn in a later chapter, the idea of the concept of an atom changed over many years. In order to understand each of the different theories of the atom according to the various scientists, models were drawn, and more easily understood.

Lesson Summary

- A natural law is an observation, or a description of a large amount of reproducible data.
- A hypothesis is a early attempt at an explanation for data.
- A theory is used to explain a law or to explain a series of facts/events.
- Theories can use qualitative analogies or models to describe results.

Review Questions

1. Jack performed an experiment where he measured the masses of two different reactants and the resulting product. His results are shown in the equation below. What law is Jack demonstrating in his experiment? **(Intermediate)**

$$\begin{array}{ccccc} S_{(s)} & + & 2\ T_{(s)} & \longrightarrow & ST_{2(s)} \\ 10\text{ g} & & 20\text{ g} & & 30\text{ g} \end{array}$$

a. law of constant composition

b. law of combining volumes

c. law of conservation of mass

d. law of conservation of energy

e. law of multiple proportions

2. Sugar dissolves in water. What kind of a statement is this? **(Beginning)**

a. a hypothesis

b. a law

c. a theory

d. a rule

e. all of the above

3. Draw a model to represent the difference between a solid, a liquid, and a gas. In your model, use symbols to represent the molecules that are present in each state. The model should then show how the molecules exist in each state. **(Intermediate)**

Further Reading / Supplemental Links

http://en.wikipedia.org/wiki/Category:Chemistry_theories

http://en.wikipedia.org/wiki/Polytetrafluoroethylene

Vocabulary

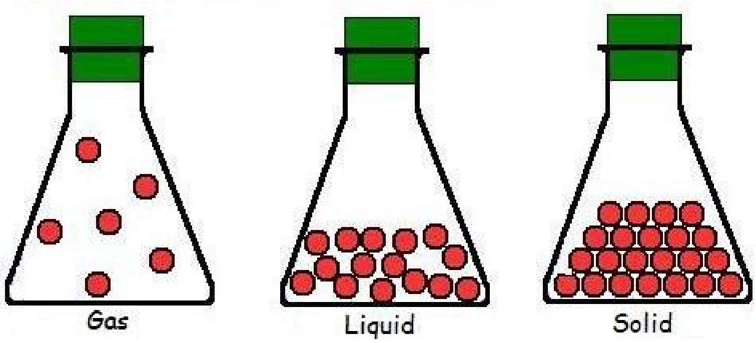
natural laws	A description of the patterns observed in the large amounts of data.
hypothesis	An educated guess as to what is going to happen in the experiment.
theory	Used to explain a law or to explain a series of facts/events.
law of conservation of mass	Matter cannot be created nor destroyed.
model	A description, graphic, or 3-D representation of theory used to help enhance understanding.
scientific method	The method of deriving the theories from hypotheses and laws through experimentation and observation.

Review Answers

1) (c)

2) (b)

3)



4. The Atomic Theory

Early Development of a Theory

Lesson Objectives

- Give a short history of the Concept of the atom.
- State the Law of Definite Proportions.
- State the Law of Multiple Proportions.
- State Dalton's Atomic Theory, and explain its historical development.

Introduction

You learned earlier how all matter in the universe is made out of tiny building blocks called atoms. The concept of the atom is accepted by all modern scientists, but when atoms were first proposed about 2500 years ago, ancient philosophers laughed at the idea. It has always been difficult to convince people of the existence of things that are too small to see. There are many observations that are made on atoms, however, that do not involve actually seeing the atom itself and science is about observing and devising a theory to explain why those observations occur. We will spend some time considering the evidence (observations) that convince scientists of the existence of atoms.

Democritus and the "Atom"

Before we discuss the experiments and evidence which have, over the years, convinced scientists that matter is made up of atoms, it's only fair to give credit to the man who proposed "atoms" in the first place. 2,500 years ago, early Greek philosophers believed the entire universe was a single, huge, entity. In other words, "everything was one." They believed that all objects, all matter, and all substance were connected as a single, big, unchangeable "thing." Now you're probably disturbed by the word *unchangeable*. Certainly you've seen the world around you change, and those early Greek philosophers must have too. Why, then, would they think that the universe was unchangeable? Well, strange as it may sound to you today, back then the generally accepted theory was that the world *didn't* change – it just looked like it did. In other words, Greek philosophers believed that all change (and all motion) was an illusion. It was all in your head! Compared to this crazy idea, the atom is looking pretty good, isn't it? One of the first people to propose "atoms" was a man known as Democritus. Democritus didn't like the idea that life was an illusion any more than you probably do. As an alternative, he suggested that the world *did* change, and he explained this change by proposing *atomos* or *atomon* – tiny, indivisible, solid objects making up all matter in the universe. Democritus then reasoned that changes occur when the many atomos

Figure 1: Democritus was known as "The Laughing Philosopher." It's a good thing he liked to laugh, because most other philosophers were laughing at his theories. (*Source:* http://en.wikipedia.org/wiki/Image:Democritus-Laughing.jpg, *License:* GNU-FDL)

in an object were reconnected or recombined in different ways. Democritus even extended his theory, suggesting that there were different varieties of atomos with different shapes, sizes, and masses. He thought, however, that shape, size and mass were the only properties differentiating the different types of atomos. According to Democritus, other characteristics, like color and taste, did not reflect properties of the atomos themselves, but rather, resulted from the different ways in which the atomos were combined and connected to one another.

Figure 2: Democritus believed that properties like color depended on how the atomos were connected to each other, and not on the atomos themselves. Interestingly, Democritus was partially right – the green emerald and the red ruby both contain atoms of aluminum, oxygen, and chromium. The emerald, however, also contains silicon and beryllium atoms.

(*Sources:* http://en.wikipedia.org/wiki/Image:Ruby_cristal.jpg; *License:* Public Domain; http://en.wikipedia.org/wiki/Image:Gachalaemerald.jpg, *License:* CC-BY-SA)

Even though the idea of the atomos seems much more reasonable than trying to explain experience as an illusion, the early Greek philosophers didn't like it, and they didn't for the following reason. If all matter consists of tiny atomos that float around, bang into each other, and connect together in various ways, these atomos must be floating *in* something. But what? Well, according to Democritus, the atoms floated around in a *void* (empty space or "nothingness"). That does seem a bit strange, doesn't it? Certainly, if you pound your fist on the desk in front of you, it doesn't *feel* like there's any empty space in it. What's more, Greek philosophers thought that empty space was illogical. In order to exist, they argued, nothing must be something, meaning nothing wasn't nothing, but that's a contradiction. Their arguments got quite confusing, but the end result was that Greek philosophers dismissed Democritus' theory entirely. Sadly, it took over two millennia before the theory of atomos (or "atoms," as they're known today) was fully appreciated.

Greek Philosophers Didn't Experiment

Early Greek philosophers disliked Democritus' theory of atomos because they believed a *void*, or complete "nothingness," was illogical. To ancient thinkers, a theory that went against "logic" was far worse than a theory that went against experience or observation. That's because Greek philosophers truly believed that, above all else, our understanding of the world should rely on "logic." In fact, they argued that the world *couldn't* be understood using our senses at all, because our senses could deceive us (these were, of course, the same people who argued that all change in the world was an illusion). Therefore, instead of relying on observation, Greek philosophers tried to understand the world using their minds and, more specifically, the power of reason. Unfortunately, when Greek philosophers applied reason to Democritus' theory, their arguments were inconsistent. Democritus' void had to be "something" to exist, but at the same time it had to be "nothing" to be a void. Greek philosophers were not willing to accept the idea that "nothing" could be "something" – that seemed illogical. Today, we call these contradictions (such as "nothing" is "something") *paradoxes*. Science is full of paradoxes. Sometimes these paradoxes result when our scientific theories are wrong or incomplete, and sometimes they

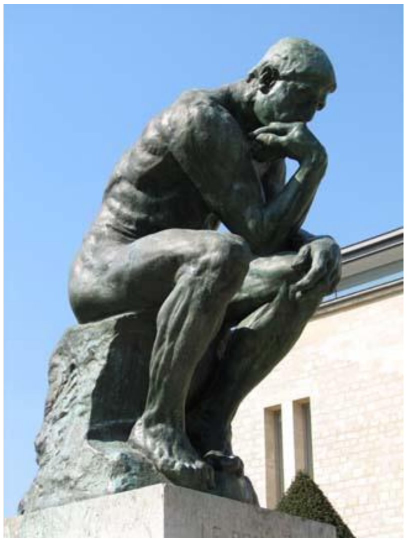


Figure 3: Greek philosophers liked to think – they didn't, however, like to experiment all that much. (*Source:* http://www.flickr.com/photos/dottie-

result because we make bad assumptions about what's "logical" and what isn't. In the case of the void, it turns out that "nothing" really can exist, so in a way, "nothing" is "something." So how could the Greek philosophers have known that Democritus had a good idea with his theory of "atomos?" It would have taken is some careful observation and a few simple experiments. Now you might wonder why Greek philosophers didn't perform any experiments to actually test Democritus' theory. The problem, of course, was that Greek philosophers didn't believe in experiments at all. Remember, Greek philosophers didn't trust their senses, they only trusted the reasoning power of the mind.

day/536278579/, *License:* CC-BY-SA)

Alchemists Experimented But Didn't Seek Explanation

As you learned in the last section, the early Greek philosophers tried to understand the nature of the world through reason and logic, but not through experiment and observation. As a result, they had some very interesting ideas, but they felt no need to justify their ideas based on life experiences. In a lot of ways, you can think of the Greek philosophers as being "all thought and no action." It's truly amazing how much they achieved using their minds, but because they never performed any experiments, they missed or rejected a lot of discoveries that they could have made otherwise. Some of the earliest *experimental* work was done by the alchemists. Remember that the alchemists were extremely interested in discovering the "philosopher's stone", which could turn common metals into gold. Of course, they also dabbled in medicines and cures, hoping to find "the elixir of life", and other such miraculous potions. On the other hand, alchemists were not overly concerned with any deep questions about the nature of the world. In contrast to the Greek philosophers, you can think of alchemists as being "all action and no thought." Alchemists experimented freely with everything that they could find. In general, though, they didn't think too much about their results and what their results might tell them about the world. Instead, they were only interested in whether or not they had made gold. To be fair, there were some alchemists who tried to use results from past experiments to help suggest future experiments. Nevertheless, alchemy always had very materialistic goals in mind – goals like producing gold and living forever. Alchemists were not troubled by philosophical questions like "what is the universe made of?" - they didn't really care unless they thought it would somehow help them find the "philosopher's stone" or the "elixir of life."

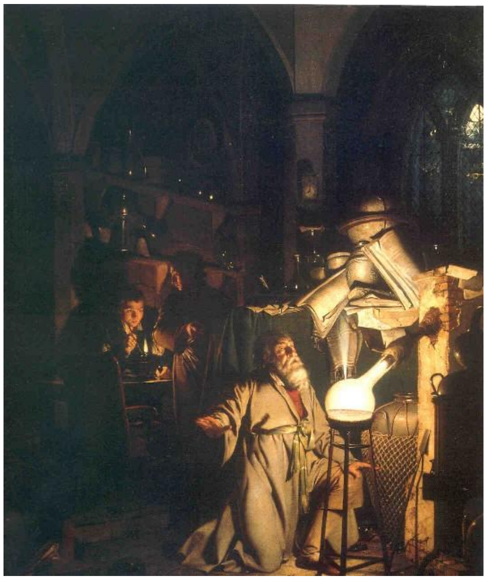


Figure 5: Yet another alchemist searching for the philosopher's stone. Notice how the alchemists used a lot of experimental techniques. It's too bad they were only interested in making gold! (*Source:* http://www.chem1.com/acad/webtext/pre/chemsci.html, *License:* CC-BY-SA)

What you've probably noticed by reading about the Greek philosophers and the alchemists is that the history of science is ironic. Greek philosophers asked deep questions about the universe but didn't believe in any of the experiments that might have led them to the answers. In contrast, alchemists believed in experimentation but weren't interested in what the experiments might tell them in terms of the nature of the world. Unbelievably, it took over 2000 years to put the questions asked by the Greek philosophers together with the experimental tools developed by the alchemists. The result was significant progress in our understanding of nature and the universe, and that's what we'll learn about next.

Dalton's Atomic Theory

Let's begin our discussion of Dalton's atomic theory by considering a simple, but important experiment that suggested matter might be made up of atoms. In the late 1700's and early 1800's, scientists began noticing that when certain substances, like hydrogen and oxygen, were combined to produce a new substance, like water, the reactants (hydrogen and oxygen) always reacted in the *same proportions by mass.* In other words, if 1 gram of hydrogen reacted with 8 grams of oxygen, then 2 grams of hydrogen would react with 16 grams of oxygen, and 3 grams of hydrogen would react with 24 grams of oxygen. Strangely, the observation that hydrogen and oxygen always reacted in the "same proportions by mass" wasn't special. In fact, it turned out that the reactants in *every* chemical reaction reacted in the same proportions by mass. Take, for example, nitrogen and hydrogen, which react to produce ammonia (a chemical you've probably used to clean your house). 1 gram of hydrogen will react with 4.7 grams of nitrogen, and 2 grams of hydrogen will react with 9.4 grams of nitrogen. Can you guess how much nitrogen would react with 3 grams of hydrogen?

Scientists studied reaction after reaction, but every time the result was the same. The reactants always reacted in the "same proportions by mass" or in what we call "definite proportions." As a result, scientists proposed the ***Law of Definite Proportions.*** This law states that:

In a given type of chemical substance, the elements are always combined in the same proportions by mass.

Earlier, you learned that an "element" is a grouping in which there is only one type of atom – of course, when the Law of Definite Proportions was first discovered, scientists didn't know about atoms or elements, so the law was stated slightly differently. We'll stick with this modern version, though, since it's easiest to understand.

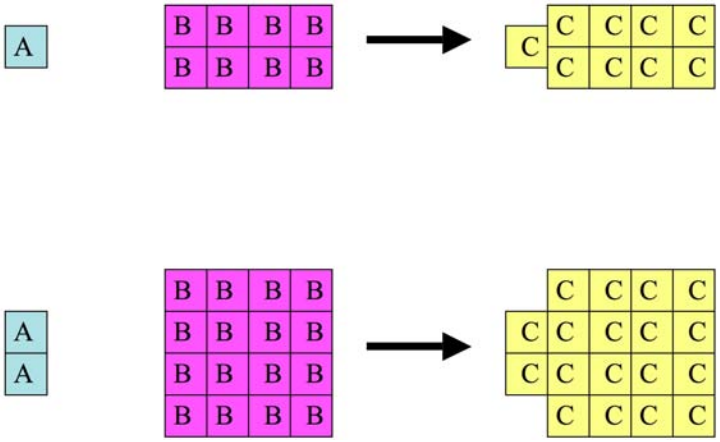


Figure 6: If 1 gram of A reacts with 8 grams of B, then by the Law of Definite Proportions, 2 grams of A must react with 16 grams of B. If 1 gram of A reacts with 8 grams of B, then by the Law of Conservation of Mass, they must produce 9 grams of C. Similarly, when 2 grams of A react with 16 grams of B, they must produce 18 grams of C.

The Law of Definite Proportions applies when elements are reacted together to form *the same* product. Therefore, while the Law of Definite Proportions can be used to compare two experiments in which hydrogen and oxygen react to form water, the Law of Definite Proportions can *not* be used to compare one experiment in which hydrogen and oxygen react to form water, and another experiment in which hydrogen and oxygen react to form hydrogen peroxide (peroxide is another material that can be made from hydrogen and oxygen).

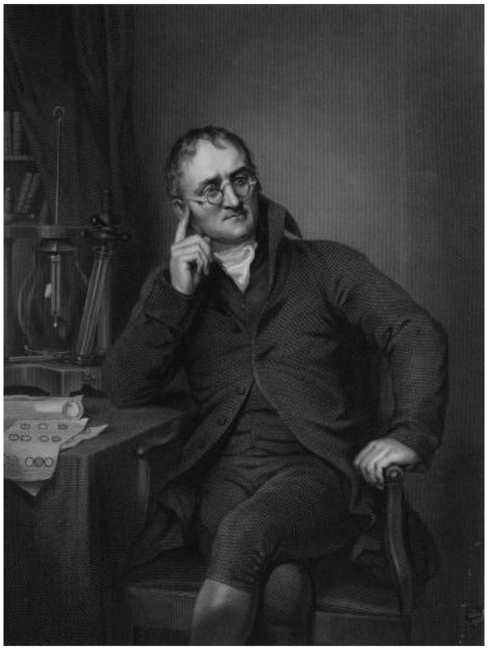


Figure 7: John Dalton was a thinker, but he was also an experimenter.

(*Source:* http://en.wikipedia.org/wiki/Image:Dalton_John_desk.jpg , *License:* Public Domain)

While scientists around the turn of the 18th century weren't making a lot of peroxide, a man named John Dalton was experimenting with several reactions in which the reactant elements formed more than one type of product, depending on the experimental conditions he used. One common reaction that he studied was the reaction between carbon and oxygen. When carbon and oxygen react, they produce two different substances – we'll call these substances "A" and "B." It turned out that, given the same amount of carbon, forming B always required *exactly twice as much oxygen* as forming A. In other words, if you can make A with 3 grams of carbon and 4 grams of oxygen, B can be made with the same 3 grams of carbon, but with *8 grams* oxygen. Dalton asked himself – why does B require 2 times as much oxygen as A? Why not 1.21 times as much oxygen, or 0.95 times as much oxygen? Why a whole number like 2?

The situation became even stranger when Dalton tried similar experiments with different substances. For example, when he reacted nitrogen and oxygen, Dalton discovered that he could make three different substances – we'll call them "C," "D," and "E." As it turned out, for the same amount of nitrogen, D always required *twice* as much oxygen as C. Similarly, E always required *exactly four times* as much oxygen as C. Once again, Dalton noticed that *small whole numbers* (2 and 4) seemed to be the rule.

Dalton used his experimental results to propose ***The Law of Multiple Proportions:***

When two elements react to form more than one substance, the different masses of one element (like oxygen) that are combined with the same mass of the other element (like nitrogen) are in a ratio of small whole numbers.

Dalton thought about his *Law of Multiple Proportions* and tried to find some theory that would explain it. Dalton also knew about the *Law of Definite Proportions* and the *Law of Conservation of Mass* (Remember that the Law of Conservation of Mass states that mass is neither created nor destroyed), so what he really wanted was a theory that would explain all *three* of these laws using a simple, plausible model. One way to explain the relationships that Dalton and others had observed was to suggest that materials like nitrogen, carbon and oxygen were composed of small, indivisible quantities which Dalton called "atoms" (in reference to Democritus' original idea). Dalton used this idea to generate what is now known as ***Dalton's Atomic Theory*** .*

Dalton's Atomic Theory 1. Matter is made of tiny particles called atoms. 2. Atoms are indivisible. During a chemical reaction, atoms are rearranged, but they do not break apart, nor are they created or destroyed. 3. All atoms of a given element are identical in mass and other properties. 4. The atoms of different elements differ in mass and other properties. 5. Atoms of one element can combine with atoms of another element to form "compounds" – new, complex particles. In a given compound, however, the different types of atoms are always present in the same relative numbers.

[*] Some people think that Dalton developed his Atomic Theory before stating the Law of Multiple Proportions, while others argue that the Law of Multiple Proportions, though not formally stated, was actually discovered first. In reality, Dalton was probably contemplating both concepts at the same time, although it is hard to tell from his laboratory notes.

Lesson Summary

- 2,500 years ago, Democritus suggested that all matter in the universe was made up of tiny, indivisible, solid objects he called "atomos."
- Democritus believed that there were different types of "atomos" which differed in shape, size, and mass.
- Other Greek philosophers disliked Democritus' "atomos" theory because they felt it was illogical. Since they didn't believe in experiments, though, they had no way to test the "atomos" theory.
- Alchemists experimented and developed experimental techniques, but they were more interested in making gold than they were in understanding the nature of matter and the universe.
- The Law of Definite Proportions states that in a given chemical substance, the elements are always combined in the same proportions by mass.
- The Law of Multiple Proportions states that when two elements react to form more than one substance, the different masses of one element that are combined with the same mass of the other element are in a ratio of small whole numbers.
- Dalton used the Law of Definite Proportions, the Law of Multiple Proportions, and The Law of Conservation of Mass to propose his Atomic Theory.
- Dalton's Atomic Theory states:

1. Matter is made of tiny particles called atoms.

2. Atoms are indivisible. During a chemical reaction, atoms are rearranged, but they do not break apart, nor are they created or destroyed.

3. All atoms of a given element are identical in mass and other properties.

4. The atoms of different elements differ in mass and other properties.

5. Atoms of one element can combine with atoms of another element to form "compounds" – new complex particles. In a given compound, however, the different types of atoms are always present in the same relative numbers.

Review Questions

1. It turns out that a few of the ideas in Dalton's Atomic Theory aren't entirely correct. Are inaccurate theories an indication that science is a waste of time? **(Intermediate)**

2. Suppose you are trying to decide whether to wear a sweater or a T-shirt. To make your decision, you phone two friends. The first friend says, "Wear a sweater, because I've already been outside today, and it's cold." The second friend, however, says, "Wear a T-shirt. It isn't logical to wear a sweater in July." Would you decide to go with your first friend, and wear a sweater, or with your second friend, and wear a T-shirt?

Why?

3. Decide whether each of the following statements is true or false. **(Beginning)**

a. Democritus believed that all matter was made of “atomos.”

b. Democritus also believed that there was only one kind of “atomos.”

c. Most early Greek scholars thought that the world was “ever-changing.”

d. If the early Greek philosophers hadn’t been so interested in making gold, they probably would have liked the idea of the “atomos.”

4. Match the person, or group of people, with their role in the development of chemistry. **(Beginning)**

(1) Early Greek philosophers	a. suggested that all matter was made up of tiny, indivisible objects
(2) alchemists	b. tried to apply logic to the world around them
(3) John Dalton	c. suggested that all matter was made up of tiny, indivisible objects
(4) Democritus	d. were primarily concerned with finding ways to turn common metals into gold

5. Early Greek philosophers felt that Democritus’ “atomos” theory was illogical because: **(Beginning)**

a. no matter how hard they tried, they could never break matter into smaller pieces.

b. it didn’t help them to make gold.

c. sulfur is yellow and carbon is black, so clearly “atomos” must be colored.

d. empty space is illogical because it implies that nothing is actually something.

6. Which Law explains the following observation: carbon monoxide can be formed by reacting 12 grams of carbon with 16 grams of oxygen? To form carbon dioxide, however, 12 grams of carbon must react with 32 grams of oxygen. **(Intermediate)**

7. Which Law explains the following observation: carbon monoxide can be formed by reacting 12 grams of carbon with 16 grams of oxygen? It can also be formed by reacting 24 grams of carbon with 32 grams of oxygen. **(Intermediate)**

8. Which Law explains the following observation: 28 grams of carbon monoxide are formed when 12 grams of carbon reacts with 16 grams of oxygen? **(Intermediate)**

9. Which Law explains the following observations: when 12 grams of carbon react with 4 grams of hydrogen, they produce methane, and there is no carbon or hydrogen left over at the end of the reaction? If, however, 11 grams of carbon react with 4 grams of hydrogen, there is hydrogen left over at the end of the reaction. **(Challenging)**

10. Which of the following is *not* part of Dalton’s Atomic Theory? **(Beginning)**

a. matter is made of tiny particles called atoms.

b. during a chemical reaction, atoms are rearranged.

c. during a nuclear reaction, atoms are split apart.

d. all atoms of a specific element are the same.

Calculations

11. Consider the following data: 3.6 grams of boron react with 1.0 grams of hydrogen to give 4.6 grams of BH_3. How many grams of boron would react with 2.0 grams of hydrogen? **(Challenging)**

12. Consider the following data: 12 grams of carbon and 4 grams of hydrogen react to give 16 grams of "compound A." 24 grams of carbon and 6 grams of hydrogen react to give 30 grams of "compound B." Are compound A and compound B the same? Why or why not? **(Challenging)**

Vocabulary

atomos (atomon)	Democritus' word for the tiny, indivisible, solid objects that he believed made up all matter in the universe.
void	Another word for empty space.
paradox	Two statements that seem to be true, but contradict each other.
law of definite proportions	In a given chemical substance, the elements are always combined in the same proportions by mass.
law of multiple proportions	When two elements react to form more than one substance, the different masses of one element that are combined with the same mass of the other element are in a ratio of small whole numbers.

Review Answers

1. Many highly successful theories were not exactly perfect when first presented. The modification of theories to make them fit all observations is a normal process in the scientific method.

2. There are arguments for either side. You might go with the sweater, because your first friend has actually *observed* the temperature. On the other hand, you might not trust your friend's observation. Perhaps your friend has a different idea of what is cold and what is warm. After all, it does seem strange to wear a sweater in July! The question here is whether to believe the observation, or common sense. As you'll see, that's a question that early Greek philosophers struggled with as well. In the end, they decided to trust common sense, but most scientists today rely more on observation.

3.

a. (T) b. (F) c. (F) d. (F)

4.

1.b. 2.d. 3.a. or c. 4.a. or c.

5. d

6. The Law of Multiple Proportions

7. The Law of Definite Proportions

8. The Law of Conservation of Mass

9. The Law of Definite Proportions

10. Even though this is a correct statement, it is not part of Dalton's Atomic Theory.

11. 7.2 grams

12. Compound A and compound B are not the same. If they were the same, 24 grams of carbon would have required 8 grams of hydrogen according to the Law of Definite Proportions. Since it only required 6 grams, compound B must be a different substance.

Further Understanding of the Atom

Lesson Objectives

- Explain the experiment that led to Thomson's discovery of the electron.
- Describe Thomson's "plum pudding" model of the atom.
- Describe Rutherford's Gold Foil experiment, and explain how this experiment proved that the "plum pudding" model of the atom was incorrect.

Introduction

In the last lesson, you learned about the atom, and the early experiments that led to the development of Dalton's Atomic Theory. But Dalton's Atomic Theory isn't the end of the story. Do you remember the scientific method introduced in early on in the book? Chemists using the scientific method make careful observations and measurements and then use these measurements to propose theories. That's exactly what Dalton did. Dalton used the following *observations*:

1. Mass is neither created nor destroyed during a chemical reaction.
2. Elements always combine in the same proportions by mass when they form a given compound.
3. When elements form *more than one* compound, the different masses of one element that are combined with the same mass of the other element are in a ratio of small whole numbers.

With these observations (which came from careful measurement), Dalton proposed his Atomic Theory – a model which suggested how the underlying structure of matter might lead to the three observations above. The scientific method, though, doesn't stop once a theory has been proposed. Instead, the theory should suggest new experiments that can be performed to test whether or not the original theory is accurate and complete.

Dalton's Atomic Theory held up well to a lot of the different chemical experiments that scientists performed to test it. In fact, for almost 100 years, it seemed as if Dalton's Atomic Theory was the whole truth. However, in 1897, a scientist named J. J. Thompson conducted some research which suggested that Atomic Theory wasn't the *entire* story. As it turns out, Dalton had a lot right. He was right in saying matter is made up of atoms; he was right in saying there are different kinds of atoms with different mass and other properties; he was "almost" right in saying atoms of a given element are identical; he was right in saying during a chemical reaction, atoms are merely rearranged; he was right in saying a given compound always has atoms present in the same relative numbers. But he was **WRONG** in saying atoms were indivisible or indestructible. As it turns out, atoms *are divisible*. In fact, atoms are composed of smaller **subatomic particles**. We'll talk about the discoveries of these subatomic particles next.

Thomson Discovered Electrons Were Part of the Atom

In the mid-1800s, scientists were beginning to realize that the study of chemistry and the study of electricity were actually related. First, a man named Michael Faraday showed how passing electricity through mixtures of different chemicals could cause chemical reactions. Shortly after that, scientists found that by forcing electricity through a tube filled with gas, the electricity made the gas glow! Scientists didn't, however, understand the relationship between chemicals and electricity until a British physicist named J. J. Thomson began experimenting with what is known as a *cathode ray tube.*

Figure 1: A portrait of J. J. Thomson.

(*Source:* http://en.wikipedia.org/wiki/Image:Jj-thomson2.jpg, *License:* Public Domain)

Figure 2 shows a basic diagram of a cathode ray tube like the one J. J. Thomson would have used. A cathode ray tube is a small glass tube with a cathode (a negatively charged metal plate) and an anode (a positively charged metal plate) at opposite ends. By separating the cathode and anode by a short distance, the cathode ray tube can generate what are known as “cathode rays” – rays of electricity that flowed from the cathode to the anode, J. J. Thomson wanted to know what cathode rays were, where cathode rays came from and whether cathode rays had any mass or charge. The techniques that J. J. Thomson used to answer these questions were very clever and earned him a Nobel Prize in physics. First, by cutting a small hole in the anode J. J. Thomson found that he could get some of the cathode rays to flow through the hole in the anode and into the other end of the glass cathode ray tube. Next, J. J. Thomson figured out that if he painted a substance known as “phosphor” onto the far end of the cathode ray tube, he could see exactly where the cathode rays hit because the cathode rays made the phosphor glow.

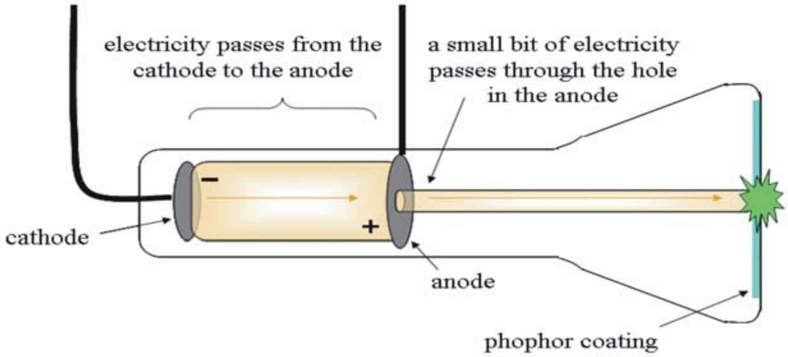


Figure 2: A cathode-ray tube.

(*Source:* Sharon Bewick, *License:* CC-BY-SA)

J. J. Thomson must have suspected that cathode rays were charged, because his next step was to place a positively charged metal plate on one side of the cathode ray tube and a negatively charged metal plate on the other side of the cathode ray tube, as shown in Figure 3. The metal plates didn’t actually touch the cathode ray tube, but they were close enough that a remarkable thing happened! The flow of the cathode rays passing through the hole in the anode was bent upwards towards the positive metal plate and away from the negative metal plate.

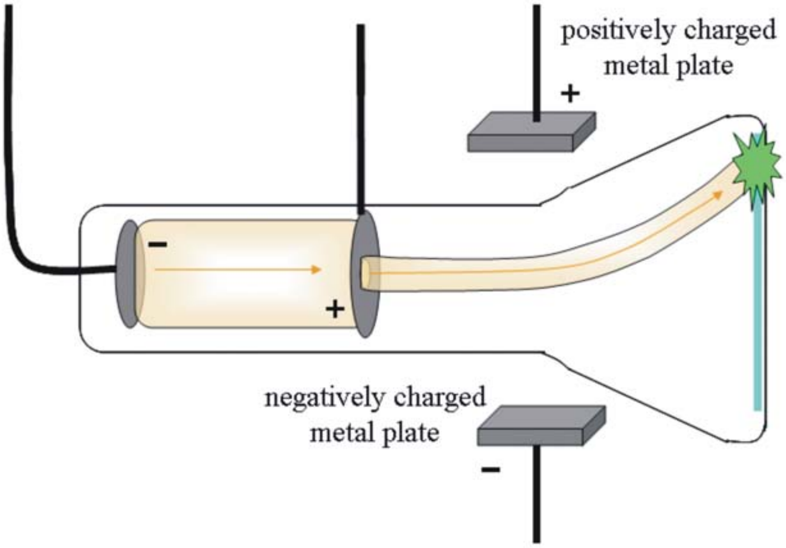


Figure 3: A cathode ray was attracted to the positively charged metal plate placed above the tube, and repelled from negatively charged metal plate placed below the tube.

(*Source by:* Sharon Bewick, *License:* CC-BY-SA)

In other words, instead of the phosphor glowing directly across from the hole in the anode (as in Figure 2), the phosphor now glowed at a spot quite a bit higher in the tube (as in Figure 3).

J. J. Thomson thought about his results for a long time. It was almost as if the cathode rays were *attracted* to the positively charged metal plate above the cathode ray tube, and *repelled* from the negatively charged metal plate below the cathode ray tube. J. J. Thomson knew that charged objects are attracted to and repelled from other charged objects according to the rule: *opposites attract, likes repel.* This means that a positive charge is attracted to a negative charge, but repelled from another positive charge. Similarly, a negative charge is attracted to a positive charge, but repelled from another negative charge. Using the “opposites attract, likes repel” rule, J. J. Thomson argued that if the cathode rays were *attracted* to the positively charged metal plate and *repelled* from the negatively charged metal plate, they themselves must have a negative charge!

J. J. Thomson then did some rather complex experiments with magnets, and used his results to prove that cathode rays were not only negatively charged, but also had mass. Remember that anything with mass is part of what we call matter. In other words, these cathode rays must be the result of negatively charged “matter” flowing from the cathode to the anode. But there was a problem. According to J. J. Thomson’s measurements, either these cathode rays had a ridiculously high charge, or else had very, very little mass – much less mass than the smallest known atom. How was this possible? How could the matter making up cathode rays be *smaller* than an atom if atoms were indivisible? J. J. Thomson made a radical proposal: maybe atoms *are* divisible. J. J. Thomson suggested that the small, negatively charged particles making up the cathode ray were actually pieces of atoms. He called these pieces “corpuscles,” although today we know them as “electrons.” Thanks to his clever experiments and careful reasoning J. J. Thomson is credited with the discovery of the electron.

Protons Were Thought to Exist but Discovered Much Later

In the last section, we learned that atoms are, in fact, divisible, and that one of the **subatomic particles** making up an atom is a small, negatively charged entity called an "electron." Now imagine what would happen if atoms were made entirely of electrons. First of all, electrons are very, very small; in fact, electrons are about 2000 times smaller than the smallest known atom, so every atom would have to contain a whole lot of electrons. But there's another, even bigger problem: electrons are *negatively charged*. Therefore, if atoms were made entirely out of electrons, atoms would be negatively charged themselves… and that would mean all matter was negatively charged as well.

Of course, matter isn't negatively charged. In fact, most matter is what we call *neutral* – it has no charge at all. If matter is composed of atoms, and atoms are composed of *negative* electrons, how can matter be *neutral*? The only possible explanation is that atoms consist of more than just electrons. Atoms must also contain some type of *positively charged* material which balances the negative charge on the electrons. Negative and positive charges of equal size cancel each other out, just like negative and positive numbers of equal size. What do you get if you add +1 and -1? You get 0, or nothing. That's true of numbers, and that's also true of charges. If an atom contains an electron with a -1 charge, but also some form of material with a +1 charge, overall the atom must have a (+1) + (-1) = 0 charge – in other words, the atom must be neutral, or have *no* charge at all.

Based on the fact that atoms are neutral, and based on J. J. Thomson's discovery that atoms contain negative subatomic particles called "electrons," scientists assumed that atoms must *also* contain a positive substance. It turned out that this positive substance was another kind of **subatomic particle**, known as the "proton." Although scientists knew that atoms had to contain positive material, protons weren't actually discovered, or understood, until quite a bit later.

Thomson's Model of the Atom

When Thomson discovered the negative electron, he realized that atoms had to contain positive material as well – otherwise they wouldn't be neutral overall. As a result, Thomson formulated what's known as the "plum pudding" model for the atom. According to the "plum pudding" model, the negative electrons were like pieces of fruit and the positive material was like the batter or the pudding. This made a lot of sense given Thomson's experiments and observations. Thomson had been able to isolate electrons using a cathode ray tube; however he had never managed to isolate positive particles. As a result, Thomson theorized that the positive material in the atom must form something like the "batter" in a plum pudding, while the negative electrons must be scattered through this "batter." (If you've never seen or tasted a plum pudding, you can think of a chocolate chip cookie instead. In that case, the positive material in the atom would be the "batter" in the chocolate chip cookie, while the negative electrons would be scattered through the batter like chocolate chips.)

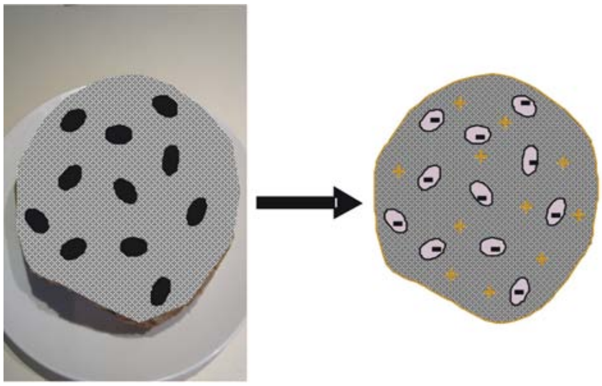


Figure 4: A plum pudding and Thomson's "plum-pudding" model for the atom. Notice how the "plums" are the negatively charged electrons, while the positive charge is spread throughout the entire pudding batter. (*Source:* http://en.wikipedia.org/wiki/Image:Christmas_Pudding.jpg, *License:* GNU-FDL)

Figure 4 shows a "plum pudding" and a "plum pudding" model for the atom. Notice how easy it would be to pick the pieces of fruit out of a plum pudding. On the other hand, it would be a lot harder to pick the batter out of the plum pudding, because the batter is *everywhere.* If an atom were similar to a plum pudding in which the electrons are scattered throughout the "batter" of positive material, then you'd expect it would be easy to pick out the electrons, but a lot harder to pick out the positive material.

Everything about Thomson's experiments suggested the "plum pudding" model was correct – but according to the scientific method, any new theory or model should be tested by further experimentation and observation. In the case of the "plum pudding" model, it would take a man named Ernest Rutherford to prove it wrong. Rutherford and his experiments will be the topic of the next section.

Rutherford's Model of the Atom

Disproving Thomson's "plum pudding" model began with the discovery that an element known as uranium emitted *positively charged* particles called **alpha particles** as it underwent radioactive decay. Radioactive decay occurs when one element decomposes into another element. It only happens with a few very unstable elements. This involves some difficult concepts so, for now, just accept the fact that uranium decays and emits alpha particles in the process. Alpha particles themselves didn't prove anything about the structure of the atom. In fact, a man named Ernest Rutherford proved that alpha particles were nothing more than helium atoms that had lost their electrons. Think about why an atom that has lost electrons will have a positive charge. Alpha particles could, however, be used to conduct some very interesting experiments. Ernest Rutherford was fascinated by all aspects of alpha particles. For the most part, though, he seemed to view alpha particles as tiny bullets that he could use to fire at all kinds of different materials. One experiment in particular, however, surprised Rutherford, and everyone else. Rutherford found that when he fired alpha particles at a very thin piece of gold foil, an interesting thing happened. Almost all of the alpha particles went straight through the foil as if they'd hit nothing at all. Every so often, though, one of the alpha particles would be deflected slightly as if it had bounced off of something hard. Even less often, Rutherford observed alpha particles bouncing straight back at the "gun" from which they had been fired! It was as if these alpha particles had hit a wall "head-on" and had ricocheted right back in the direction that they had come from.

Figure 5: A photograph of Ernest Rutherford. (*Source:* http://en.wikipedia.org/wiki/Image:Ernest_Rutherford2.jpg, *License:* GNU-FDL)

Rutherford thought that these experimental results were rather odd. Rutherford described firing alpha particles at gold foil like shooting a high-powered rifle at tissue paper. Would you ever expect the bullets to hit the tissue paper and bounce back at you? Of course not! The bullets would break through the tissue paper and keep on going, almost as if they'd hit nothing at all. That's what Rutherford had expected would happen when he fired alpha particles at the gold foil. Therefore, the fact that most alpha particles passed through didn't shock him. On the other hand, how could he explain the alpha particles that got deflected? Even worse, how could he explain the alpha particles that bounced right back as if they'd hit a wall?

Rutherford decided that the only way to explain his results was to assume that the positive matter forming the gold atoms was *not*, in fact, distributed like the batter in plum pudding, but rather, was concentrated in one spot, forming a small positively charged particle somewhere in the center of the gold atom. We now call this clump of positively charged mass the **nucleus.** According to Rutherford, the presence of a nucleus explained his experiments, because it implied that most alpha particles passed through the gold foil without hitting anything at all. Once in a while, though, the alpha particles would actually collide with a gold nucleus, causing the alpha particles to be deflected, or even to bounce right back in the direction they came from.

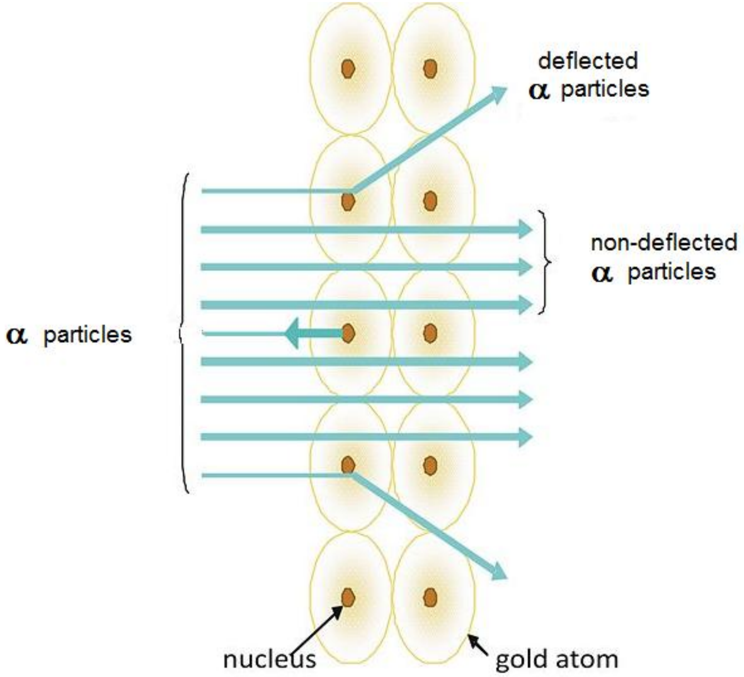


Figure 6: Ernest Rutherford's Gold Foil Experiment.

(*Source: Created by:* Sharon Bewick, *License:* CC-BY-SA)

Rutherford Suggested Electrons "Orbited"

While Rutherford's discovery of the positively charged atomic nucleus offered insight into the structure of the atom, it also led to some questions. According to the "plum pudding" model, electrons were like plums embedded in the positive "batter" of the atom. Rutherford's model, though, suggested that the positive charge wasn't distributed like batter, but rather, was concentrated into a tiny particle at the center of the atom, while most of the rest of the atom was empty space. What did that mean for the electrons? If they weren't *embedded* in the positive material, exactly what were they doing? And how were they held in the atom? Rutherford suggested that the electrons might be circling or "orbiting" the positively charged nucleus as some type of negatively charged cloud, but at the time, there wasn't much evidence to suggest exactly how the electrons were held in the atom.

Despite the problems and questions associated with Rutherford's experiments, his work with alpha particles definitely seemed to point to the existence of an atomic "nucleus." Between J. J. Thomson, who discovered the electron, and Rutherford, who suggested that the positive charges in an atom were concentrated at the atom's center, the 1890s and early 1900s saw huge steps in understanding the atom at the "subatomic" (or smaller than the size of an atom) level. Although there was still some uncertainty with respect to exactly how subatomic particles were organized in the atom, it was becoming more and more obvious that atoms were indeed divisible. Moreover, it was clear that the pieces an atom could be separated into negatively charged electrons and a nucleus containing positive charges. In the next lesson, we'll look more carefully at the structure of the nucleus, and we'll learn that while the atom is made up of positive and negative particles, it also contains *neutral* particles that neither Thomson, nor Rutherford, were able to detect with their experiments.

Lesson Summary

- Dalton's Atomic Theory wasn't entirely correct. It turns out that atoms *can* be divided into smaller subatomic particles.

- A cathode ray tube is a small glass tube with a cathode and an anode at one end. Cathode rays flow from the cathode to the anode.

- When cathode rays hit a material known as "phosphor" they cause the phosphor to glow. J. J. Thomson used this phenomenon to reveal the path taken by a cathode ray in a cathode ray tube.

- J. J. Thomson found that the path taken by the cathode ray could be bent towards a positive metal plate, and away from a negative metal plate. As a result, he reasoned that the particles in the cathode ray were negative.

- Further experiments with magnets proved that the particles in the cathode ray also had mass. Thomson's measurements indicated, however, that the particles were much smaller than atoms.

- J. J. Thomson suggested that these small, negatively charged particles were actually subatomic particles. We now call them "electrons."

- Since atoms are neutral, atoms that contain negatively charged electrons must also contain positively charged material.

- According to Thomson's "plum pudding" model, the negatively charged electrons in an atom are like the pieces of fruit in a plum pudding, while the positively charged material is like the batter.

- When Ernest Rutherford fired alpha particles at a thin gold foil, most alpha particles went straight through; however, a few were scattered at different angles, and some even bounced straight back.

- In order to explain the results of his Gold Foil experiment, Rutherford suggested that the positive matter in the gold atoms was concentrated at the center of the gold atom in what we now call the nucleus of the atom.

- Rutherford's model of the atom didn't explain where electrons were located in an atom.

Review Questions

Concepts

1. Decide whether each of the following statements is true or false. **(Beginning)**

a. Cathode rays are positively charged.

b. Cathode rays are rays of light, and thus they have no mass.

c. Cathode rays can be repelled by a negatively charged metal plate.

d. J.J. Thomson is credited with the discovery of the electron.

e. Phosphor is a material that glows when struck by cathode rays.

2. Match each observation with the correct conclusion. **(Beginning)**

a. Cathode rays are attracted to a positively charged metal plate.	i. Cathode rays are positively charged.
	ii. Cathode rays are negatively charged.
	iii. Cathode rays have no charge.
b. Electrons have a negative charge.	i. atoms must be negatively charged.

	ii. atoms must be positively charged.
	iii. atoms must also contain positive subatomic material.
c. Alpha particles fired at a thin gold foil are occasionally scattered back in the direction that they came from	i. the positive material in an atom is spread throughout like the “batter” in pudding
	ii. atoms contain neutrons
	iii. the positive charge in an atom is concentrated in a small area at the center of the atom.

3. Alpha particles are: **(Beginning)**

a. Helium atoms that have extra electrons.

b. Hydrogen atoms that have extra electrons.

c. Hydrogen atoms that have no electrons.

d. Electrons.

e. Helium atoms that have lost their electrons.

f. Neutral helium atoms.

4. What is the name given to the tiny clump of positive material at the center of an atom? **(Beginning)**

5. Choose the correct statement. **(Beginning)**

a. Ernest Rutherford discovered the atomic nucleus by performing experiments with aluminum foil.

b. Ernest Rutherford discovered the atomic nucleus using a cathode ray tube.

c. When alpha particles are fired at a thin gold foil, they never go through.

d. Ernest Rutherford proved that the “plum pudding model” was incorrect.

e. Ernest Rutherford experimented by firing cathode rays at gold foil.

6. Answer the following questions: **(Beginning)**

a. Will the charges + 2 and -2 cancel each other out?

b. Will the charges +2 and -1 cancel each other out?

c. Will the charges +1 and +1 cancel each other out?

d. Will the charges -1 and +3 cancel each other out?

e. Will the charges +9 and -9 cancel each other out?

7. Electrons are _______ negatively charged metals plates and _______ positively charged metal plates? **(Beginning)**

8. What was J. J. Thomson's name for electrons? **(Beginning)**

9. A "sodium cation" is a sodium atom that has lost one of its electrons. Would the charge on a sodium cation be positive, negative or neutral? Would sodium cations be attracted to a negative metal plate, or a positive metal plate? Would electrons be attracted to or repelled from sodium cations? **(Intermediate)**

10. Suppose you have a cathode ray tube coated with phosphor so that you can see where on the tube the cathode ray hits by looking for the glowing spot. What will happen to the position of this glowing spot if: **(Intermediate)**

a. a negatively charged metal plate is placed above the cathode ray tube

b. a negatively charged metal plate is placed to the right of the cathode ray tube

c. a positively charged metal plate is placed to the right of the cathode ray tube

d. a negatively charged metal plate is placed above the cathode ray tube, and a positively charged metal plate is placed to the left of the cathode ray tube

e. a positively charged metal plate is placed below the cathode ray tube, and a positively charged metal plate is also placed to the left of the cathode ray tube.

Vocabulary

subatomic particles	Particles that are smaller than the atom. The three main subatomic particles are electrons, protons and neutrons.
cathode rays	rays of electricity that flow from the cathode to the anode. J.J. Thomson proved that these rays were actually negatively charged subatomic particles (or electrons).
cathode	A negatively charged metal plate.
anode	A positively charged metal plate.
cathode ray tube	A glass tube with a cathode and anode, separated by some distance, at one end. Cathode ray tubes generate cathode rays.
phosphor	A chemical that glows when it is hit by a cathode ray.
plum pudding model	A model of the atom which suggested that the negative electrons were like plums scattered through the positive material (which formed the batter).
alpha (α) **particles**	Helium atoms that have lost their electrons. They are produced by uranium as it decays.
nucleus	The small central core of the atom where most of the mass of the atom (and all of the atoms positive charge) is located.

Review Answers

1. a. (F) b. (F) c. (T) d. (T) e. (T)

2. a. ii. b. iii. c. iii.

3. e.

4. Nucleus

5. d.

6.

a. yes b. no c. no d. no e. yes

7. repelled from; attracted to

8. corpuscules

9. positive negative attracted to

10.

a. it will move down

b. it will move to the left

c. it will move to the right

d. it will move down and to the left

e. it will move down and to the left

Atomic Terminology

Lesson Objectives

- Describe the properties of electrons, protons, and neutrons.
- Define and use an atom's atomic number (Z) and mass number (A).
- Define an isotope, and explain how isotopes affect an atom's mass, and an element's atomic mass.

Introduction

Dalton's Atomic Theory explained a lot about matter, chemicals, and chemical reactions. Nevertheless, it wasn't entirely accurate, because contrary to what Dalton believed, atoms can, in fact, be broken apart into smaller subunits or **subatomic particles**. One type of subatomic particle found in an atom is the negatively charged **electron**. Since atoms are neutral, though, they also have to contain positive material. At first, scientists weren't sure exactly what this positive material was, or how it existed in the atom. Thomson thought it was distributed throughout the atom like batter in a plum pudding. Rutherford, however, showed that this was not the case. In his Gold Foil experiment, Rutherford proved that the positive substance in an atom was concentrated in a small area at the center of the atom, leaving most the rest of the atom as empty space (possibly with a few electrons, or an "electron cloud").

Both Thomson's experiments and Rutherford's experiments answered a lot of questions, but they also raised a lot of questions, and scientists wanted to know more. How were the electrons connected to the rest of the atom? What was the positive material at the center of the atom like? Was it one giant clump of positive mass, or could it be divided into smaller parts as well? In this lesson, we'll look at the atom a little more closely.

Electrons, Protons, and Neutrons

The atom is composed of three different kinds of subatomic particles. First, there are the electrons, which we've already talked about, and which J. J. Thomson discovered. Electrons have a negative charge. As a result they are attracted to positive objects, and repelled from negative objects, which means that they actually repel each other.

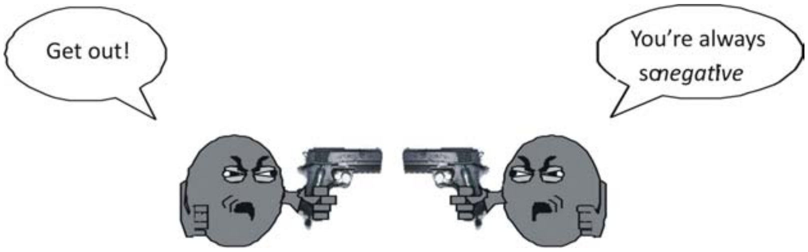


Figure 1: Electrons repel each other because they are both negatively charged.

(*Source:* http://en.wikipedia.org/wiki/Image:BB_gun_with_CO2_and_BBs.jpg, *License:* GNU-FLD)

Still, most atoms have more than one electron. That's because atoms are big enough to hold many electrons without those electrons ever colliding with each other. As you might expect, the bigger the atom, the more electrons it contains.

Protons are another type of subatomic particle found in atoms. Protons have a positive charge. As a result they are *attracted to negative objects*, and *repelled from positive objects*. Again, this means that protons *repel each other*. Unlike electrons, however, which manage to stake out a 'territory' and 'defend' it from other electrons, protons are bound together by what are termed **strong nuclear forces**. Therefore, even though they repel each other, protons are forced to group together into one big clump. This clump of protons helps to form the **nucleus** of the atom. Remember, the nucleus of the atom is the mass of positive charge at the atom's center.

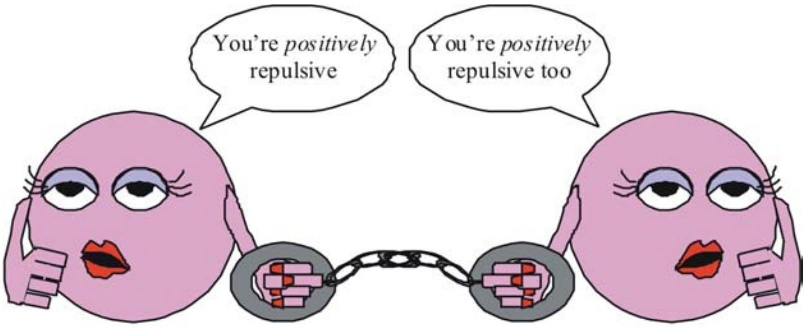


Figure 2: Protons repel each other because they are both positively charged. Despite this repulsion, protons are bound together in the atomic nucleus as a result of the strong nuclear force.

(*Source by:* Sharon Bewick, *License:* CC-BY-SA)

Electrons were the first subatomic particles discovered and protons were the second. There's a third kind of subatomic particle, though, known as a **neutron**, which wasn't discovered until much later. As you might have already guessed from its name, the neutron is neutral. In other words, it has no charge whatsoever, and is therefore neither attracted to nor repelled from other objects. That's part of the reason why the neutron wasn't discovered until long after people knew about electrons and protons – because it has no charge, it's really hard to detect. Neutrons are in every atom (with one exception), and they're bound together with other neutrons and protons in the atomic nucleus. Again, the binding forces that help to keep neutrons fastened into the nucleus are known as strong nuclear forces.

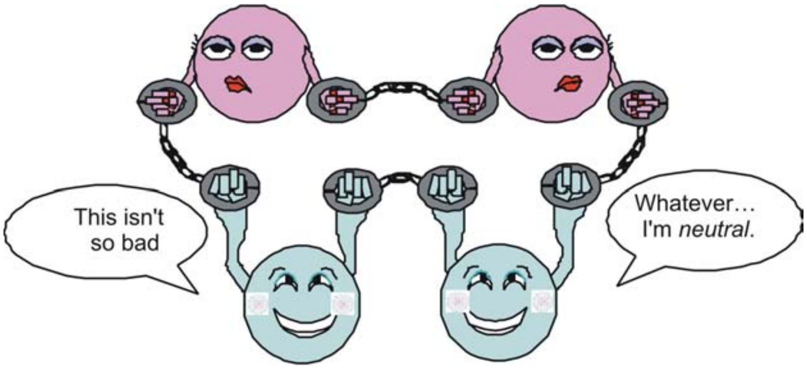


Figure 3: Protons aren't the only subatomic particles bound together in the atomic nucleus. Neutrons are also bound in nucleus as a result of the strong nuclear force.

(*Source by:* Sharon Bewick, *License:* CC-BY-SA)

Before we move on, we must discuss how the different types of subatomic particles interact with each other. When it comes to neutrons, the answer is obvious. Since neutrons are neither attracted to, nor repelled from objects, they don't really interact with protons or electrons (beyond being bound into the nucleus with the protons). Protons and electrons, however, do interact. Using what you know about protons and electrons, what do you think will happen when an electron approaches a proton - will the two subatomic particles be attracted to each other, or repelled from each other? Here's a hint: *"opposites attract, likes repel."* Electrons and protons have *opposite* charges (one negative, the other positive), so you'd expect them to be attracted to each other and that's exactly what happens.

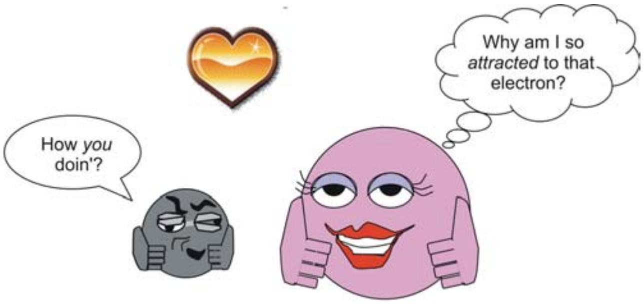


Figure 4: Protons and electrons are attracted to each other because they have opposite charges. Protons are positively charged, while electrons are negatively charged.

(*Source by:* Sharon Bewick, *License:* CC-BY-SA)

Relative Mass and Charge

Even though electrons, protons, and neutrons are all types of subatomic particles, they are not all the same size. When you compare the masses of electrons, protons and neutrons, what you find is that electrons have an extremely small mass, compared to either protons or neutrons. On the other hand, the masses of protons and neutrons are fairly similar, although technically, the mass of a neutron is slightly larger than the mass of a proton. Because protons and neutrons are so *much* more massive than electrons, almost all of the atomic mass in any atom comes from the nucleus, which contains all of the neutrons and protons.

	Mass in Grams (g)	**Mass in Atomic Mass Units (amu)**
Electron	9.109383×10^{-28}	$5.485799095 \times 10^{-4}$

Proton	1.6726217 × 10^{-24}	1.0072764669
Neutron	1.6749273 × 10^{-24}	1.0086649156

Table 1: Masses of the Different Subatomic Particles

Table 1 gives the masses of electrons, protons, and neutrons. The second column shows the masses of the three subatomic particles in grams (which is related to the SI unit kilograms according to the relationship 1 kg = 1000 g). The third column, however, shows the masses of the three subatomic particles in "atomic mass units". Atomic mass units (amu) are useful, because, as you can see, the mass of a proton and the mass of a neutron are almost exactly 1.0 in this unit system. We'll discuss atomic mass units in a later section.

Unfortunately, the numbers in Table 1 probably don't give you a very good sense of just how big protons and neutrons are compared to electrons, so here's a comparison that might help. If an electron were the size of a penny, then a proton (or a neutron) would be about the size of a large bowling ball. Obviously, if you were told to lift a box containing several bowling balls and several pennies, you wouldn't really care about the pennies, because they wouldn't change the weight of the box all that much. What you'd want to know, though, would be the number of bowling balls in the box. That's exactly what happens when scientists try to figure out the masses of atoms. They don't really care how many electrons the atoms have (because electrons are like pennies), but they *do* care how many protons and neutrons the atoms have (because protons and neutrons are like bowling balls). In addition to mass, another important property of subatomic particles is their charge. You already know that neutrons are neutral, and thus have no charge at all. Therefore, we say that neutrons have a charge of ***zero*** . What about electrons and protons? You know that electrons are negatively charged and protons are positively charged, but what's amazing is that the *positive* charge on a *proton* is ***exactly equal in magnitude*** (magnitude means "absolute value" or "size when you ignore positive and negative signs") to the *negative* charge on an *electron*.

Figure 5: Electrons are much smaller than protons or neutrons. How much smaller? If an electron was the size of a penny, a proton or a neutron would have the mass of a large bowling ball! (*Sources:* http://en.wikipedia.org/wiki/Image:2005-Penny-Uncirculated-Obverse-cropped.png, *License:* Public Domain; http://en.wikipedia.org/wiki/Image:Bowlingball.jpg, *License:* Public Domain)

Table 2 gives the charges on electrons, protons, and neutrons. The second column shows the charges of the three subatomic particles in the SI unit of Coulombs (a Coulomb is a unit that we use to measure charge, just like a kilogram is a unit that we use to measure mass, and a meter is a unit that we use to measure distance). The third column, however, shows the charges of the three subatomic particles using "elementary charge units"* or "elementary charges." Elementary charge units (e) are appealing, because the charge on a proton and the charge on an electron are exactly 1.0 in this unit system.

	Charge in Coulombs (C)	**Mass in Elementary Charges (e)**
Electron	-1.6021765 × 10^{-19}	-1
Proton	1.6021765 × 10^{-19}	1
Neutron	0	0

Table 2: Charges on the Different Subatomic Particles

Notice that whether you use Coulombs or elementary charge units, when you ignore the positive and negative signs, the charge on the proton and the charge on the electron have the same *magnitude.*

Previously, you learned that negative and positive charges of equal magnitude cancel each other out. This means that the negative charge on an electron perfectly balances the positive charge on the proton. In other words, a neutral atom must have *exactly one electron for every proton*. If a neutral atom has 1 proton, it must have 1 electron. If a neutral atom has 2 protons, it must have 2 electrons. If a neutral atom has 10 protons, it must have 10 electrons. You get the idea. In order to be neutral, an atom must have the same number of electrons and protons, but what kinds of numbers are we talking about? That's what we'll look at in the next section.

- Most scientists don't refer to "elementary charges" as a *unit.* Nevertheless, if you treat elementary charges just like you'd treat any another non-SI unit, like a pound (lb) or a foot (ft), they become a lot easier to understand.

Atomic Number (Z) Identifies the Element

How do you tell the difference between a bike and a car? What about the difference between a car and a unicycle? Take a look at figure 6.

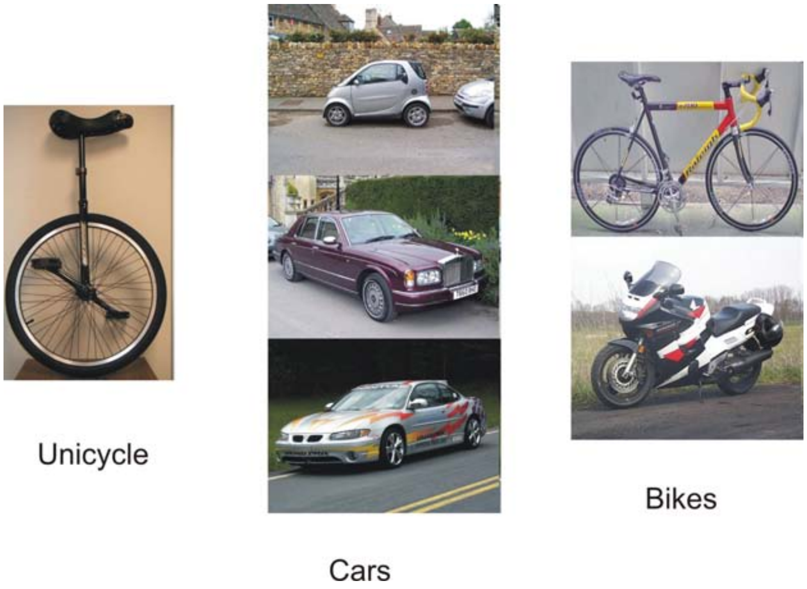


Figure 6: A unicycle, three examples of cars, and 2 examples of bikes. Can you think of some rule that might allow you to tell all unicycles, cars and bikes apart?

(*Sources:* http://en.wikipedia.org/wiki/Image:Torker_Unicycle.jpg,, *License:* GNU-FDL; http://en.wikipedia.org/wiki/Image:RacingBicycle-non.jpg, *License:* GNU-FDL; http://en.wikipedia.org/wiki/Image:Rolls.arp.850pix.jpg, *License:* Public Domain; http://en.wikipedia.org/wiki/Image:HondaCBR1000F.jpg, *License:* GNU-FDL; http://en.wikipedia.org/wiki/Image:01pacecar.jpg, *License:* Public Domain, http://www.flickr.com/photos/76074333@N00/269798915, *License:* CC-BY-SA)

If you had to make a rule to distinguish between a unicycle, a bike, a car, what would it be? You can't use color, because different cars can be different colors and, even worse, a car can be the same color as a bike or unicycle. The same goes for weight. While most cars would weigh more than most bikes, which would weigh more than most unicycles, that isn't always the case. In fact, that the little grey "Smart Car" in figure 6 probably weighs less than a large motorbike.

What you really need to distinguish between a car, a bike and a unicycle is a property that is the same within each category, but different between the categories. A good choice would be the number of wheels. All unicycles have one wheel, all bikes have two wheels, and all cars have four wheels. If you count wheels, you will most likely never confuse a unicycle with a bike, or a bike with a car (even a motorbike with a Smart Car!). In other words, if you know the number of wheels, you know which type of vehicle you're dealing with.

Just as we can tell between cars, bikes, and unicycles by counting the number of wheels, scientists can tell between different **elements** (remember, an element is a specific type of atom) by counting the number of protons. If a vehicle has only one wheel, we know it's a unicycle. If an atom has only *one proton,* we know it's *a hydrogen atom* or, said differently, it's *an atom of the element hydrogen*. Similarly, a vehicle with two wheels is always a bike, just like an atom with *two protons* is always a *helium atom,* or *an atom of the element helium*. When we count four wheels on a vehicle, we know it's a car, and when scientists count *four protons* in an atom, they know it's *a beryllium atom*, or *an atom of the element beryllium*. The list goes on: an atom with three protons is a lithium atom, an atom with five protons is a boron atom, an atom with six protons is a carbon atom… in fact, we have names for atoms containing everything from 1 proton all the way up to 117 protons. So far, the maximum number of protons scientists have been able to pack into a single atom is 117, and thus there are 117 known elements. (On Earth, only atoms with a maximum of 92 protons occur naturally.)

Figure 7: You can't really distinguish between sulfur and gold based on color because both are yellowish. You could say that gold was shiny, but then how would you tell the difference between gold and silicon? Each element, however, does have a unique number of protons. Sulfur has 16 protons, silicon has 14 protons, and gold has 79 protons.

(*Sources:* http://en.wikipedia.org/wiki/Image:Sulfur.jpg, *License:* Public Domain; http://en.wikipedia.org/wiki/Image:Native_gold_nuggets.jpg, *License:* Public Domain; http://en.wikipedia.org/wiki/Image:SiliconCroda.jpg, *License:* Public Domain)

Since an atom of one element can be distinguished from an atom of another element by the number of protons in its nucleus, scientists are always interested in this number, and how this number differs between different elements. Therefore, scientists give this number a special name and a special symbol. An element's **atomic number (Z)** is equal to the number of protons in the nuclei of any of its atoms. The atomic number for hydrogen is $Z = 1$, because every hydrogen atom has 1 proton. The atomic number for helium is $Z = 2$ because every helium atom has 2 protons. What's the atomic number of carbon?

Mass Number (A) is the Sum of Protons and Neutrons

In the last section we learned that each type of atom or element has a specific number of protons. This specific number was called the element's **atomic number**. Of course, since neutral atoms have to have one electron for every proton, an element's atomic number also tells you how many electrons are in a neutral atom of that element. For example, hydrogen has atomic number $Z = 1$. This means that an atom of hydrogen has one proton, and, if it's neutral, one electron as well. Gold, on the other hand, has atomic number $Z = 79$, which means that an atom of gold has 79 protons if it's neutral, and 79 electrons as well. So we know the number of protons, and we know the number of electrons, but what about the third type of subatomic particle? What about the number of neutrons in an atom?

The number of neutrons in an atom isn't important for determining atomic number; in fact, it doesn't even tell you which *type* of atom (or which element) you have. The number of neutrons is important, though, if you want to find a quantity known as the **mass number (A)**. The mass number of any atom is defined as the sum of the protons and neutrons in the atom:

mass number A = (number of protons) + (number of neutrons)

An atom's mass number is a very easy to calculate provided you know the number of protons and neutrons in an atom

Example 1:

What is the mass number of an atom that contains 3 protons and 4 neutrons?

Solution:

(number of protons) = 3

(number of neutrons) = 4

mass number, A = (number of protons) + (number of neutrons)

mass number, A = (3) + (4)

mass number A = 7

Example 2:

What is the mass number of an atom of helium that contains 2 neutrons?

Solution:

(number of protons) = 2 Remember that an atom of helium always has 2 protons.

(number of neutrons) = 2

mass number, A = (number of protons) + (number of neutrons)

mass number, A = (2) + (2)

mass number A = 4

Why do you think that the "mass number" includes protons and neutrons, but not electrons? You have already learned that the mass of an electron is very, very small compared to the mass of either a proton or a neutron (like the mass of a penny compared to the mass of a bowling ball). Counting the number of protons and neutrons tells scientists about the total mass of an atom, but counting the number of electrons would only confuse things.

Think of it this way – you're asked to lift a box containing some bowling balls and some pennies, but the box has already been taped closed. Now, if you have to decide whether or not to get help lifting the box, which would you prefer to know, the total number of bowling balls *and* pennies, or the just the total number of bowling balls? Suppose you were told only the number of bowling balls. If you knew that there were 20 bowling balls in the box, you wouldn't lift the box on your own, but if you knew that there was only 1, you probably would, even if that box contained 19 pennies that you didn't know about. On the other hand, if, instead of being told the number of bowling balls, you were told the number bowling balls *and* pennies, your decision would be more difficult. What if you were given the number 20? That could mean 20 bowling balls and no pennies, or it could mean 1 bowling ball and 19 pennies. In fact, it could even mean 20 pennies. Unfortunately, you would have no way of knowing what was meant by the number 20. Certainly, you wouldn't choose to lift 20 bowling balls, but lifting 20 pennies would be no problem. Just like you wouldn't care about the number of pennies in the box you were about to lift, scientists don't care about the number of electrons when they calculate the mass number. That's why the mass number is *only* the sum of the protons and neutrons in the atom.

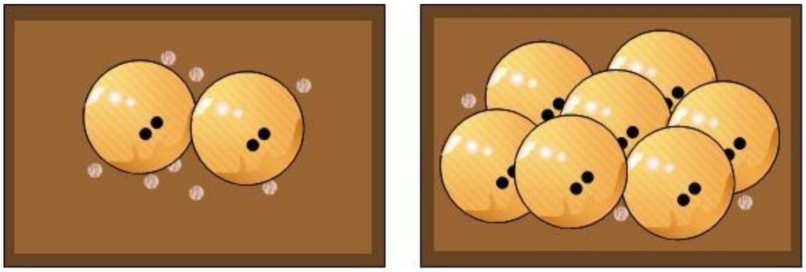


Figure 8: Each of the boxes above contains a total of 10 items. If you had to choose one to lift, though, you'd want to know the number of bowling balls in the each box, not the total number of items in each box. Obviously, you'd rather lift the box with 2 bowling balls than the box with 7 bowling balls.

(*Source by:* Sharon Bewick, *License:* CC-BY-SA)

Isotopes Have Varying Numbers of Neutrons

If you were reading the last section carefully, you'll already know that you can't use the number of neutrons in an atom to decide which *type* of atom (or which element) you have. Unlike the *number of protons,* which is always the *same* in *atoms of the same element*, the *number of neutrons* can be *different,* even in *atoms of the same element*. Atoms of the same element, containing the same number of protons, but *different numbers of neutrons* are known as **isotopes**. Since the isotopes of any given element all contain the same number of protons, they have the same atomic number (for example, the atomic number of helium is *always* 2). However, since the isotopes of a given element contain different numbers of neutrons, *different isotopes* have *different mass numbers*. The following two examples should help to clarify this point.

Example 3:

What is the atomic number (Z), and the mass number of an isotope of lithium containing 3 neutrons. A lithium atom contains 3 protons in its nucleus.

Solution:

atomic number Z = (number of protons) = 3

(number of neutrons) = 3

mass number, A = (number of protons) + (number of neutrons)

mass number, A = (3) + (3)

mass number, A = 6

Example 4:

What is the atomic number (Z), and the mass number of an isotope of lithium containing 4 neutrons. A lithium atom contains 3 protons in its nucleus.

Solution:

atomic number Z = (number of protons) = 3

(number of neutrons) = 4

mass number, A = (number of protons) + (number of neutrons)

mass number, A = (3) + (4)

mass number, A = 7

Notice that because the lithium atom *always* has 3 protons, the atomic number for lithium is *always* Z = 3. The mass number, however, is A = 6 in the isotope with 3 neutrons, and A = 7 in the isotope with 4 neutrons.

In nature, only certain isotopes exist. For instance, lithium exists as an isotope with 3 neutrons, and as an isotope with 4 neutrons, but it doesn't exists as an isotope with 2 neutrons, or as an isotope with 5 neutrons. Scientists can make isotopes of lithium with 2 or 5 neutrons, but they aren't very stable (they fall apart easily), so they don't exist outside of the laboratory.

Atomic Mass is a Calculated Value

Of course, this whole discussion of isotopes brings us back to Dalton's Atomic Theory. According to Dalton, atoms of a given element are identical. But if atoms of a given element can have different numbers of neutrons, then they can have different masses as well! How did Dalton miss this? It turns out that elements found in nature always exist as *constant uniform mixtures* of their naturally occurring isotopes. In other words, a piece of lithium always contains both types of naturally occurring lithium (the type with 3 neutrons and the type with 4 neutrons). Moreover, it always contains the two in the same relative amounts (or "relative abundances"). In a chunk of lithium, 93% will always be lithium with 4 neutrons, while the remaining 7% will always be lithium with 3 neutrons.

Unfortunately, Dalton always experimented with large chunks of an element – chunks that contained all of the naturally occurring isotopes of that element. As a result, when he performed his measurements, he was actually observing the averaged properties of all the different isotopes in the sample. Luckily, aside from having different masses, most other properties of different isotopes are similar. As a result, the fact that atoms of a given element aren't, strictly speaking, identical, isn't all that important for most chemistry problems.

Knowing about the different isotopes is important, however, when it comes to calculating atomic mass. The **atomic mass** of an element is the *average* mass of the masses of its isotopes and their relative percentages, and is typically given in "atomic mass units" (u). (Remember that an "atomic mass unit" is a convenient unit to use when studying atoms, because a proton is almost exactly 1.0 u). You can calculate the atomic mass of an element provided you know the relative abundances the element's naturally occurring isotopes, and the masses of those different isotopes. The examples below show how this is done.

Example 5:

Boron has two naturally occurring isotopes. In a sample of boron, 20% of the atoms are B-10, which is an isotope of boron with 5 neutrons and a mass of 10 amu. The other 80% of the atoms are B-11, which is an isotope of boron with 6 neutrons and a mass of 11 amu. What is the atomic mass of boron?

Solution:

To do this problem, we will calculate 20% of the mass of B-10, which is how much the B-10 isotope contributes to the "average boron atom." We will also calculate 80% of the mass of B-11, which is how much the B-11 isotope contributes to the "average boron atom."

Step One: Convert the percentages given in the question into their decimal forms by dividing each by 100:

Decimal form of 20% = $\frac{20}{100}$ = 0.20

Decimal form of 80% = $\frac{80}{100}$ = 0.80

Step Two: Multiple the mass of each isotope by its relative abundance (percentage) in decimal form:

20% of the mass of B-10 = 0.20 x 10 amu = 2.0 amu

80% of the mass of B-11 = 0.80 x 11 amu = 8.8 amu

Step Three: Find the total mass of the “average atom” by adding together the contributions from the different isotopes:

Total mass of average atom = 2.0 u + 8.8 u = 10.8 u

The mass of an average boron atom, and thus boron’s **atomic mass,** is 10.8 u.

Example 6:

Neon has three naturally occurring isotopes. In a sample of neon, 90.92% of the atoms are Ne-20, which is an isotope of neon with 10 neutrons and a mass of 19.99 u. Another 0.3% of the atoms are Ne-21, which is an isotope of neon with 11 neutrons and a mass of 20.99 u. The final 8.85% of the atoms are Ne-22, which is an isotope of neon with 12 neutrons and a mass of 21.99 u. What is the atomic mass of neon?

Solution:

To do this problem, we will calculate 90.9% of the mass of Ne-20, which is how much Ne-20 contributes to the “average neon atom”. We will also calculate 0.3% of the mass of Ne-21 and 8.8% of the mass of Ne-22, which are how much the Ne-21 isotope and the Ne-22 isotope contribute to the “average neon atom” respectively.

Step One: Convert the percentages given in the question into their decimal forms by dividing each by 100:

Decimal form of 90.92% = $\frac{90.92}{100}$ = 0.9092

Decimal form of 0.30% = $\frac{0.30}{100}$ = 0.0030

Decimal form of 8.85% = $\frac{8.85}{100}$ = 0.0885

Step Two: Multiple the mass of each isotope by its relative abundance (percentage) in decimal form:

90.92% of the mass of Ne-20 = 0.909 x 20.00 = 18.18 amu

0.3% of the mass of Ne-21 = 0.003 x 21.00 = 0.063 amu

8.85% of the mass of Ne-22 = 0.088 x 22.00 = 1.93 amu

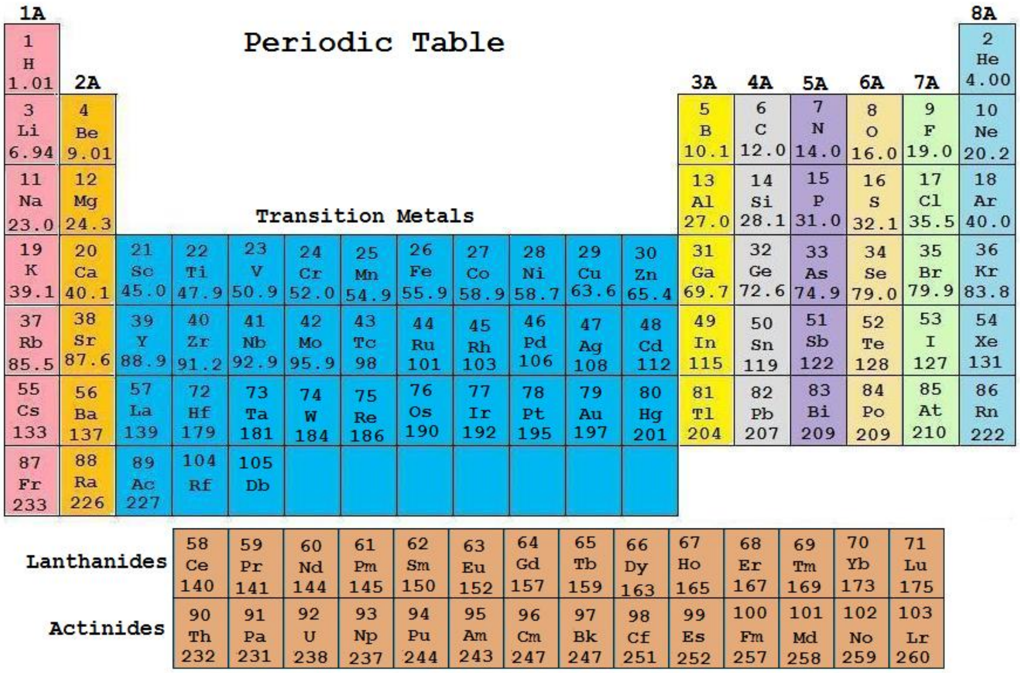
Step Three: Find the total mass of the “average atom” by adding together the contributions from the different isotopes:

Total mass of average atom = 18.18 amu + 0.06 amu + 1.93 amu = 20.17 amu

The mass of an average neon atom, and thus neon’s **atomic mass,** is 20.17 amu.

Atomic Information in the Periodic Table

Most scientists don’t want to have to calculate the atomic mass of an element every time they do an experiment. Nor do they want to memorize the number of protons, or the atomic number, of each of the 117 elements that have been discovered. As a result, this information is stored in the periodic table. Figure 9 shows a periodic table that contains more detail than the periodic table you saw back in Chapter 1.



Periodic Table

Transition Metals

1A	2A											3A	4A	5A	6A	7A	8A
1 H 1.01																	2 He 4.00
3 Li 6.94	4 Be 9.01											5 B 10.1	6 C 12.0	7 N 14.0	8 O 16.0	9 F 19.0	10 Ne 20.2
11 Na 23.0	12 Mg 24.3											13 Al 27.0	14 Si 28.1	15 P 31.0	16 S 32.1	17 Cl 35.5	18 Ar 40.0
19 K 39.1	20 Ca 40.1	21 Sc 45.0	22 Ti 47.9	23 V 50.9	24 Cr 52.0	25 Mn 54.9	26 Fe 55.9	27 Co 58.9	28 Ni 58.7	29 Cu 63.6	30 Zn 65.4	31 Ga 69.7	32 Ge 72.6	33 As 74.9	34 Se 79.0	35 Br 79.9	36 Kr 83.8
37 Rb 85.5	38 Sr 87.6	39 Y 88.9	40 Zr 91.2	41 Nb 92.9	42 Mo 95.9	43 Tc 98	44 Ru 101	45 Rh 103	46 Pd 106	47 Ag 108	48 Cd 112	49 In 115	50 Sn 119	51 Sb 122	52 Te 128	53 I 127	54 Xe 131
55 Cs 133	56 Ba 137	57 La 139	72 Hf 179	73 Ta 181	74 W 184	75 Re 186	76 Os 190	77 Ir 192	78 Pt 195	79 Au 197	80 Hg 201	81 Tl 204	82 Pb 207	83 Bi 209	84 Po 209	85 At 210	86 Rn 222
87 Fr 233	88 Ra 226	89 Ac 227	104 Rf	105 Db													

Lanthanides	58 Ce 140	59 Pr 141	60 Nd 144	61 Pm 145	62 Sm 150	63 Eu 152	64 Gd 157	65 Tb 159	66 Dy 163	67 Ho 165	68 Er 167	69 Tm 169	70 Yb 173	71 Lu 175
Actinides	90 Th 232	91 Pa 231	92 U 238	93 Np 237	94 Pu 244	95 Am 243	96 Cm 247	97 Bk 247	98 Cf 251	99 Es 252	100 Fm 257	101 Md 258	102 No 259	103 Lr 260

Figure 9: A periodic table showing both the atomic number (Z) of each element and the mass number (A) of each element.

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Notice that each box still contains the symbol (a capital letter or a capital letter followed by a lower case letter) for one of the elements, but now there are two new numbers that have been added to each square, one number above the element's symbol, and another number below the element's symbol.

The number above the element's symbol in each square is the element's atomic number. Just as you learned previously, hydrogen (symbol H) has atomic number Z = 1, helium (symbol He) has atomic number Z = 2, lithium (symbol Li) has atomic number Z = 3, beryllium (symbol Be) has atomic number Z = 4, boron (symbol B) has atomic number Z = 5, and carbon (symbol C) has atomic number Z = 6. The number below the element's symbol in each square is the element's atomic mass. Notice that atomic mass of boron (symbol B) is 10.8, which is what we calculated in example 5, and the atomic mass of neon (symbol Ne) is 20.18, which is what we calculated in example 6. Observe how compactly the periodic table stores and presents a large amount of information about each element. Take time to notice that not all periodic tables have the atomic number above the element's symbol and the mass number below it. If you are ever confused, remember that the *atomic number (Z)* should always be the *smaller of the two,* while the *atomic mass* should always be the *larger of the two.* (The average mass must include both the number of protons (Z) *and* the average number of neutrons).

Lesson Summary

- Electrons are a type of subatomic particle with a negative charge. As a result, electrons repel each other, but are attracted to protons.
- Protons are a type of subatomic particle with a positive charge. As a result, protons repel each other, but are attracted to electrons. Protons are bound together in an atom's nucleus as a result of the strong nuclear force.
- Neutrons are a type of subatomic particle with no charge (they're neutral). Like protons, neutrons are bound into the atom's nucleus as a result of the strong nuclear force.

- Protons and neutrons have approximately the same mass, but they are both much more massive than electrons (approximately 2,000 times as massive as an electron).
- The positive charge on a proton is equal in magnitude ("size when you ignore positive and negative signs") to the negative charge on an electron. As a result, a neutral atom must have an equal number of protons and electrons.
- Each element has a unique number of protons. An element's atomic number (Z) is equal to the number of protons in the nuclei of any of its atoms.
- The mass number (A) of an atom is the sum of the protons and neutrons in the atom

mass number A = (number of protons) + (number of neutrons)

- Isotopes are atoms of the same element (same number of protons) that have different numbers of neutrons in their atomic nuclei.
- An element's atomic mass is the average mass of one atom of that element. An element's atomic mass can be calculated provided the relative abundances of the element's naturally occurring isotopes, and the masses of those isotopes are known.
- The periodic table is a convenient way to summarize information about the different elements. In addition to the element's symbol, most periodic tables will also contain the element's atomic number (Z), and element's atomic mass.

Review Questions

1. Decide whether each of the following statements is true or false. **(Intermediate)**

a. The nucleus of an atom contains all of the protons in the atom.

b. The nucleus of an atom contains all of the neutrons in the atom.

c. The nucleus of an atom contains all of the electrons in the atom.

d. Neutral atoms of a given element must contain the same number of neutrons.

e. Neutral atoms of a given element must contain the same number of electrons.

2. Match the subatomic property with its description. **(Beginning)**

(1) electron	a. has an atomic charge of + 1 e
(2) neutron	b. has a mass of 9.109383×10^{-28} grams
(3) proton	c. is neither attracted to, nor repelled from charged objects

3. Arrange the electron, proton, and neutron in order of decreasing mass. **(Beginning)**

4. Decide whether each of the following statements is true or false. **(Intermediate)**

a. An element's atomic number is equal to the number of protons in the nuclei of any of its atoms.

b. The symbol for an element's atomic number is (A).

c. A neutral atom with Z = 4 must have 4 electrons.

d. A neutral atom with A = 4 must have 4 electrons.

e. An atom with 7 protons and 7 neutrons will have A = 14.

f. An atom with 7 protons and 7 neutrons will have Z = 14.

g. A neutral atom with 7 electrons and 7 neutrons will have A = 14.

5. Use the periodic table to find the symbol for the element with: **(Intermediate)**

a. 44 electrons in a neutral atom

b. 30 protons

c. Z = 36

d. an atomic mass of 14.007 amu

6. When will the mass number (A) of an atom be… **(Challenging)**

a. bigger than the atomic number (Z) of the atom?

b. smaller than the atomic number (Z) of the atom?

c. equal to the atomic number (Z) of the atom?

7. Column One contains data for 5 different elements. Column Two contains data for the same 5 elements, however different isotopes of those elements. Match the columns by connecting isotopes of the same element. **(Challenging)**

Column One	Column Two
a. an atom with 2 protons and 1 neutron	i. a C (carbon) atom with 6 neutrons
b. a Be (beryllium) atom with 5 neutrons	ii. an atom with 2 protons and 2 neutrons
c. an atom with Z = 6 and A = 13	iii. an atom with Z = 7 and A = 15
d. an atom with 1 proton and A = 1	iv. an atom with A = 2 and 1 neutron
e. an atom with Z = 7 and 7 neutrons	v. an atom with Z = 4 and 6 neutrons

Calculations:

8. Match the following isotopes with their respective mass numbers. **(Intermediate)**

a. an atom with Z = 17 and 18 neutrons	i. 35
b. an H atom with no neutrons	ii. 4
c. A He atom with 2 neutrons	iii. 1
d. an atom with Z = 11 and 11 neutrons	iv. 23
e. an atom with 11 neutrons and 12 protons	v. 22

9. Match the following isotopes with their respective atomic numbers. **(Challenging)**

a. a B (boron) atom with A = 10	i. 8
b. an atom with A = 10 and 6 neutrons	ii. 2
c. an atom with 3 protons and 3 neutrons	iii. 3
d. an oxygen atom	iv. 4
e. an atom with A = 4 and 2 neutrons	v. 5

10. Answer the following questions: **(Beginning)**

a. What's the mass number of an atom that contains 13 protons and 13 neutrons?

b. What's the mass number of an atom that contains 24 protons and 30 neutrons?

11. Answer the following questions: **(Intermediate)**

a. What's the mass number of the isotope of manganese (Mn) containing 28 neutrons?

b. What's the mass number of the isotope of calcium (Ca) containing 20 neutrons?

12. Answer the following questions: **(Challenging)**

a. What's the atomic number of an atom that has 30 neutrons, and a mass number of A = 70?

b. What's the atomic number of an atom with 14 neutrons, if the mass number of the atom is A = 28?

13. Answer the following questions: **(Challenging)**

a. What's the mass number of a neutral atom that contains 7 protons and 7 neutrons?

b. What's the mass number of a neutral atom that contains 7 electrons and 7 neutrons?

c. What's the mass number of a neutral atom that contains 5 protons, 5 electrons and 6 neutrons?

d. What's the mass number of a neutral atom that contains 3 electrons and 4 neutrons

14. Answer the following questions: **(Challenging)**

a. What element has 32 neutrons in an atom with mass number A = 58?

b. What element has 10 neutrons in an atom with mass number A = 19?

15. Copper has two naturally occurring isotopes. 69.15% of copper atoms are Cu-63 and have a mass of 62.93 amu. The other 30.85% of copper atoms are Cu-65 and have a mass of 64.93 amu. What is the atomic mass of copper? **(Challenging)**

Vocabulary

electron	A type of subatomic particle with a negative charge.
proton	A type of subatomic particle with a positive charge. Protons are found in the nucleus of an atom.
neutron	A type of subatomic particle with no charge. Neutrons are found in the nucleus of an atom.
the strong nuclear force	The force that holds protons and neutrons together in the nucleus of the atom. The strong nuclear force is strong enough to overcome the repulsion between protons.
atomic mass units (amu)	A unit used to measure the masses of small quantities like protons, neutrons, electrons and atoms. It is useful, because the mass of a proton is very close to 1.0 amu.
elementary charge (e)	The magnitude of charge on one electron or one proton. You can treat elementary charges as a unit of charge.
atomic number (Z)	An element's atomic number is equal to the number of protons in the nuclei of any of its atoms.

mass number (A)	The mass number of an atom is the sum of the protons and neutrons in the atom.

Review Answers

1. a. (T) b. (T) c. (F) d. (F) e. (T)

2. 1.b., 2.c., 3.a.

3. neutron > proton > electron

4.

a. (T) b. (F) c. (T) d. (F) e. (T) f. (F) g. (T)

5. a. (Ru) b. (Zn) c. (Kr) d. (N)

6.

a. when the atom has 1 or more neutrons

b. never

c. when the atom has no neutrons. This is true of one commonly occurring isotope of hydrogen

7. a.ii., b.v., c.i., d.iv., e.iii.

8. a.i., b.iii., c.ii., d.v., e.iv.

9. a.v., b.iv., c.iii., d.i., e.ii.

10.

a. A = 26 b. A = 54

11.

a. A = 53 b. A = 40

12.

a. Z = 40 b. Z = 14

13.

a. A = 14 b. A = 14 c. A = 11 d. A = 7

14.

a. Fe, since Z = 26

b. F, since Z = 9

15. 63.55 amu

5. The Bohr Model of the Atom

The Wave Form of Light

Lesson Objectives

- The student will define the terms wavelength and frequency with respect to wave-form energy.
- The student will state the relationship between wavelength and frequency with respect to electromagnetic radiation.
- The student will state the respective relationship between wavelengths and frequencies of selected colors on the electromagnetic spectrum.

Introduction

Our entire universe is made up of matter, which is anything that has mass and occupies space. You now know that matter is composed of small building blocks known as atoms, and that these small building blocks are composed of even smaller subatomic particles called protons, electrons and neutrons. Matter is all around you and you can use the atomic, or subatomic, description of matter to understand anything from the cells in your body to the planet Earth!

Any object that you can hold or touch is matter. But our universe contains something else – something that you can't really touch, but that you can certainly see (in fact, you can't see without it!), and that you can often feel. It isn't matter, because it doesn't have any mass, nor does it occupy any space. Still it's fundamentally important to our everyday lives, and we most definitely have a name for it. Can you think of what it is? If you haven't guessed by now, the answer is light.

Think about it for a minute – can you really talk about light using any of the ideas that we've considered so far in our study of matter and the universe? Light doesn't have any mass. Light doesn't occupy any space either. Try sticking your hand into the beam of light shining out of a flashlight. Your hand goes straight through as if there was nothing there! And yet there must be *something* there... how else can you explain the "brightness" that you see? If you have trouble understanding light and trying to define exactly what light is, you're not alone. Scientists had trouble explaining light too. In fact, we've only really understood light for about 100 years.

Wave Form Energy

The wave model of energy can be partially demonstrated with waves in a rope. Suppose we tie one end of a rope to a tree and hold the other end at a distance from the tree such that the rope is fully extended.

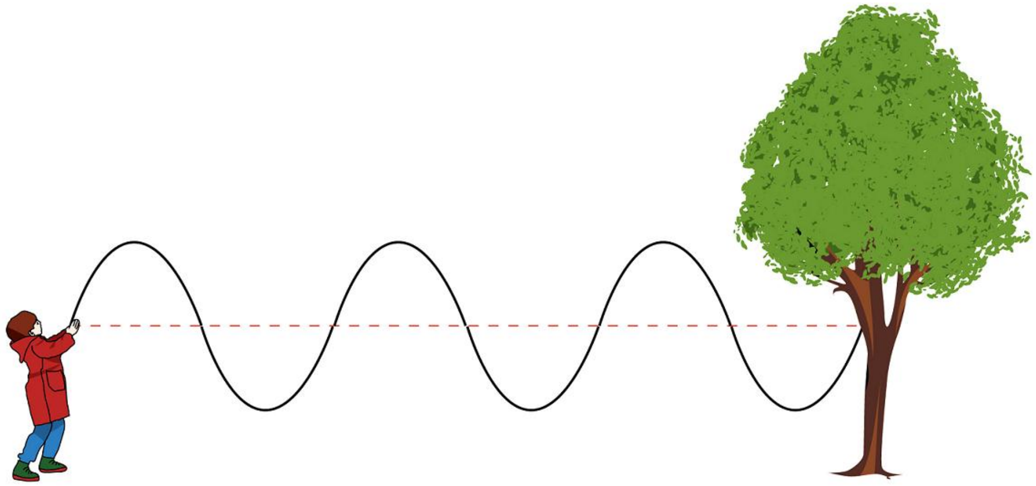


Figure 1: Wave in a rope.

(*Source:* CK-12 Foundation, *License:* CC-BY-SA)

If we then jerk the end of the rope up and down in a rhythmic way, the end of the rope we are holding goes up and down. When the piece of rope we are holding goes up and down, it pulls on the neighboring part of the rope which then also goes up and down. The up and down motion will be passed along to each succeeding part of the rope so that after a short time, the entire rope will contain a wave as shown in Figure 1. The red dotted line in the figure shows the undisturbed position of the rope before the wave was initiated. The humps above the undisturbed line are called ***crests*** and the dips below the undisturbed position are called ***troughs*** . It is important for you to recognize that the individual particles of the rope DO NOT move horizontally. The particles of rope only move up and down and if the wave is allowed to dissipate, all the particles of rope will be in exactly the same position they were in before the wave started. Each hump in the rope moves horizontally from the person to the tree but the particles of rope only move vertically. The energy that is put into the rope by jerking it up and down also moves horizontally from the person to the tree. The feeling that parts of the rope are moving horizontally is a visual illusion.

If we jerk the rope up and down with a different rhythm, the wave in the rope will change its appearance in terms of crest height, distance between crests, and so forth, but the general shape of the wave will remain the same. We can characterize the wave in the rope with a few measurements. An instantaneous photo of the rope will freeze it so we can indicate some of the characteristic values.

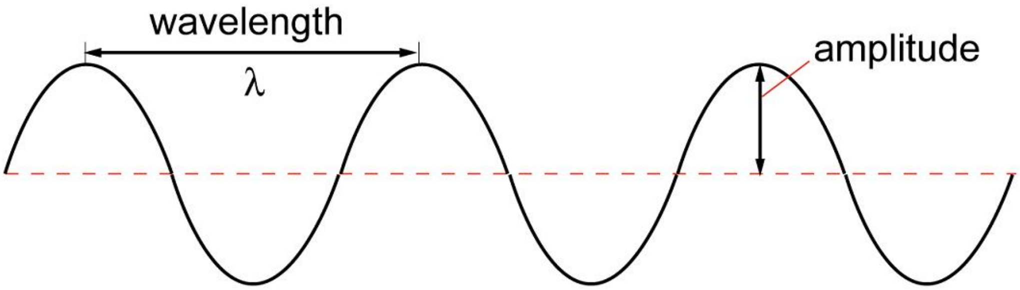


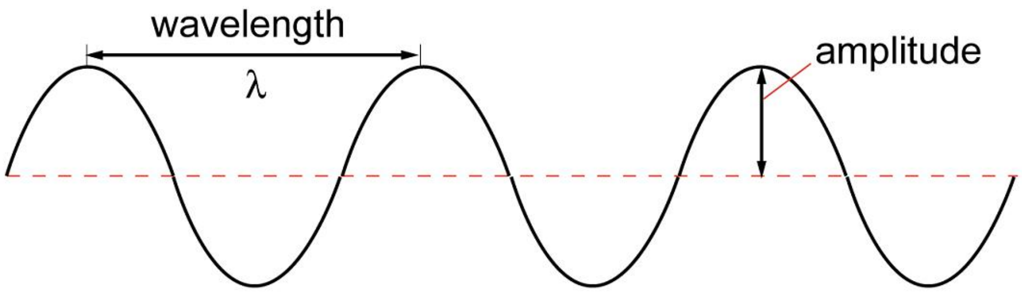
Figure 2: Characteristics of waves.

(*Source:* CK-12 Foundation, *License*: CC-BY-SA)

The distance from one crest to the next crest is called the ***wavelength*** of the wave. You could also measure the wavelength from one trough to the next or, in fact, between any two identical positions on successive waves. The symbol used for wavelength is the Greek letter lambda, λ. The distance from the maximum height of a crest to the undisturbed position is called the ***amplitude*** of the wave. We could measure a ***velocity*** for the wave if we measure how far horizontally a crest travels in a unit of time. The unit for velocity would be the normal meters/second. We also need to determine a very important characteristic of waves called ***frequency***. If we choose an exact position along the path of the wave and count how many crests pass the position per unit time, we would get a value for frequency. In everyday life, frequency values are often expressed as "cycles/second" or "waves/second" but when you try to use these units in calculations, the word "cycles" or "waves" will not cancel. The proper unit for frequency has seconds in the denominator and "1" in the numerator. It is simple 1/s or s^{-1}. This unit has been named "Hertz." Frequencies are often expressed in Hertz but when you are plugging numbers into mathematical formulas and wish to keep track of units, it is best to express frequency in units of s^{-1}. The symbol used for frequency is the Greek letter nu, ν. Unfortunately, this Greek letter looks a very great deal like an italicized v. You must be very careful reading equations to be sure whether they are representing velocity, v, or frequency, ν. To avoid this problem, this material will use a lower case **f** as the symbol for frequency. The velocity, wavelength, and frequency of a wave are related as indicated by the formula, $\mathbf{v = f \lambda}$. If the wavelength is expressed in meters and the frequency is expressed in s^{-1}, then multiplying the wavelength times the frequency will yield m/s, which is the unit for velocity.

Electromagnetic Waves

Electromagnetic radiation (light) waves are somewhat like waves in a rope . . . except without the rope. Light waves do not need a medium through which to travel. They can travel through a vacuum, which is obvious since they come to us from the sun. The energy of an electromagnetic wave travels in a straight line along the path of the wave just as did the energy in a rope wave. The moving light has associated with it an oscillating electric field and an oscillating magnetic field. This means that along the straight line path of the wave, there exists a positive electric field that will reach maximum positive charge, then slowly collapse to zero charge, and then expand to a maximum negative charge. Along the path of the electromagnetic wave, this changing electric field repeats its oscillating charge over and over again. There is also a changing magnetic field that oscillates from maximum north pole field to maximum south pole field. When scientists try to draw a picture to represent this concept, they use the same picture of a wave that was used for rope waves and water waves.



You should not allow yourself to think that the light travels in this weaving pattern. The light travels along the straight red line that represents the undisturbed position. For an electromagnetic wave, the crests and troughs represent oscillating fields, not the path of the light. We can still characterize light waves by their wavelength, frequency, and velocity but these values will be significantly different numerically from water and rope waves.

At some point along the path of the electromagnetic wave, the electric field will reach a maximum value (crest) and then, as the electromagnetic wave continues to move along its straight line path, the electric field will decrease, through zero, increase to a maximum trough, collapse back to zero again, and then expand to another maximum crest. We can measure along the path of the wave, the distance the wave travels between one crest and the succeeding crest and this distance will be the wavelength of the wave. The frequency of electromagnetic waves are determined in the same way as the frequency of a rope wave, that is, the number of full cycles that pass a point in a unit of time. The velocity of electromagnetic waves (in a vacuum) is the same for all waves regardless of frequency or wavelength. Every electromagnetic wave has a velocity of 3.00 x 10^8 m/s in a vacuum. The velocity of electromagnetic waves in air is slightly less than in a vacuum but so close that we will use the value for the velocity. The speed of light in a vacuum is symbolized by a lower case *c*. The relationship for the velocity, wavelength, and frequency of electromagnetic waves is **$c = \lambda f$**.

In rope waves and water waves, the amount of energy possessed by the wave is related to the amplitude of the wave; more energy is put into the rope if the end of the rope is jerked higher and lower. But, in electromagnetic radiation, the amount of energy possessed by the wave is related only to the frequency of the wave. In fact, the frequency of an electromagnetic wave can be converted directly to energy in Joules by multiplying by a conversion factor. The conversion factor is called ***Planck's constant*** and is equal to 6.63 x 10^{-34} J·s. Sometimes, the unit for Planck's constant is given as Joules/Hertz but you can work that out to see the units are the same. The equation for the conversion of frequency to energy is ***$E = hf$***, where E is the energy in Joules, *h* is Planck's constant in J·s, and f is the frequency in s^{-1}.

The Electromagnetic Spectrum

Electromagnetic waves have an extremely wide range of wavelengths, frequencies, and energies. The highest energy form of electromagnetic waves are gamma rays and the lowest energy form (that we have named) are radio waves.

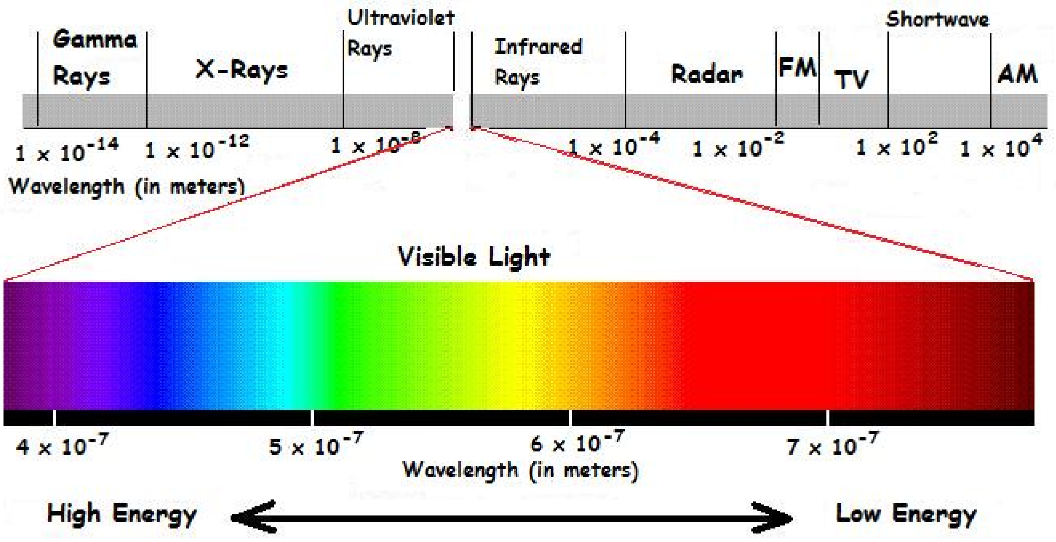


Figure 4: The Electromagnetic Spectrum.

(*Source: Created by:* Richard Parsons, *License:* CC-BY-SA)

On the far left of Figure 4 are the highest energy electromagnetic waves. These are called gamma rays and can be quite dangerous, in large numbers, to living systems. The next lower energy form of electromagnetic waves are called x-rays. Most of you are familiar with the penetration abilities of these waves. They can also be dangerous to living systems. Humans are advised to limit as much as possible the number of medical x-rays they have per year. Next lower, in energy, are ultraviolet rays. These rays are part of sunlight and the upper end of the ultraviolet range can cause sunburn and perhaps skin cancer. The tiny section next in the spectrum is the visible range of light . . . this section has been greatly expanded in the bottom half of the figure so it can be discussed in more detail. The visible range of electromagnetic radiation are the frequencies to which the human eye responds. Lower in the spectrum are infrared rays and radio waves.

The light energies that are in the visible range are electromagnetic waves that cause the human eye to respond when those frequencies enter the eye. The eye sends a signal to the brain and the individual "sees" various colors. The highest energy waves in the visible region cause the brain to see violet and as the energy decreases, the colors change to blue, green, yellow, orange, and red. When the energy of the wave is above or below the visible range, the eye does not respond to them. When the eye receives several different frequencies at the same time, the colors are blended by the brain. If all frequencies of light strike the eye together, the brain sees white and if there are no visible frequencies striking the eye, the brain sees black. The objects that you see around you are light absorbers - that is, the chemicals on the surface of the object will absorb certain frequencies and not others. Your eyes detect the frequencies that strike your eye. Therefore, if your friend is wearing a red shirt, it means the dye in that shirt absorbs every frequency except red and the red frequencies are reflected. If your only light source was one exact frequency of blue light and you shined it on a shirt that was red in sunlight, the shirt would appear black because no light would be reflected. The light from fluorescent types of lights do not contain all the frequencies of sunlight and so clothes inside a store may appear to be a slightly different color than when you get them home.

Lesson Summary

- One model of light is that of wave-form electromagnetic radiation.
- Light, in wave form, is characterized by its wavelength, λ , frequency, f, and velocity, c.
- The unit for wavelength is meters and the unit for frequency is either s^{-1} or Hertz.
- The full spectrum of electromagnetic radiation has radio waves as its lowest energy, lowest frequency, longest wavelength end and gamma rays as its highest energy, highest frequency, shortest wavelength end.
- The colors we see for an object are the blending of all the frequencies of light reflected by the object.

Review Questions

1. Choose the correct word in each of the following statements. **(Intermediate)**

a. Blue light has a (longer/shorter) wavelength than red light.

b. Yellow light has a (higher/lower) frequency than blue light.

c. Green light has a (larger/smaller) energy than red light.

2. Choose the correct word in each of the following statements. **(Intermediate)**

a. If ‘light A’ has a longer wavelength than ‘light B’, then ‘light A’ has (a lower frequency than/a higher frequency than/the same frequency as) ‘light B.’

b. If ‘light C’ has a shorter wavelength than ‘light D’, then ‘light C’ has (a larger energy than/a smaller energy than/the same energy as) ‘light D.’

c. If ‘light E’ has a higher frequency than ‘light F’, then ‘light E’ has (a longer wavelength than/a shorter wavelength than/ the same wavelength as) ‘light F.’

d. If ‘light G’ has a higher frequency than ‘light H’, then ‘light G’ has (a larger energy than/ a smaller energy than/ the same energy as) ‘light H.’

e. If ‘light J’ has a larger energy than ‘light K’, then ‘light J’ has (a shorter wavelength than/ a longer wavelength than/ the same wavelength as) ‘light K.’

Vocabulary

crest	High point in a wave pattern (hill).
trough	Low point in a wave pattern (valley).
amplitude of a wave	The ‘height’ of a wave. In light waves, the amplitude is proportional to the brightness of the wave.

frequency of a wave (ν)	The 'number' of waves passing a specific reference point per unit time. The frequency of a light wave determines the color of the light.
hertz (Hz)	The SI unit used to measure frequency. One Hertz is equivalent to 1 event (or one full wave passing by) per second.
wavelength (λ)	The length of a single wave from peak to peak (or trough to trough). The wavelength of a light wave determines the color of the light.
electromagnetic spectrum	A list of all the possible types of light in order of decreasing frequency, or increasing wavelength, or decreasing energy. The electromagnetic spectrum includes gamma rays, X-rays, UV rays, visible light, IR radiation, microwaves and radio waves.

Review Answers

1.

a. shorter b. lower c. larger

2.

a. a lower frequency than

b. a larger energy than

c. a shorter wavelength than

d. a larger energy than

e. a shorter wavelength than

The Dual Nature of Light

Lesson Objectives

- Explain the double-slit experiment and the photoelectric effect.
- Explain why light is both a particle and a wave.
- Use and understand the formula relating a light's velocity, frequency, and wavelength, $c = f\lambda$.
- Use and understand the formula relating a light's frequency and energy, $E = hf$.

Introduction

Developing a theory to explain the nature of light was a difficult task. An acceptable theory in science is required to explain ALL the observations made on a particular phenomenon. Light, appears to have two different sets of behaviors under different circumstances. As you will see, sometimes light behaves like wave-form energy and sometimes it behaves like an extremely tiny particle. It required the very best scientific minds from all over the world to put together a theory to deal with the nature of light.

The Difficulties of Defining Light Solved by Einstein and Planck

Why was light so hard to understand? Part of the problem was that when scientists performed different experiments on light, they got conflicting results. Some experiments suggested that light was like a wave, while others suggested that light was like a particle! Let's take a look at what's meant by "like a wave" and "like a particle".

Figure 1: Water diffracting into circular waves as it passes through the small opening between two rocks.

(*Source:* <http://www.flickr.com/photos/framesofmind/554402976/>, *License:* CC-BY-SA, *Modified by:* Sharon Bewick)

Since you're probably familiar with water waves, we'll use water to explain wave behavior. Whenever a water wave is forced through a small opening, such as the space between the two rocks in Figure 1, it spreads out into a circular shape through a process known as *diffraction.* If several of these circular waves run into each other, they can interfere with one another and produce interesting patterns in the water.

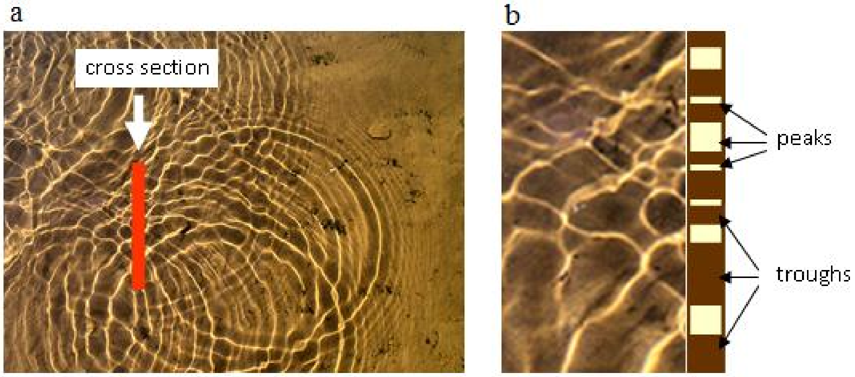


Figure 2: Patterns formed by colliding diffraction waves.

(*Source:* <http://www.flickr.com/photos/clearlyambiguous/46198862/>, *License:* CC-BY-SA, *Modified by:* Sharon Bewick)

Figure 2 shows some of these patterns. Look carefully at the red line in Figure 2a, which defines a cross-section of the pattern. That same cross-section is blown up in Figure 2b, where you can clearly see how it is composed of alternating "peaks" and "troughs." The peaks are actually extra high points in the waves (hills), while the troughs are extra low points (valleys).

Imagine how surprised scientists were when they shone light through two narrow slits in a solid plate and saw a similar pattern of peaks (bright spots) and troughs (dark spots) on the wall opposite the plate. Obviously, this proved that light had some very wave-like properties. In fact, by assuming that light was a wave and that it diffracted through the two narrow slits in the plate, just like water waves diffract when they pass between rocks, scientists were even able to predict *where* the bright spots would occur! Figure 3 shows how the results of the "**double-slit**" experiment could be understood in terms of light waves.

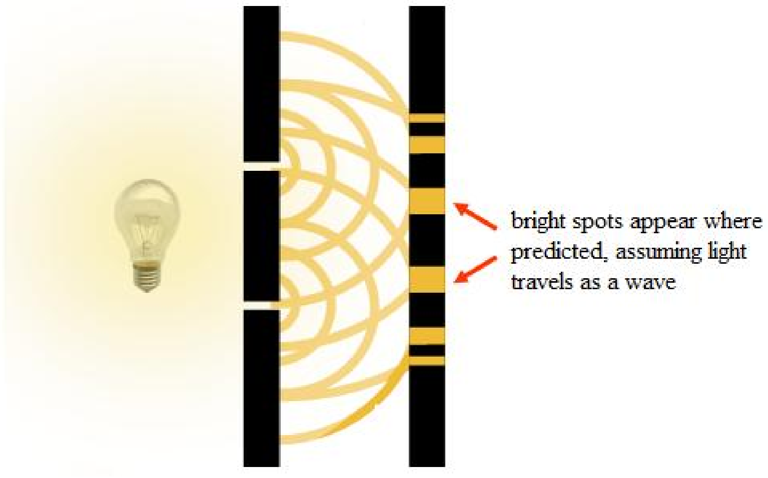


Figure 3: Waves of light also diffract when they pass through narrow slits.

(*Source:* <http://en.wikipedia.org/wiki/Image:Gluehlampe_01_KMJ.jpg>, *License:* GNU-FDL, *Modified by:* Sharon Bewick)

What was also obvious from the double-slit experiment was that light could not be understood as a particle. Imagine rolling a particle (like a marble) through a small opening. Would you expect it to diffract? Of course not! You'd expect the marble to role in a straight line from the opening to the opposite wall, as shown in Figure 4. Light traveling as a particle, then, should make a single bright spot directly across from each slit opening. Since that wasn't what scientists observed, they knew that light couldn't be composed of tiny particles.

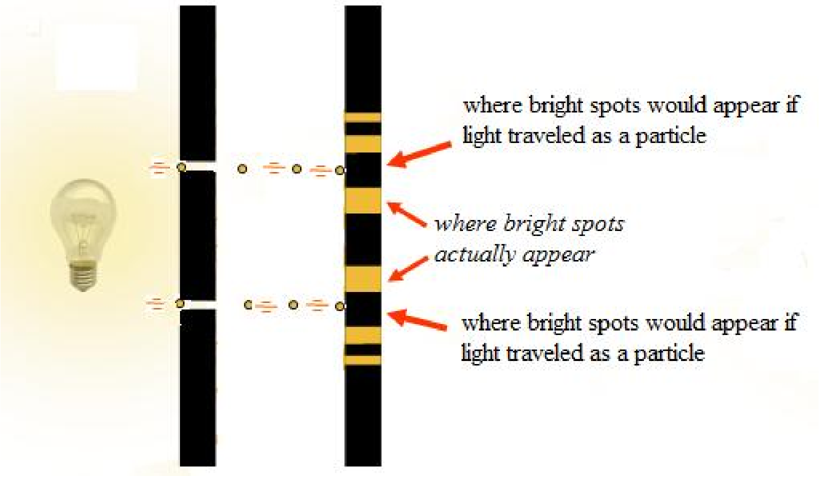


Figure 4: The bright spots formed when light shines through narrow slits are not straight through the openings.

(*Source:* <http://en.wikipedia.org/wiki/Image:Gluehlampe_01_KMJ.jpg>, *License:* GNU-FDL, *Modified by:* Sharon Bewick)

The wave theory of light seemed to work, at least for the double-slit experiment. Remember, though, that according to the scientific method, a theory should be tested with further experiments to make sure that it's accurate and complete. Unfortunately, the next experiment that scientists performed suggested that light was *not* a wave, but was, instead, a stream of particles! By shining light on a flat strip of metal, scientists found that they could knock electrons off of the metal surface. They called this phenomenon the **photoelectric effect,** and they called electrons that were bumped off **photoelectrons.** Why did the photoelectric effect prove that light wasn't a wave? The problem was that the number of photoelectrons produced by a beam of light didn't depend on how bright the light was, but instead depended on the light's color. To see why this was so important, we need to talk a little bit more about waves and light waves in particular.

Suppose you were sitting on a pier looking out at the Atlantic Ocean. Which do you think would be more likely to knock you off the pier, a huge tidal wave or a wave like the type you might find on a calm day at the beach? Obviously, the tidal wave would have a better chance of knocking you off the pier, and that's because the tidal wave has more energy as a result of its bigger **amplitude** (amplitude is really just another name for the 'height' of the wave). The energy of a *wave* depends on its amplitude, and only on its amplitude. What does amplitude mean in terms of light waves? It turns out that in light waves, the amplitude is related to the brightness of the light – the brighter the light, the bigger the amplitude of the light wave. Now, based on what you know about tidal waves and piers, which do you think would be better at producing photoelectrons, a bright light, or a dim light? Naturally, you'd think that the bright light with its bigger amplitude light waves would have more energy and would therefore knock more electrons off… but that's **NOT** the case.

It turns out that bright light and dim light knock exactly the *same number* of electrons off a strip of metal. What matters, instead of the brightness of the light, is the *color* of the light. Red light doesn't produce any photoelectrons, while blue light produces a lot of photoelectrons. Unlike brightness, which depends on the amplitude of the light waves, color depends on their *frequency* (for a discussion of frequency, see the box below).

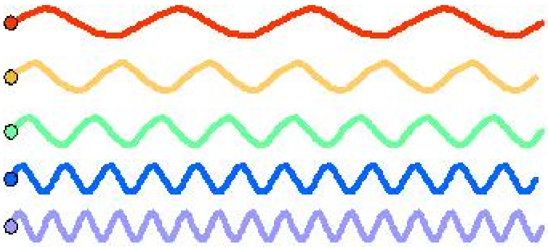


Figure 5: The wavelengths of the different colors in the visible light spectrum.

(*Source: Created by:* Sharon Bewick, *License:* CC-BY-SA)

This made the photoelectric effect very puzzling to scientists because they knew that the energy of a wave doesn't depend on its frequency, only on its amplitude. So why did frequency matter when it came to photoelectrons? It was all rather mysterious.

What is frequency? Frequency can be a difficult concept to understand, but it's really just a measure of how many times an event occurs in a given amount of time. In the case of waves, it's the number of waves that pass by a specific reference point per unit time. Figure 6 shows two different types of waves, one red and one blue. Notice how, in a single second (one full turn of the clock hand), 4 red waves pass by the dotted black line while 16 blue waves pass by the same reference point. We say that the blue waves have a higher frequency than the red waves. The SI unit used to measure frequency is the Hertz (Hz). One *Hertz* is equivalent to *one event (or one full wave passing by) per second.*

How does the frequency of the light affect the length of the light waves? Take a close look at Figure 6 again. What do you notice about the lengths of the blue and red waves? Obviously, the blue waves (higher frequency) have a shorter wavelength, while the red waves (lower frequency) have a longer wavelength. This has to be true, provided that the waves are traveling at the same speed. You can tell that the red and blue waves *are* traveling at the same speed, because their leading edges (marked by a red dot and a blue dot respectively) keep pace with each other. All light waves travel at the same speed.

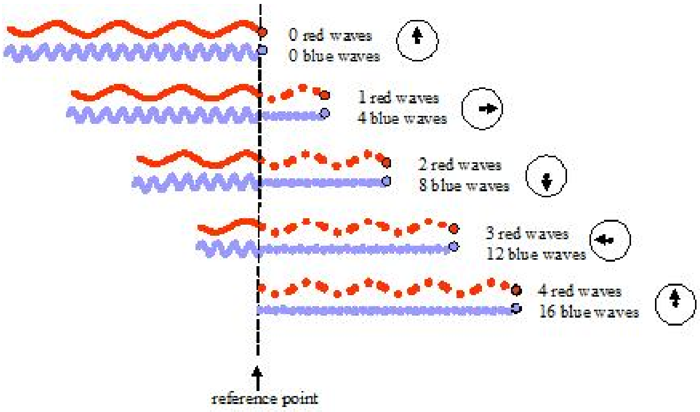


Figure 6: Red and blue light have different wavelengths but travel at the same speed.

(*Source: Created by:* Sharon Bewick, *License:* CC-BY-SA)

The explanation of the photoelectric effect began with a man named Max Planck. Max Planck wasn't actually studying the photoelectric effect himself. Instead, he was studying something known as **black-body radiation.** Black-body radiation is the light produced by a black object when you heat it up (think, for example, of a stove element that glows red when you turn it on). Like the photoelectric effect, scientists couldn't explain black-body radiation using the wave theory of light either. Max Planck, however, realized that black-body radiation *could* be understood by treating light like a stream of tiny energy packets (or *particles*). We now call these packets of energy "**photons**" or "**quanta**", and say that light is **quantized**.

Albert Einstein applied the theory of quantized light to the photoelectric effect and found that the energy of the photons, or quanta of light, *did* depend on the light's frequency. In other words, all of a sudden Einstein could explain why the frequency of a beam of light and the energy of a beam of light were related. That made it a lot easier to understand why the number of photoelectrons produced by the light depended on the light's color (frequency). The only assumption that Einstein needed to make was that light was composed of particles.

Wait! Sure the particle theory of light explained black-body radiation and the photoelectric effect, but what about the double-slit experiment? Didn't that require that light behave like a wave? Either the double-slit experiment was wrong, or else the photoelectric effect and black-body radiation were wrong. Surely, light had to be either a wave or a particle. Surely, it couldn't be both. Or could it? Albert Einstein suggested that maybe light wasn't exactly a wave *or* a particle. Maybe light was *both.* Albert Einstein's theory is known as the **wave-particle duality** of light, and is now fully accepted by modern scientists.

Light Travels as a Wave

You just learned that light can act like a particle *or* a wave, depending entirely on the situation. Did you ever play with Transformers when you were younger? If you did, maybe you can answer the following question: are Transformers vehicles (cars and aircraft) or are they robots? It's kind of a stupid question, isn't it? Obviously Transformers are *both* vehicles and robots. It's the same with light – light is *both* a wave and a particle.

Even though Transformers are both vehicles and robots, when they want to get from one place to another quickly, they usually assume their vehicle form and use all of their vehicle properties (like wheels or airplane wings). Therefore, if you were trying to explain how a Transformer sped off in search of an enemy, you'd probably describe the Transformer in terms of its car or aircraft properties.

Just as it's easiest to talk about Transformers traveling as vehicles, it's easiest to talk about light traveling as a wave. When light moves from one place to another, it uses its wave properties. That's why light passing through a thin slit will diffract; in the process of traveling through the slit, the light behaves like a wave. Keeping in mind that light travels as a wave, let's discuss some of the properties of its wave-like motion.

First, and most importantly, *all light waves travel, in a vacuum, at a speed of 299,792,458 m/s (or approximately* 3.00 x 10^8 m/s*. Imagine a tiny ant trying to surf by riding on top of a light wave. Provided the ant could balance on the wave, it would move through space at 3.00 x 10^8 m/s.*

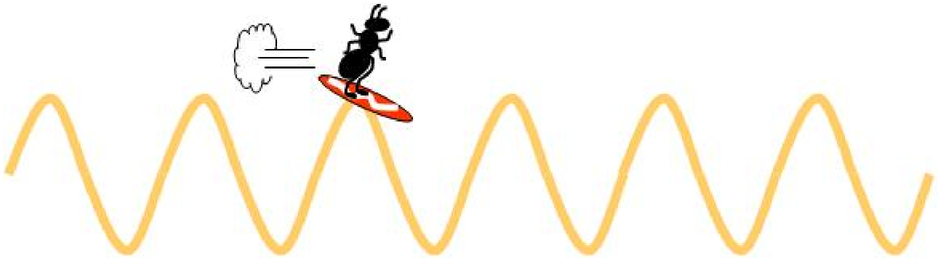


Figure 7: An ant surfing a light wave.

(*Source: Created by:* Sharon Bewick, *License:* CC-BY-SA)

To put that number into perspective, when you go surfing at the beach, the waves you catch are moving at about 9 m/s. Unlike light waves, though, which all travel at exactly the same speed, ocean waves travel at different speeds depending on the depth of the ocean, the temperature, and even the wind!

Previously, you learned that light can have different frequencies and different wavelengths. You also learned that because light always travels at the same speed 3.00 x 10^8 m/s, light waves with higher frequencies must have smaller wavelengths, while light waves with lower frequencies must have longer wavelengths. Scientists state this relationship mathematically using the formula

c	$=$	f	$\times$	λ
speed of light (3.00 x 10^8 m/s)		frequency (Hz or s^{-1})		wavelength (m)

where c is the speed of light, 3.00 x 10^8 m/s, f is the frequency and λ is the wavelength. Remember that the unit we use to measure frequency is the Hertz (Hz), where 1 *Hertz* (Hz) is equal to 1 *per second*, s^{-1}. Wavelength, since it is a distance, should be measured in the SI unit of distance, which is the meter (m). Let's see how the formula can be used to calculate the frequency or the wavelength of light.

Example 1:

What is the frequency of a purple colored light, if the purple light's wavelength is 4.45 x 10^{-7} m?

speed of light, c = 3.00 x 10^8 m/s You *always* know the speed of light, even if the question doesn't give it to you.

wavelength, λ = 4.45 x 10^{-7} m

c	$=$	f	$\times$	λ
3.00 x 10^8 m/s	=	f	x	4.45 x 10^{-7} m

To solve for frequency, f, divide *both* sides of the equation by 4.45 x 10^{-7} m.

$$\frac{3.00 \times 10^{8} m/s}{4.45 \times 10^{-7} m} = f \times \frac{4.45 \times 10^{-7} m}{4.45 \times 10^{-7} m}$$

$6.74 \text{ x } 10^{14} \text{ s}^{-1} = f \text{ x } (1)$

$f = 6.74 \text{ x } 10^{14}$ Hz

The frequency of the purple colored light is $6.74 \text{ x } 10^{14}$ Hz.

Example 2:

What is the frequency of a red colored light, if the red light’s wavelength is 650 nm?

speed of light, $c = 3.00 \text{ x } 10^{8}$ m/s

$\lambda = 650$ nm

$\lambda = (650 \text{ nm})(1 \text{ x } 10^{-9} \text{ m/nm}) = 6.50 \text{ x } 10^{-7}$ m

$$c = f \times \lambda$$

$$3.00 \text{ x } 10^{8} \text{ m/s} = f \text{ x } 6.50 \text{ x } 10^{-7} \text{ m}$$

To solve for frequency, f, divide *both* sides of the equation by $6.50 \text{ x } 10^{-7}$ m.

$$\frac{3.00 \times 10^{8} m/s}{6.50 \times 10^{-7} m} = f \text{ x } \frac{6.50 \times 10^{-7} m}{6.50 \times 10^{-7} m}$$

$4.61 \text{ x } 10^{14} \text{ s}^{-1} = f \text{ x } (1)$

$f = 4.61 \text{ x } 10^{14}$ Hz

The frequency of the red colored light is $4.61 \text{ x } 10^{14}$ Hz.

Notice that the wavelength in Example 1, $4.45 \text{ x } 10^{-7}$ m, is smaller than the wavelength in Example 2, $6.50 \text{ x } 10^{-7}$ m, while the frequency in Example 1, $6.74 \text{ x } 10^{14}$ Hz is *bigger* than the frequency in Example 2, $4.61 \text{ x } 10^{14}$ Hz. Just as you’d expect, a small wavelength corresponds to a big frequency, while a big wavelength corresponds to a small frequency. (If you’re still not comfortable with that idea, take another look at Figure 6 and convince yourself of why this must be so, provided the waves travel at the same speed.) Let’s take a look at one final example, where you have to solve for the wavelength instead of the frequency.

Example 3:

Scientists have measured the frequency of a particular light wave at $6.10 \text{ x } 10^{14}$ Hz. What is the wavelength of the light wave?

speed of light, $c = 3.00 \text{ x } 10^{8}$ m/s

frequency, $f = 6.10 \text{ x } 10^{14}$ Hz

$f = 6.10 \text{ x } 10^{14} \text{ s}^{-1}$(To do dimensional analysis, it is easiest to change Hertz to *per second* 1 Hz = 1 s^{-1})

$c = f \text{ x } \lambda$

$3.00 \text{ x } 10^{8} \text{ m/s} = 6.10 \text{ x } 10^{14} \text{ s}^{-1} \text{ x } \lambda$

To solve for wavelength, λ, divide both sides of the equation by 6.10 x 10^{14} s^{-1}.

$$\frac{3.00 \times 10^{8}\ m/s}{6.10 \times 10^{14}\ s^{-1}} = \frac{6.10 \times 10^{14}\ s^{-1}}{6.10 \times 10^{14}\ s^{-1}} \times \lambda$$

4.92×10^{-7} m = (1) x λ

$\lambda = 4.92 \times 10^{-7}$ m

The wavelength of the light is 4.92 x 10^{-7} m (or 492 nm, if you do the conversion).

Light Consists of Energy Packets Called Photons

We have already seen how the photoelectric effect proved that light wasn't *completely* wave-like, but rather, had particle-like properties too. Let's return to our comparison between Transformers and light. Transformers travel as vehicles; however, when Transformers battle each other, they fight as robots, not as cars and planes. The situation with light is similar. Light may travel as a wave, but as soon as it strikes an object and transfers its energy to that object, the light behaves as if it's made up of tiny energy packets, or particles, called **photons.**

Remember, the energy of a wave depends only on the wave's amplitude, but not on the wave's frequency. The energy of a photon, or a light "particle", however, *does* depend on frequency. The relationship between a photon's energy and a photon's frequency is described mathematically by the formula

E	$=$	h	$\times$	f
energy (J)		Planck's constant (h = 6.63 x 10^{-34} J·s)		frequency (Hz or s^{-1})

where E is the energy of the photon, h is Planck's **constant** (which always has the value h = 6.63 x 10^{-34} J·s), and f is the frequency of the light. The SI unit for energy is the Joule (J); the SI unit for frequency is the Hertz (or per second, s^{-1}); the SI unit for Planck's constant is the Joule-second (J·s). Although this equation came from complex mathematical models of black-body radiation, its meaning should be clear – the larger the frequency of the light beam, the more energy in each photon of light.

Example 4:

What is the energy of a photon in a stream of light with frequency 4.25 x 10^{14} Hz?

Planck's constant, 6.63 x 10^{-34} J·s

frequency, 4.25 x 10^{14} Hz

f = 4.25 x 10^{14} s^{-1}

(To do dimensional analysis, it is easiest to change Hertz to *per second*, 1 Hz = 1 s^{-1})

$$E = h \times f$$

$$E = 6.63 \times 10^{-34}\ J{\cdot}s \times 4.25 \times 10^{14}\ s^{-1}$$

$$E = 2.82 \times 10^{-19}\ J$$

The energy of a photon of light with frequency 4.25 x 10^{14} s^{-1} is 2.82 x 10^{-19} J.

Example 5:

What is the frequency (in Hz) of a beam of light if each photon in the beam has energy 4.44×10^{-22} J?

Planck's constant, 6.63×10^{-34} J·s

energy, $E = 4.44 \times 10^{-22}$ J

$$E = h \times f$$

$$4.44 \times 10^{-22}\ \text{J} = 6.63 \times 10^{-34}\ \text{J·s} \times f$$

To solve for frequency (f), divide *both* sides of the equation by 6.63×10^{-34} J·s.

$$\frac{4.44 \times 10-22\ J}{6.63 \times 10^{-34}\ J.s} = \frac{6.63 \times 10^{-34}\ J.s}{6.63 \times 10^{-34}\ J.s} \times f$$

$$6.70 \times 10^{11}\ s^{-1} = (1) \times f$$

$f = 6.70 \times 10^{11}$ Hz

The frequency of the light is 6.70×10^{11} Hz.

The Electromagnetic Spectrum

When scientists speak of light in terms of its wave-like properties, they are often interested in the frequency and wavelength of the light. One way that we, as humans, can distinguish between light beams of different frequencies (and thus different wavelengths) is to use their colors. Light that is reddish colored has large wavelengths and small frequencies, while light that is bluish colored has small wavelengths and large frequencies. Humans can't, however, see all types of light. We can only see visible light. In fact, if the light's wavelength gets too small, the light becomes invisible to our eyes. We call this light **ultraviolet (UV)** radiation. Similarly, if the light's wavelength gets too large, the light also becomes invisible to our eyes. We call this light **infrared (IR)** radiation.

Believe it or not, there are types of light with wavelengths even shorter than those of ultraviolet radiation. We call these types of light **X-rays** and **gamma rays.** We can use X-rays to create pictures of our bones, and gamma rays to kill bacteria in our food, but our eyes can't see either (you can see the picture that an X-ray makes, but you can't actually see the X-ray itself). On the other side of the spectrum, light with wavelengths even longer than those of infrared radiation are called **microwaves** and **radio waves.** We can use microwaves to heat our food, and radio waves to broadcast music, but again, our eyes can't see either.

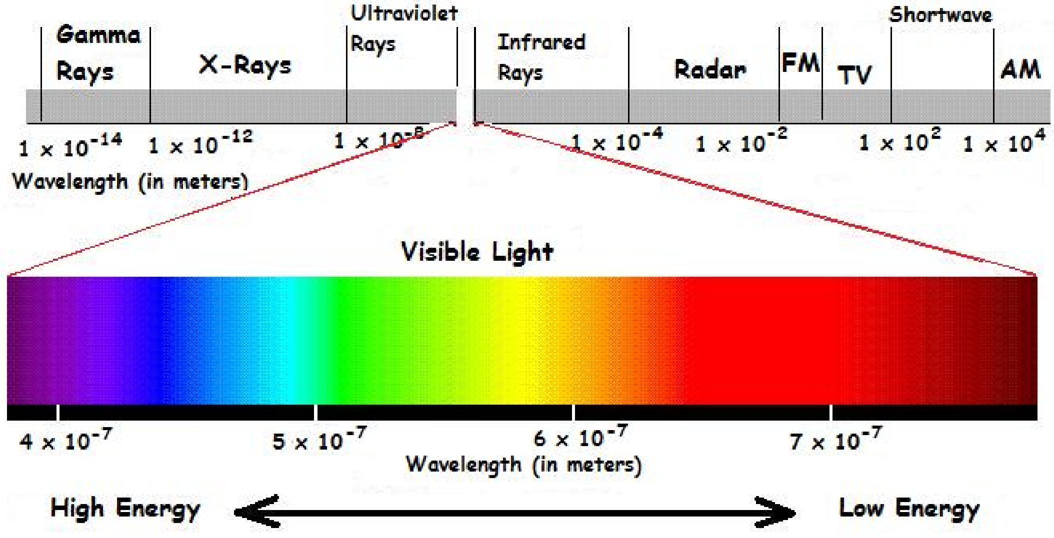


Figure 8: The electromagnetic spectrum.

(*Source: Created by:* Richard Parsons, *License:* CC-BY-SA)

Scientists summarize all the possible types of light in what's known as the **electromagnetic spectrum.** Figure 8 shows a typical electromagnetic spectrum. As you can see, it's really just a list of all the possible types of light in order of increasing wavelength. Notice how visible light is right in the middle of the electromagnetic spectrum. Since light with a large wavelength has a small frequency and light with a small wavelength has a large frequency, arranging light in order of "increasing wavelength," is the same as arranging light in order of "decreasing frequency." This should be obvious from Figure 8 where, as you can see, wavelength increases to the right (decreases to the left), while frequency increases to the left (decreases to the right).

Unlike wavelength and frequency, which are typically shown on the electromagnetic spectrum, energy is rarely included. You should, however, be able to predict how the energy of the light photons changes along the electromagnetic spectrum. Light with large frequencies contains photons with large energies, while light with small frequencies contains photons with small energies. Therefore energy, like frequency, increases to the left (decreases to the right).

Lesson Summary

- When waves pass through narrow openings, they spread out into a circular shape through a process known as diffraction.
- When circular waves interact, they produce predictable patterns of peaks and troughs.
- When light is passed through two narrow slits, the light appears to interact in a manner similar to two circular waves spreading out from the slits. This suggests that light diffracts into circular waves when it passes through the slits and that these circular waves interact with each other. As a result, many scientists believed that light was wave-like.
- Shining light on a flat strip of metal knocks electrons off of the metal surface through what is known as the photoelectric effect.
- The number of photoelectrons produced by a beam of light depends on the color (wavelength) of the light but not on the brightness (amplitude) of the light.
- Since the energy of a wave should depend on the amplitude of the wave, scientists couldn't understand why a brighter light didn't knock more photoelectrons off of the metal. This led them to question of whether light was truly wave-like.

- Together Max Planck and Albert Einstein explained the photoelectric effect by assuming that light was actually a stream of little particles, or packets of energy known as photons or quanta.
- Scientists now believe that light is both a wave and a particle – a property which they term the wave-particle duality.
- Light travels as a wave. The speed of a light wave is always c = 3.00×10^8 m/s. The frequency, f, and wavelength, λ, of a light wave are related by the formula $c = f\lambda$.
- Light gives up its energy as a particle or photon. The energy (E) of a photon of light is related to the frequency, f, of the light according to the formula $E = hf$.
- The relationship between the frequency, the wavelength, and the energy of light are summarized in what's known as the electromagnetic spectrum. The electromagnetic spectrum is a list of light waves in order of increasing wavelength, decreasing frequency, and decreasing energy.

Review Questions

1. Decide whether each of the following statements is true or false: **(Beginning)**

a. Light always behaves like a wave.

b. Light always behaves like a particle.

c. Light travels like a particle and gives up its energy like a wave.

d. Light travels like a wave and gives up its energy like a particle.

2. Which of the following experiments suggested that light was a wave, and which suggested that light was a particle? **(Intermediate)**

a. the double-slit experiment

b. the photoelectric effect

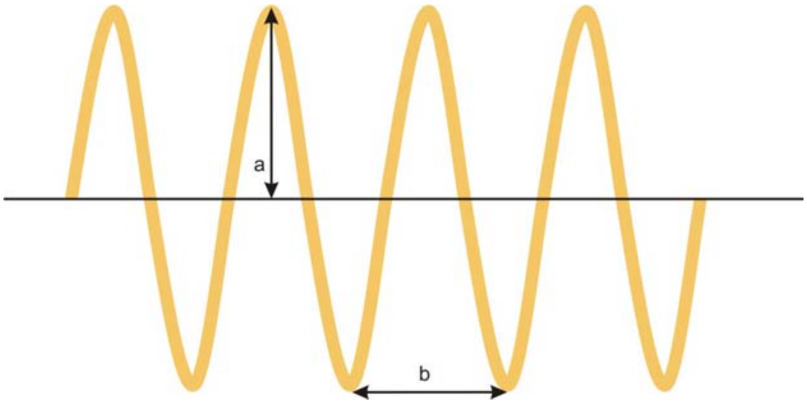
c. black-body radiation

3. Fill in each of the following blanks. **(Beginning)**

a. The brightness of a beam of light is determined by the ___________ of the light wave.

b. The color of a beam of light is determined by the _____________ of the light wave (frequency is also an acceptable answer)

4. What is the name of the quantity depicted by each of the arrows in the diagram below? **(Intermediate)**



(*Source: Created by:* Sharon Bewick, *License:* CC-BY-SA)

5. Consider light with a frequency of 4.4×10^{14} Hz. What is the wavelength of this light? **(Intermediate)**

6. What is the frequency of light with a wavelength of 3.4×10^{-9} m? **(Intermediate)**

7. What is the frequency of light with a wavelength of 575 nm? **(Intermediate)**

8. What is the energy of a photon in a beam of light with a frequency of 5.66×10^{8} Hz?

(Intermediate)

Vocabulary

diffraction	The tendency of a wave to spread out in a circular shape when passed through a small opening.
double-slit experiment	When light is passed through two narrowly separated openings (slits), the light produces a resulting pattern of peaks and troughs that suggests that light behaves like a wave.
photoelectric effect	The process whereby light shone on a metal surface knocks electrons (called photoelectrons) off of the surface of the metal.
black-body radiation	Light produced by a black object when the object is heated.
photon or quanta of light	A tiny particle-like packet of energy.
wave-particle duality of light	Einstein's theory, which concluded that light exhibits both particle and wave properties.
electromagnetic spectrum	A list of all the possible types of light in order of decreasing frequency, or increasing wavelength, or decreasing energy. The electromagnetic spectrum includes gamma rays, X-rays, UV rays, visible light, IR radiation, microwaves and radio waves.

Review Answers

1.

a. false b. false c. false d. true

2.

a. a wave b. a particle c. a particle

3.

a. amplitude b. wavelength

4.

a. amplitude b. wavelength

5. (6800 m)

6. 8.8×10^{16} Hz

7. 5.22×10^{14} Hz

8. 3.75×10^{-25} J

Light and the Atomic Spectra

Lesson Objectives

- Distinguish between continuous and discontinuous spectra.
- Recognize that white light is actually a continuous spectrum of all possible wavelengths of light.
- Recognize that all elements have unique atomic spectra.

Introduction

We now know how light can act as a wave or a particle, depending on the situation. You might wonder, though, why a chemistry textbook would waste a whole lesson on light. Light, like matter, is part of the universe, but chemists aren't responsible for studying the *entire* universe. *Chemists* are responsible for studying *chemicals.* What does light have to do with chemicals? Why do chemists need to know about light?

It turns out that scientists can actually learn a lot *about* chemicals by observing how they interact with light. Different chemicals behave differently when struck with a beam of light. In fact, the same chemical will interact differently with differently colored beams of light. To understand what light can tell us about different chemicals, though, we must first look at the electromagnetic spectrum a little more carefully.

Continuous Spectra Compared to Discontinuous Spectra

If you have a class that requires a lot of work, you might find yourself saying something like, "I'm *continuously* doing homework for this class". Think about what you mean by that. You probably mean that the homework seems to be *non-stop.* Every time you finish one assignment, the teacher gives another, so you **never get a break.** When scientists use the word **continuous,** it has a similar meaning. It means **no gaps, no holes,** and **no breaks** of any kind.

Scientists don't use the word continuous to describe homework, but they do use it to describe electromagnetic spectra (spectra is just the plural word for spectrum). In the last section, you learned that an electromagnetic spectrum was a list of light arranged in order of increasing wavelength. A continuous electromagnetic spectrum, then, includes *every possible* wavelength of light between the wavelength at the beginning of the list and the wavelength at the end. If you find that definition confusing, consider the following example.

Suppose you have a continuous spectrum that begins with light at a wavelength of 500 nm, and ends with light at a wavelength of 600 nm. Because it's continuous, that spectrum contains light with any wavelength between 500 nm and 600 nm. It contains light with a wavelength of 550 nm. It contains light with a wavelength of 545 nm. It contains light with a wavelength of 567.3 nm. It even contains light with a wavelength of 599.99999 nm. Write down any number (including a number with decimal places) that is bigger than 500 and smaller than 600. A continuous electromagnetic spectrum between 500 nm and 600 nm will include light with a wavelength equal to the number you've written down.

As shown in the last section, within the visible range of the electromagnetic spectrum, a light's wavelength corresponds to its color. Therefore, another way of defining a continuous spectrum in the visible range is to say that it is a spectrum which contains *every possible* color between the color at the beginning of the list and the color at the end. Figure 1 shows several examples of continuous spectra in the visible light range. The first continuous spectrum starts with a deep indigo blue and ends with red. Notice how the colors in this spectrum change smoothly all the way from indigo to red. There are no gaps, or missing colors. The same is true of the second continuous spectrum. The second spectrum again starts with a deep indigo blue, but this time ends with yellow. Once more the colors in the spectrum change smoothly without any gaps or holes, which makes the spectrum continuous. The third spectrum is also continuous, only this time it starts with the color green and ends with the color orange.

Figure 1: Several examples of continuous spectra in the visible range. (*Source:* <http://en.wikipedia.org/wiki/Image:Spectrum4websiteEval.svg, *License:* CC-BY-SA)

Not all electromagnetic spectra are continuous. Sometimes they contain gaps or holes. Scientists call electromagnetic spectra that contain gaps or holes **discontinuous.** Let's reexamine spectra that start at 500 nm and end at 600 nm. Discontinuous spectra in this range will include light with *some, but not all* wavelengths of light greater than 500 nm and less than 600 nm. A discontinuous spectrum might, for example, *only* contain light with wavelengths of 500 nm, 523 nm and 600 nm. Obviously you can think of many numbers that lie between 500 and 600 which aren't included in that list (534 is one example). Therefore, the spectrum is discontinuous. A different discontinuous spectrum between 500 nm and 600 nm might contain every wavelength of light *except* 533 nm. In this case, *almost* every wavelength of light is included, but since 533 nm is missing, the spectrum is still discontinuous.

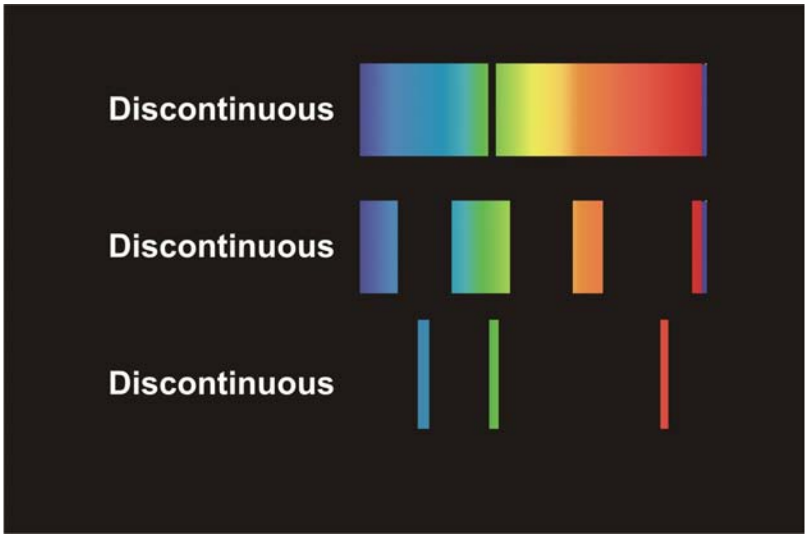


Figure 2: Several examples of discontinuous spectra in the visible range.

(*Source:* <http://en.wikipedia.org/wiki/Image:Spectrum4websiteEval.svg, *License:* CC-BY-SA)

Figure 2 shows several examples of discontinuous spectra in the range of visible light. Again, since the wavelength of a beam of light corresponds to its color, you can clearly see when an electromagnetic spectrum in the visible range is discontinuous – there will be colors missing! In the first example, only a few shades of green are missing from the middle of the spectrum. Nevertheless, the missing shades of green make the spectrum discontinuous. The next two examples in Figure 2 have even bigger gaps of missing color, so it's even more obvious that they are discontinuous.

The concept of a continuous spectrum compared to a discontinuous spectrum may seem a little silly. So what if one spectrum contains *every* possible wavelength, while another skips wavelengths here and there! Why does that matter? To understand the importance of continuous and discontinuous spectra, we have to look a little more closely at the ways in which light interacts with matter, and how those interactions can actually produce electromagnetic spectra.

Each Element Has Its Own Spectrum

Light from the sun is a continuous spectrum. In other words, when you go to the beach and sunbathe, you are bombarded by light beams of *every* different wavelength in the electromagnetic spectrum. Certain wavelengths bounce off your skin, while others interact in ways that lead to a tan or even sun burn. For example, you've probably seen sunscreens that offer UV protection. Ultraviolet light has wavelengths that are smaller than those of visible blue light. In addition to the white light that we see, the continuous spectrum of light from the sun contains UV light, and light with that range of wavelengths can be dangerous to human skin cells.

Figure 3: A sunbather trying to avoid tan lines and possibly too much UV radiation.

(*Source:* http://en.wikipedia.org/wiki/Image:Sunbathing.jpg, *License:* Public Domain)

Of course, when you're lying in the sun on the beach, you don't actually see a rainbow shining down on you, do you? Instead, you see white light. As a result, you might be skeptical and find it hard to believe that sunlight forms a continuous spectrum. Surely, the beams of light coming from the sun don't contain *every possible* wavelength of light… surely, they only contain the wavelengths of light corresponding to the 'color' white. That argument might seem logical to you, but you've fallen into a common trap – white *isn't* a color. If you take a careful look at the electromagnetic spectrum, what you'll notice is that there is *no* 'white' light in the visible range. It turns out that white light does *not* come from light of any specific wavelength or range of wavelengths. Rather, in order for our eyes to see white, they must actually receive light of *every* wavelength in the entire visible spectrum.

Figure 4: When sunlight passes through water, the white sunlight is spread out so that you can actually see the entire spectrum of brightly colored light composing it. This is what we know as a rainbow.

(*Source:* http://en.wikipedia.org/wiki/Image:Surfing_Rainbow.jpg, *License:* GNU-FDL)

White is *not* a color, and there is no light with a wavelength corresponding to 'white'. Instead, white light is formed when light of *every* wavelength in the visible spectrum is mixed together.

Remember that by passing white light through a prism, you were able to split the light into a rainbow, revealing all of the different colors, or different wavelengths of light that make up white light.

Now that we know where to find *continuous* spectra (light from the sun or any other source of pure white light), let's discuss where and when *discontinuous* spectra appear in our world. By passing an electric current or an electric spark through certain types of matter, it's possible to make that matter glow. Neon lights are one common example of this phenomenon. When an electric current travels through neon gas, the neon glows bright orange.

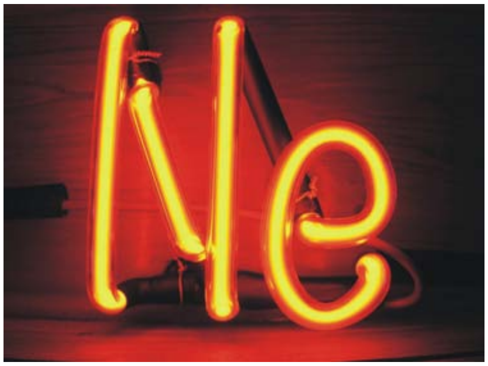


Figure 5: When an electric current is passed through neon gas, the gas glows orange.

(*Source:* http://en.wikipedia.org/wiki/Image:NeTube.jpg, *License:* CC-BY-SA)

Neon isn't the only gas that lights up when electricity passes through it. Electricity causes argon to glow blue and helium to glow pink. In fact, electricity causes *every* element in the entire periodic table to glow with a distinct color. As you might have guessed, the light from a glowing sample of neon or argon is very different from the light shining down from the sun. Unlike sunlight, which is white, elements such as neon and argon glow in *colors,* which means that the light they *emit* (or send forth) is missing certain wavelengths – if it wasn't, it would appear white to our eyes.

Figure 6: When an electric current is passed through argon gas, the gas glows blue. (*Source:* http://en.wikipedia.org/wiki/Image:Ar-Tube.jpg, *License:* CC-BY-SA) (

Remember how sunlight spread out into a rainbow, or a continuous spectrum, when you passed it through a prism? Well, when you pass light from a sample of glowing hydrogen through a prism, it doesn't spread out into a continuous spectrum. Instead, it spreads out into a discontinuous spectrum, with only four lines of colored light. A similar thing happens when you pass the light from a sample of glowing neon, or argon, or even sodium through a prism. Instead of getting a continuous spectrum, you get a discontinuous spectrum composed of a series of colored lines. The particular series of colored lines that you get out of any specific element is called the element's **atomic spectrum** or **emission spectrum.** Each element has an emission spectrum that is characteristic to that element. In other words, the emission spectrum from sodium is always the same and is different than the emission spectrum from any other element, like calcium or helium, or gold.

Figure 7: The emission spectrum for hydrogen.

(*Source:* http://en.wikipedia.org/wiki/Atomic_emission_spectrum, *License:* CC-BY-SA)

Figure 8: The emission spectrum for sodium.

(*Source:* http://en.wikipedia.org/wiki/Atomic_emission_spectrum, *License:* CC-BY-SA)

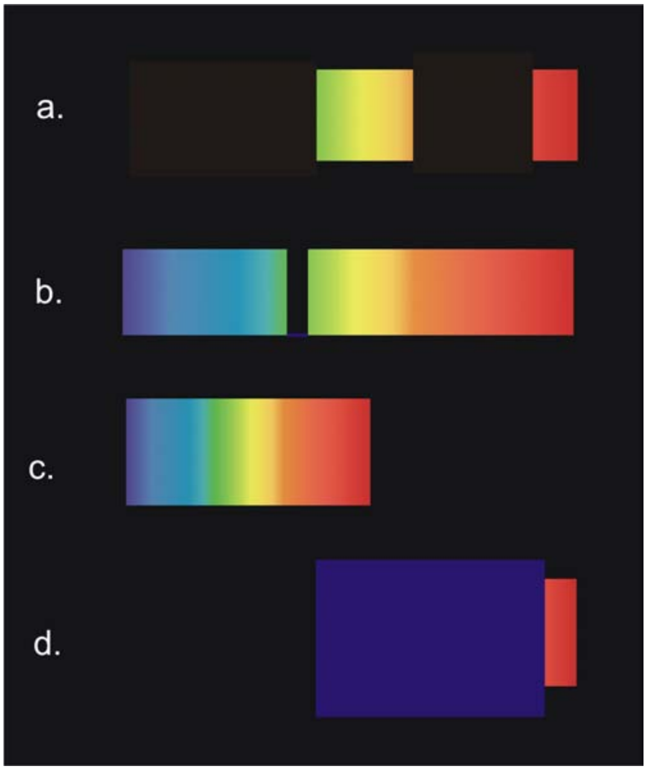
Emission spectra are important to scientists for two reasons. First, because an element's emission spectrum is characteristic of the element, scientists can often use emission spectra to determine which elements are present or absent in an unknown sample. If the emission spectrum from the sample contains lines of light that correspond to sodium's emission spectrum, then the sample contains sodium. You may have heard or read about scientists discussing what elements are present in some distant star, and after hearing that, wondered how scientists could know what elements are present in a place no one has ever been. Scientists determine what elements are present in distant stars by analyzing the light that comes from stars and finding the atomic spectrum of elements in that light. If the emission spectrum from the sample contains lines of light that correspond to helium's emission spectrum, then the sample contains helium. Second, and perhaps more importantly, the existence of atomic spectra and the fact that atomic spectra are discontinuous, can tell us a lot about how the atoms of each element are constructed. In general, an element's atomic spectrum results from the interaction between the electrons and protons within an atom of that element. The relationship between atomic spectra and the components of the atom will be the topic of the next lesson.

Lesson Summary

- When scientists use the word continuous, they mean something with no holes, no gaps, and no breaks.
- A continuous electromagnetic spectrum contains every wavelength between the wavelength on which the spectrum starts and the wavelength on which the spectrum ends.
- A discontinuous electromagnetic spectrum is a spectrum that contains gaps, holes, or breaks in terms of the wavelengths that it contains.
- Light from the sun and, in fact, any pure white light source, produces light that contains a continuous spectrum of wavelengths.
- White is not a color of light itself, but rather, results when light of every other color is mixed together.
- When an electric current or an electric spark is passed through an element, the element will give off a colored glow. This glow is actually composed of light from a discontinuous spectrum that is unique to the each and every element.
- We call the discontinuous spectrum produced by passing an electric current through an element the element's atomic spectrum or emission spectrum.
- Atomic spectra can be used to identify elements. They also tell us a lot about the nature of matter.

Review Questions

1. Decide whether each of the following spectra is continuous or discontinuous. **(Beginning)**



(*Source: Created by:* Sharon Bewick, *License:* CC-BY-SA)

2. Decide whether each of the following statements is true or false. **(Intermediate)**

a. White light has a wavelength of 760 nm.

b. Sodium's atomic spectrum is an example of a discontinuous spectrum.

c. Hydrogen's atomic spectrum is an example of a continuous spectrum.

3. Fill in each of the following blanks with the words 'must', 'may' or 'does not.' **(Intermediate)**

a. A continuous spectrum between 300 nm and 565 nm _____ contain light with a wavelength of 356 nm.

b. A continuous spectrum between 1000 cm and 1.500 m _____ contain light with a wavelength of 1.234 m.

c. A discontinuous spectrum between 234 mm and 545 mm ____ contain light with a wavelength of 300 mm.

4. Choose the correct word in each of the following statements. **(Intermediate)**

a. A continuous spectrum between 532 nm and 894 nm contains light of every wavelength (greater than/less than) 532 nm and (greater than/ less than) 894 nm

b. A discontinuous spectrum between 532 nm and 894 nm contains light of every wavelength between 532 nm and 894 nm (including/except for) light with a wavelength of 650 nm

5. What is another name for an atomic spectrum? **(Beginning)**

6. When an electric current is passed through neon, it glows __________. **(Beginning)**

7. When an electric spark is passed through argon, it glows _________. **(Beginning)**

8. When an electric current is passed through helium, it glows _________. **(Beginning)**

9. Suppose you had a solution which contained both dissolved hydrogen and dissolved sodium. If an electric current was passed through this solution, how many lines would you see in the emission spectrum? **(Intermediate)**

10. LEDs, or light emitting diodes, produce light by passing an electric current through a mixture of different atoms (or molecules) and then using their combined emission spectra to light up a room, or a string of Christmas tree lights. Why are white LEDs difficult and expensive to make? **(Challenging)**

Vocabulary

continuous electromagnetic spectrum	A spectrum that contains every possible wavelength of light between the wavelength at the beginning of the list and the wavelength at the end. In the visible range of light, it is a spectrum which contains every possible color between the color at the beginning of the list and the color at the end.
discontinuous electromagnetic spectrum	A spectrum that includes some, but not all of the wavelengths in the specified range. In the visible spectrum there are gaps or missing colors.
pure white light	A continuous spectrum of all possible wavelengths of light

atomic spectrum (emission spectrum)	A unique, discontinuous spectrum emitted by an element when an electric current is passed through a sample of that element

Review Answers

1.

a. discontinuous

b. discontinuous

c. continuous

d. continuous

2.

a. false b. true c. false

3.

a. must b. must c. may

4.

a. greater than, less than

b. except for

5. an emission spectrum

6. red/orange

7. blue

8. pink

9. 6

10. In order to produce pure white light, you would need an atom or molecule which produced an emission line at every possible wavelength in the entire visible spectrum. Obviously that would require an enormous number of different atoms and molecules in very specific combinations! In reality, LEDs are always slightly off-white.

The Bohr Model

Lesson Objectives

- Define an energy level in terms of the Bohr model.
- Find the energy of a given Bohr orbit using the equation $E_n = \frac{-Rhc}{n^2}$.

- Discuss how the Bohr model can be used to explain atomic spectra.

Introduction

In the last lesson, you learned that atoms of different elements produce different *atomic spectra* when they are struck by an electric spark or an electric current. This phenomenon is really rather puzzling. Why do atoms emit light when they are exposed to an electric current? Why is the emitted light *only* at specific wavelengths? Why do different elements have different atomic spectra? Surely these atomic spectra must tell us something about the atoms that they came from, but what does it all mean? These were the types of questions that scientists were asking in the early 1900s when a Danish physicist named Niels Bohr became interested in atomic spectra and the nature of the atom.

Figure 1: A photograph of Niels Bohr.

(*Source:* http://en.wikipedia.org/wiki/Image:Niels_Bohr.jpg, *License:* Public Domain)

Bohr Used Atomic Spectra to Develop His Model

We have learned that light travels as a wave and gives up its energy as a particle. As a result, the wavelength (or color) of a light is related to the light's frequency which is, in turn, related to the light's energy. All of these relationships were summarized in the electromagnetic spectrum. Remember the smaller the wavelength of the light (blue end of the visible spectrum), the larger the frequency and the larger energy. Similarly, the larger the wavelength of the light (red end of the visible spectrum), the smaller the frequency and the smaller the energy.

When Niels Bohr began thinking about the atom and atomic spectra in general, he was aware of the wave-particle duality of light that had just been discovered. He knew that a specific wavelength (or color) of light was related to the light's energy. As a result, Bohr realized that the lines of color appearing in an element's atomic spectrum corresponded not only to those wavelengths of light but also, to the specific frequencies and, more importantly, to the specific energies of light. The important question, then, was why the atoms were *only* emitting light at *very specific energies.* Niels Bohr realized that this unusual result could be explained by proposing what he termed **energy levels.** What are energy levels?

Electron Energy Is Quantized

You have learned that a rock held above the ground would release potential energy as it fell. Niels Bohr realized that in order for atoms to release energy, there must be a similar 'falling' process going on *inside* the atom. Since Bohr, like Rutherford, knew that the protons in the atom were bound up in the tiny nucleus, the obvious sub-atomic objects that could be 'falling' inside the atom were the electrons. Therefore, Bohr proposed a model in which electrons circled around the nucleus and, on occasion, fell closer to the nucleus, releasing energy in the process. According to Bohr, the energy that came out of the atoms as their electrons fell towards the nucleus appeared as light. This light, he argued, produced the atomic spectra that could be seen whenever electric current was passed through an element.

Of course, none of Bohr's arguments thus far explain why only *certain* energies appear in each element's atomic spectrum. If you hold a rock above the ground and drop it, it will release a specific amount of energy. If you raise that rock higher by a tiny amount, it will release slightly more energy. If you lower that rock by a tiny amount, it will release slightly less energy. In fact, it would seem you can get that rock to release *any* quantity of energy that you'd like, just by raising and lowering it to different levels above ground. But with electrons, the situation is clearly different. With electrons, it seems as if there are only a few **levels** from which electrons can fall. At least, that's what Bohr decided, and that's why he proposed the existence of the atomic **energy level.**

According to Bohr, the electrons in an atom were only allowed to exist at certain energy levels. The electrons could jump from a lower level to a higher level when they gained energy (which they could get from a passing electric current, electric spark, heat, or light), and they could drop from a higher level to a lower level when they lost energy (which they released in the form of light). Most importantly, though, the electrons could *not exist in between the allowed energy levels.* Many people have compared Bohr's energy levels to a set of stairs. Think about a child jumping up and down a set of stairs. The child can rest at any one of the stairs and stay there. If he puts energy in, he can jump up to a higher stair. If he allows himself to fall, he can drop to a lower stair. The child *cannot,* however, hover at a level in between two of the stairs, just as an electron *cannot* hover in between two of the atom's energy levels.

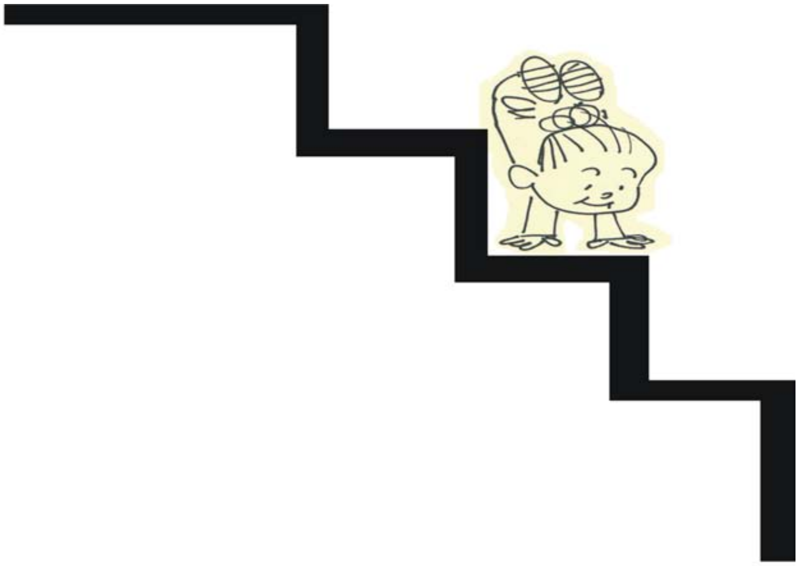


Figure 2: Just as children cannot hover between two steps on a staircase, Bohr suggested that electrons cannot hover between to energy levels in the atom.

(*Source:* http://www.flickr.com/photos/veganstraightedge/327066889/, *License:* CC-BY-SA)

Bohr developed his energy level model further using principles from physics. In physics, the energy of a positive charge and a negative charge depends on the distance between them. Therefore, Bohr decided that his energy levels must correspond to orbits, or circular paths centered around the nucleus of the atom. Since an electron that was trapped in one of these orbits remained a constant distance from the nucleus, Bohr stated that within an orbit an electron had a constant energy. Of course, the fact that only certain energy levels were allowed, also meant that only certain orbits were allowed. Figure 3 shows a schematic illustration of Bohr's model. In the diagram, each circle from n = 1 to n = 4 is an allowed orbit.

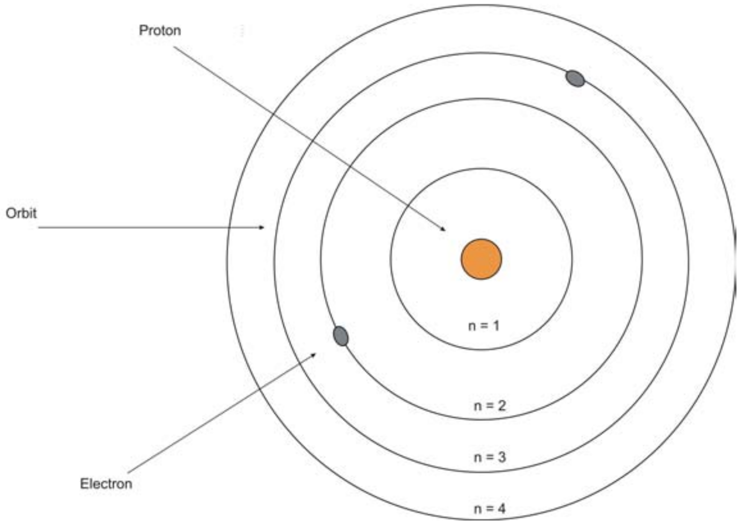


Figure 3: A schematic illustration of the Bohr model of the atom

(*Source: Created by:* Sharon Bewick, *License:* CC-BY-SA)

Notice how the negative electron, in any given orbit, is always the same distance from the positive nucleus at any place on the orbit. As a result electrons within an orbit always have the same energy. When an electron is hit by electricity, it can gain energy and can be bumped up to a higher energy orbit further away from the nucleus. On the other hand, when an electron loses energy, it falls back down to a lower energy orbit closer to the nucleus. The electron can never exist at distances in between allowed orbits. Notice how this limits the number of different transitions that the electron can make. Because the electron can only exist in certain orbits, and thus can have only certain energies, we say that the energy of the electron is **quantized.**

Bohr Used a Formula to Determine Allowed Energy Levels

Although Bohr's descriptive model of atomic orbits gives a nice explanation as to why atoms should have *discontinuous* atomic spectra, it's hard to test experimentally. Luckily, using advanced physics, the Bohr model can be used to derive a mathematical expression for the energies of the allowed orbits in the hydrogen atom. As you'll see in the next section, the energies of these orbits actually determine which wavelengths of light appear in hydrogen's atomic spectrum, meaning that Bohr's model can, *in* fact, be tested experimentally. The equation predicting the energies of the allowed hydrogen orbits is:

Rydberg constant, $R = 1.097 \times 10^{7}\ \text{m}^{-1}$

Planck's constant, $h = 6.63 \times 10^{-34}\ \text{J}\cdot\text{s}$

speed of light, $c = 3.00 \times 10^{8}\ \text{m/s}$

$$E_n = \frac{-R \times h \times c}{n^2}$$

Here E_n is the energy of the n^{th} orbit (in other words the energy of the 1^{st}, 2^{nd}, 3^{rd}, 4^{th}, etc. orbit), R is the Rydberg **constant** for hydrogen (which always has the value $R = 1.097 \times 10^7\ m^{-1}$, h is Planck's **constant** (which always has the value $h = 6.63 \times 10^{-34}$ J·s, c is the speed of light (which always has the value $c = 3.00 \times 10^8$ m/s, and n is the number of the orbit you are interested in. n can have any integer value (no decimals!) from 1 to infinity, n = 1, 2, 3, 4... infinity. As was shown in Figure 3, n = 1 is the orbit closest to the atomic nucleus, n = 2 is the next orbit out, n = 3 is the one after that, and so on. In other words, *n increases with increasing distance from the nucleus.* Let's take a look at several examples using this equation.

Example 1:

What is the energy of the 3rd allowed orbit in the hydrogen atom?

Planck's constant, 6.63×10^{-34} J·s

Rydberg constant for hydrogen $R = 1.097 \times 10^7\ m^{-1}$ (Notice how you do not need to be given h, R or c, since they are all constants)

speed of light, 3.00×10^8 m/s

n = 3

$$E_n = \frac{-R \times h \times c}{n^2}$$

$$E_n = -\frac{(1.097 \times 10^7\ m^{-1}) \times (6.63 \times 10^{-34}\ J.s) \times (3.00 \times 10^8\ m/s)}{(3)^2}$$

$$E_n = -\frac{(7.27 \times 10^{-27}\ J.s/m) \times (3.00 \times 10^8\ m/s)}{9}$$

$$E_n = -\frac{(2.18 \times 10^{-18}\ J)}{9}$$

$E_n = -2.42 \times 10^{-19}$ J

(Be careful not to drop the negative sign! These energies should always be negative)

Example 2:

What is the energy of the 2nd allowed orbit in the hydrogen atom?

Planck's constant, $h = 6.63 \times 10^{-34}$ J·s

Rydberg constant for hydrogen, $R = 1.097 \times 10^7\ m^{-1}$ (Notice, again, how you do not need to be given h, R or c, since they are all constants)

speed of light, $c = 3.00 \times 10^8$ m/s

n = 2

$$E_n = \frac{-R \times h \times c}{n^2}$$

$$E_n = -\frac{(1.097 \times 10^7\ m^{-1}) \times (6.63 \times 10^{-34}\ J.s) \times (3.00 \times 10^8\ m/s)}{(2)^2}$$

$$E_n = -\frac{(7.27 \times 10^{-27}\ J.s/m) \times (3.00 \times 10^8\ m/s)}{4}$$

$$E_n = -\frac{(2.18 \times 10^{-18}\ J)}{4}$$

$$E_n = -5.45 \times 10^{-19}\ J$$

(Again, be careful not to drop the negative sign!)

At the moment, these probably seem like fairly boring calculations, but in the next section, we'll see how energy level calculations like the two above can actually be used to predict the atomic spectrum of hydrogen. When scientists first did this in the early 1900s, they were amazed at how well this simple equation predicted the colors of light emitted by hydrogen atoms.

Atomic Spectra Produced by Electrons Changing Energy Levels

Suppose you have $10 in your wallet when you go to the store, and you only have $4 when you come home. How much money have you spent at the store? The answer is simple – you've obviously spent $6. With electrons, the situation is similar. If they start with 10 units of energy, and fall down to 4 units of energy, they lose 6 units of energy in the process. To state this mathematically, we write:

$$\underset{\text{Change in energy going from the initial state, i, to the final state, f}}{\Delta E_{i \rightarrow f}} = \underset{\text{Energy in the final state, f}}{E_f} - \underset{\text{Energy in the initial state, i}}{E_i}$$

When electrons 'lose' energy, though, they lose it by giving it off in the form of light. We have calculated the energy of an electron in the 3rd hydrogen orbit, -2.42×10^{-19} J, and the energy of an electron in the 2nd hydrogen orbit, -5.45×10^{-19} J. An electron falling from the 3rd hydrogen orbit to the 2nd hydrogen orbit begins with -2.42×10^{-19} J, and ends with -5.45×10^{-19} J, thus it loses -3.03×10^{-19} J in the process. This can be worked out mathematically. (Don't worry too much about the fact that this *lost* energy has a negative sign. Any time that an atom gains energy, the sign will be positive, and any time that an atom *loses* energy, the sign will be negative).

initial state, i = 3

final state, f = 2

$$\Delta E_{i\rightarrow f} = \Delta E_{3\rightarrow 2}$$

$$E_f = E_2 = -5.45 \times 10^{-19}\ J$$

$$E_i = E_3 = -2.42 \times 10^{-19}\ J$$

$$\Delta E_{3\rightarrow 2} = E_2 - E_3$$

$$\Delta E_{i\rightarrow f} = (-5.45 \times 10^{-19}\ J) - (-2.42 \times 10^{-19}\ J)$$

Remember, subtracting a negative number is the same as adding a positive number!

$$\Delta E_{i\rightarrow f} = (-5.45 \times 10^{-19}\ J) + (2.42 \times 10^{-19}\ J)$$

$$\Delta E_{i\rightarrow f} = -3.03 \times 10^{-19}\ J$$

All of the energy lost when an electron falls from a higher energy orbit to a lower energy orbit is turned into light, thus when an electron falls from the 3rd hydrogen orbit to the 2nd hydrogen orbit, it emits a beam of light with an energy of 3.03×10^{-19} J. You should now be able convert this energy into a wavelength (first convert the energy into a frequency and then, convert that frequency into a wavelength). The wavelength turns out to be 656 nm and, amazingly, if you look at hydrogen's atomic spectrum, shown in Figure 4, you'll notice that hydrogen clearly has a line of red light at exactly 656 nm! What's more, the green 486 nm line in hydrogen's atomic spectrum corresponds to an electron falling from the 4th hydrogen orbit to the 2nd hydrogen orbit, the blue 434 nm line corresponds to an electron falling from the 5th hydrogen orbit to the 2nd hydrogen orbit, and the purple 410 nm line corresponds to an electron falling from the 6th hydrogen orbit to the 2nd hydrogen orbit. In other words, Bohr's model can be used to predict the exact wavelengths of the four visible lines in hydrogen's atomic spectrum.

Figure 4: The wavelengths of the four visible lines in hydrogen's emission spectrum

(*Source:* http://en.wikipedia.org/wiki/Atomic_emission_spectrum, *License:* CC-BY-SA)

What about all of the other transitions that could occur between the allowed hydrogen orbits? For example, where is the line that corresponds to an electron falling from the 4th orbit to the 3rd orbit? It turns out that the energies of all the other transitions don't lie within range of energies included in the visible spectrum. As a result, even though these transitions occur, your eyes can't see the light that's given off as a result. Clearly, then, the predictions from Bohr's model give a perfect fit when compared to the hydrogen atomic spectrum. There's only one small problem…

Bohr's Model Only Worked for Hydrogen

If you take a look at the periodic table, what you'll notice is that hydrogen is a very special element. Hydrogen is the *first* element, and thus, it only has one electron. It turns out that Bohr's model of the atom worked very well provided it was used to describe atoms with only one electron. The moment that the Bohr model was applied to an element with *more* than one electron (which, unfortunately, includes every element except hydrogen), the Bohr model failed miserably.

Bohr's model failed because it treated electrons according to the laws of *classical physics.* Unfortunately, those laws only apply to fairly large objects. Back when Bohr was developing his model, scientists were only beginning to realize that the laws of classical physics didn't apply to matter as tiny as the electron. Electrons are actually quantum objects, meaning that they can only be described using the laws of quantum physics. Many of the differences between classical physics and quantum physics become particularly important when two or more quantum objects interact. As a result, while Bohr's model worked for hydrogen, it became worse and worse at predicting the atomic spectra for atoms with more and more electrons. Even helium, with two electrons, was something of a disaster!

Bohr's model explained the emission spectrum of hydrogen which previously had no explanation. The invention of precise energy levels for the electrons in an electron cloud and the ability of the electrons to gain and lose energy by moving from one energy level to another offered an explanation for how atoms were able to emit exact frequencies of light. Bohr calculated energies for the energy levels of hydrogen atoms that yielded the exact frequencies found in the hydrogen spectrum. Furthermore, those same energy levels predicted that hydrogen atoms would also emit frequencies of light in the infrared and ultraviolet regions that no one had observed previously. The subsequent discovery that those exact frequencies of infrared and ultraviolet light were present in the hydrogen spectrum provided even greater support for the ideas in the Bohr model.

One of the problems with Bohr's theory was that it was already known that when electrons were accelerated, they emitted radio waves. When you study physics, you will learn that acceleration applies to speeding up, slowing down, and traveling in a curved path. When charged particles are accelerated, they emit radio waves. In fact, that is how we create radio signals . . . by forcing electrons to accelerated up and down in an antenna. Scientists were creating radio signals in this way since 1895. Since Bohr's electrons were supposedly traveling around the nucleus in a circular path, they MUST emit radio waves, hence lose energy and collapse into the nucleus. Since the electrons in the electron cloud of an atom did not emit radio waves, lose energy, and collapse into the nucleus, there was some immediate doubt that the electrons could be traveling in a curved path around the nucleus. Bohr attempted to deal with this problem by suggesting that the electron cloud contained a certain number of energy levels, that each energy level could hold only a single electron, and that in ground state, all electrons were in the lowest available energy level. Under these conditions, no electron could lose energy because there was no lower energy level available. Electrons could gain energy and go to a higher energy level and then fall back down to the now open energy level thus emitting energy, but once in ground state, no lower positions were open. This explained why electrons circling the nucleus did not emit energy and spiral into the nucleus. Bohr did not, however, offer an explanation for why only the exact energy levels he calculated were present, that is, what is there about electrons in electron clouds that produce only a specific set of energy levels.

Another problem with Bohr's model was the predicted positions of the electrons in the electron cloud. If Bohr's model was correct, the hydrogen atom electron in ground state would always be the same distance from the nucleus. If we could take a series of photographic snapshots of a hydrogen electron cloud that would freeze the position of the electron so we could see exactly where it was located at different times, we still wouldn't know the path the electron followed to get from place to place, but we could see a few positions for the electron. Such an image of electron positions would show the electron could actually be various distances from the nucleus rather that at a constant distance.

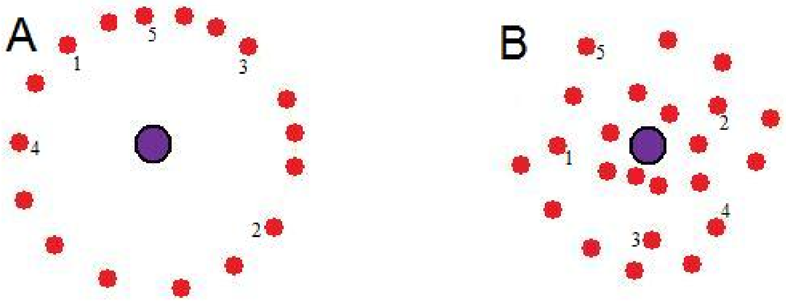


Figure 5: The electrons are NOT a constant distance from the nucleus.

(*Source: Created by:* Richard Parsons, *License:* CC-BY-SA)

If the electron circled the nucleus as suggested by Bohr's model, the electron positions would always be the same distance from the nucleus as shown in figure A above. In reality, however, the electron is found at many different distances from the nucleus as in figure B. To solve all these discrepancies, scientists would need a completely new way of looking at not just energy but at matter as well.

The development of Bohr's model of the atom is a good example of the scientific method. It shows how the observations of atomic spectra lead to the invention of a hypothesis about the nature of matter to explain the observations. The hypothesis also made predictions about spectral lines that should exist in the infrared and ultraviolet regions and when these observations were found to be correct, it provided even more supportive evidence for the theory. Of course, further observations can also provide contradictory evidence that will cause the downfall of the theory which also occurred with Bohr's model. Bohr's model was not, however, a failure. It provided the insights that allowed the next step in the development of our concept of the atom.

Bohr's Model Unacceptable

You have just seen that the Bohr model applied classical physics to electrons when electrons can only be described using quantum mechanics. In addition, it turns out that Bohr’s description of electrons as tiny little objects circling the nucleus along fixed orbits is incorrect as well. Bohr was picturing an atom that looked very much like a small solar system. The nucleus at the center of the atom was like the sun at the center of the solar system, while the electrons circling the nucleus were like the planets circling the sun. However, in quantum mechanics, electrons are thought of more like clouds rather than planets. Rather than 'circling' the nucleus confined to orbits, electrons can seem to be everywhere at once, like a fog.

The fact that Bohr's model worked as well as it did for hydrogen is actually quite remarkable! Of course, Bohr's fictional 'solar system atom' wasn't a random guess. Bohr had actually thought quite a bit about what might be going on inside the atom, and his work marked the first major step towards understanding where electrons are found in the atom. Therefore, despite the fact that the Bohr model wasn't entirely correct, Niels Bohr was awarded a Nobel Prize for his theory in 1922. It turns out that a complete description of the atom and atomic spectra, requires an understanding of quantum physics. Quantum physics describes a bizarre world that behaves according to rules which only apply to very, very small objects like electrons. Back when Bohr developed his model of the atom, scientists had never heard of quantum physics. In fact, most scientists at the beginning of the 20th century thought that everything could be described using classical physics. Even today, scientists still don't fully understand quantum physics and the world that quantum physics describes.

Lesson Summary

- Niels Bohr suggested that electrons in an atom were restricted to specific orbits around the atom's nucleus.
- Bohr argued that an electron in a given orbit has a constant energy, thus he named these orbits energy levels.
- When an electron gains energy (from an electric current or an electric spark), it can use this energy to jump from a lower energy orbit (closer to the nucleus) to a higher energy orbit (farther from the nucleus).
- When an electron falls from a higher energy orbit (farther from the nucleus) to a lower energy orbit (closer to the nucleus) it releases energy in the form of light.
- White is not a color of light itself, but rather, results when light of every other color is mixed together
- In Bohr's model, electrons can only exist in certain orbits and thus, can only have certain energies. As a result, we say that the energies of the electrons are quantized.
- Bohr used the formula $E_n = \frac{-Rhc}{n^2}$ to predict he energy level of an electron in the nth energy level (or orbit) of a hydrogen atom.
- Because, the electron is only allowed to exist at certain energy levels according to the Bohr model, there are only a few possible energies of light which can be released when electrons fall from one energy level to another. As a result, the Bohr model explains why atomic spectra are discontinuous.
- The Bohr model successfully predicts the four colored lines in hydrogen's atomic spectrum, but it fails miserably when applied to any atom with more than one electron. This is due to the differences between the laws of classical physics and the laws of quantum physics.
- The Bohr model is no longer accepted as a valid model of the atom.

Review Questions

1. Decide whether each of the following statements is true or false: **(Intermediate)**

a. Niels Bohr suggested that the electrons in an atom were restricted to specific orbits and thus could only have certain energies.

b. Bohr's model of the atom can be used to accurately predict the emission spectrum of hydrogen.

c. Bohr's model of the atom can be used to accurately predict the emission spectrum of neon.

d. According to the Bohr model, electrons have more or less energy depending on how far around an orbit they have traveled.

2. According to the Bohr model, electrons in an atom can only have certain, allowable energies. As a result, we say that the energies of these electrons are _______. **(Beginning)**

3. The Bohr model accurately predicts the emission spectra of atoms with... **(Beginning)**

a. less than 1 electron.

b. less than 2 electrons.

c. less than 3 electrons.

d. less than 4 electrons.

4. Consider an He^+ atom. Like the hydrogen atom, the He^+ atom only contains 1 electron, and thus can be described by the Bohr model. Fill in the blanks in the following statements. **(Challenging)**

a. An electron falling from the n = 2 orbit of He^+ to the n = 1 orbit of He^+ releases ______ energy than an electron falling from the n = 3 orbit of He^+ to the n = 1 orbit of He^+.

b. An electron falling from the n = 2 orbit of He^+ to the n = 1 orbit of He^+ produces light with a ______ wavelength than the light produced by an electron falling from the n = 3 orbit of He^+ to the n = 1 orbit of He^+.

c. An electron falling from the n = 2 orbit of He^+ to the n = 1 orbit of $He\^{}^+$ produces light with a ______ frequency than the light produced by an electron falling from the n = 3 orbit of He^+ to the n = 1 orbit of He^+.

5. According to the Bohr model, higher energy orbits are located (closer to/further from) the atomic nucleus. This makes sense since negative electrons are (attracted to/repelled from) the positive protons in the nucleus, meaning it must take energy to move the electrons (away from/towards) the nucleus of the atom. **(Intermediate)**

6. According to the Bohr model, what is the energy of an electron in the first Bohr orbit of hydrogen? **(Intermediate)**

7. According to the Bohr model, what is the energy of an electron in the tenth Bohr orbit of hydrogen? **(Intermediate)**

8. According to the Bohr model, what is the energy of an electron in the seventh Bohr orbit of hydrogen? **(Intermediate)**

9. If an electron in a hydrogen atom has an energy of -6.06×10^{-20} J, which Bohr orbit is it in? **(Intermediate)**

10. If an electron in a hydrogen atom has an energy of -2.69×10^{-20} J, which Bohr orbit is it in? **(Intermediate)**

11. If an electron falls from the 5th Bohr orbital of hydrogen to the 3rd Bohr orbital of hydrogen, how much energy is released (you can give the energy as a positive number)? **(Intermediate)**

12. If an electron falls from the 6th Bohr orbital of hydrogen to the 3rd Bohr orbital of hydrogen, what wavelength of light is emitted? Is this in the visible light range? **(Intermediate)**

Vocabulary

Bohr energy level	Distinct energies corresponding to the orbits (or circular paths) of electrons around the atomic nucleus, according to Bohr's model of the atom
Bohr model of the atom	Bohr's explanation of why elements produced discontinuous atomic spectra when struck by an electric current. According to this model, electrons were restricted to specific orbits around the nucleus of the atom in a solar system like manner.
classical physics	The laws of physics that describe the interactions of large objects
quantum mechanics	The laws of physics that describe the interactions of very small (atomic or subatomic) objects. Also known as "wave mechanics" and "quantum physics".

Review Answers

1.

a. true b. true c. false d. false

2. quantized

3. b. less than 2 electrons

4.

a. less b. longer c. lower

5. further from, attracted to, away from

6. -2.18×10^{-18} J

7. -2.18×10^{-20} J

8. -4.45×10^{-20} J

9. the 6th

10. the 9th

11. 1.55×10^{-19} J

12. 1090 nm, no

6. Quantum Mechanics Model of the Atom

The Wave Particle Duality

Lesson Objectives

- Explain the wave-particle duality of matter.
- Define the de Broglie relationship and give a general description of how it was derived.
- Use the de Broglie relationship to calculate the wavelength of an object given the object's mass and velocity.

Introduction

In The Bohr Model of the Atom chapter you learned about the double-slit experiment. The double-slit experiment proved that light passing through two closely spaced slits *diffracted* into circular waves, which then interfered with each other and made interesting patterns on the opposite wall. From the double-slit experiment, it was obvious that light behaved like a wave. But then along came a new set of results from black body radiation and the photoelectric effect. Both of these experiments could only be understood by assuming that light was a particle! Eventually, scientists had no choice but to accept the fact that light was actually *both* a wave *and* a particle – hence the wave-particle duality of light. Now, you probably didn't find the arguments in the previous chapter all that hard to accept. You probably thought to yourself "Fine. If Einstein says light is a wave *and* a particle, I'll believe him. He's the super-genius scientist, and I've never understood light anyhow."

Now let's talk about something that you probably *do* understand (or at least *think* you do). Let's talk about matter. Before reading any further, answer the following question – "Does matter behave like a wave, or a particle?" *Obviously* it behaves like a particle, right? Didn't we *already* decide that matter was made up of tiny *particles* called atoms, and that those atoms were, themselves, made up of even tinier *particles* called electrons, protons and neutrons? Don't worry. Everything that you've learned so far is absolutely true. Atoms, electrons, protons and neutrons *do* behave like particles. But that's not the whole story. Atoms, electrons, protons and neutrons *also* behave like waves! In other words, matter is just like light in that it has *both* wave-like *and* particle-like properties.

Electrons Were First Only Considered to Have Particle Properties

Do you remember how electrons were first discovered? It was all thanks to J. J. Thompson, with his clever cathode ray tube experiment. Briefly, J. J. Thompson cut a small hole into the anode of a cathode ray tube. This allowed cathode rays to pass through the anode and strike phosphor-coated glass on the other side. Since the phosphor glowed when it was struck by the cathode rays J. J. Thompson could actually visualize how the cathode ray traveled through the cathode ray tube.

What J. J. Thompson noticed, of course, was that the cathode rays hit the glass of the cathode ray tube directly opposite the hole in the anode. In other words, the cathode rays traveled in a straight line from the cathode, through the anode, to the glass at the end of the cathode ray tube. That sounds pretty much like a particle, doesn't it? After all, if the electrons in the cathode ray were wave-like, wouldn't they have *diffracted* when they passed through the hole in the anode? In that case, a huge glowing circle should have appeared on the phosphor painted glass, rather than just a tiny glowing spot.

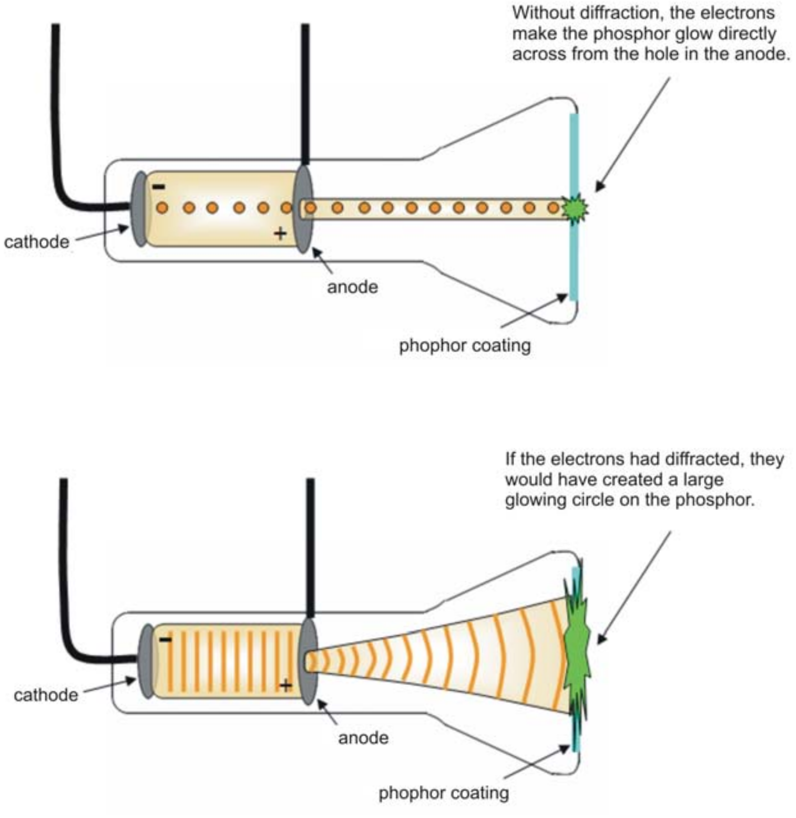


Figure 1: Early experiments didn't show any evidence of electron diffraction, so most scientists believed that electrons were particles. It turned out, though, that electrons really do have wave-like properties. The wavelengths were just too small to diffract in the cathode ray experiment.

In addition, by experimenting with magnets, J. J. Thompson had proven that the electron had mass. Up until the 1920s, scientists had *never* observed wave-like behavior from an object with mass. In fact, you probably can't think of *anything* with mass that exhibits obvious wave properties. Baseballs don't diffract; bullets fired from neighboring rifles at a shooting range never form interference patterns.

You might ask about water waves, like the type you see in the ocean. Technically speaking, the *water* in the ocean *doesn't* behave like a wave. Instead, it's the *energy* traveling *through* the water that behaves like a wave. Water may have mass, but the energy traveling *through* the water is 'mass-less.' So far we've established the fact that you never see an object with mass exhibit wave-like properties. Why, then, would *anyone* suggest that matter, even matter as small as an electron, could be described in terms of a wave-particle duality?

Figure 2: What we know as ocean waves are actually energy waves passing through the water. Source: http://en.wikipedia.org/wiki/Image:Waves_in_pacifica_1.jpg,

License: GNU-FDL)

de Broglie Proposed That Electrons are Particles and Waves

We never see matter behaving like a wave, but in 1924 a French graduate student named Louis de Broglie suggested that matter *did* in fact, have wave-like properties. It was a strange proposal on de Broglie's part, but even stranger was the fact that no one laughed at him! Instead, de Broglie was awarded a Nobel Prize in 1929. So how did de Broglie convince the scientists of his day to believe his theory? In order to argue against de Broglie's wave-particle duality of matter, scientists would have had to argue with Einstein – and no one argues with Einstein!

Figure 3: Louis de Broglie Source: http://en.wikipedia.org/wiki/Image:Broglie_Big.jpg, *License:* Public Domain)

Einstein is most famous for saying ' **mass** is **related** to **energy** '. Of course, this is usually written out as an equation, rather than as words:

$$E = m \times c \times c$$

or

$$\underset{\substack{\downarrow \\ \text{Energy in} \\ \text{Joules}}}{E} = \underset{\substack{\downarrow \\ \text{Mass in kg}}}{m} \times c^2 \longrightarrow \text{Speed of Light } (c = 3.00 \times 10^8 \text{ m/s})$$

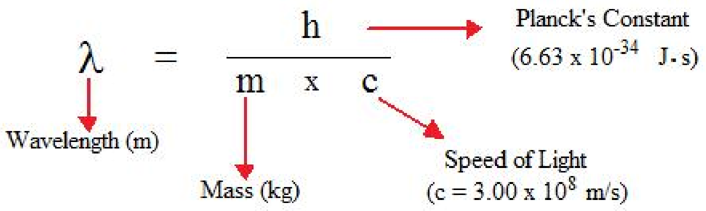
(In The Science of Chemistry chapter, you were told that you didn't need to know where the equation $E = mc^2$ comes from. You still don't need to know where it comes from, but you *do* need to know what it means!) So Einstein was responsible for defining the amount of energy in any object with mass. Remember, though, that Einstein was *also* responsible for proposing the wave-particle duality of light. In section 5.1.3 you learned that, because of the wave-particle duality of light, the *energy* of a wave can be related to the wave's *frequency* by the equation:

$$\underset{\substack{\downarrow \\ \text{Energy} \\ \text{(Joules)}}}{E} = \underset{\substack{\downarrow \\ \text{Planck's Constant} \\ (6.63 \times 10^{-34} \text{ J}\cdot\text{s})}}{h} \times f \longrightarrow \text{Frequency (Hz or s}^{-1}\text{)}$$

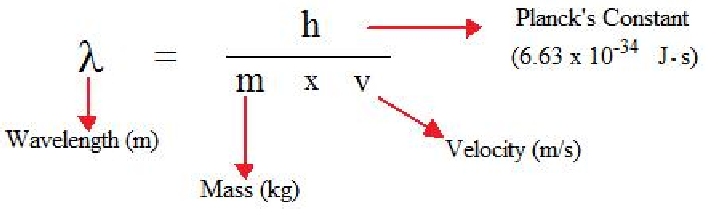
Louis de Broglie looked at Einstein's first equation relating mass and energy. Then he looked at Planck's equation, relating energy and frequency (remember, in The Bohr Model of the Atom chapter you learned that frequency is a property associated with all waves, and is related to wavelength according to the equation $c = f\lambda$). After thinking for a while, de Broglie said to himself, "If **mass** is related to **energy,** and **energy** is related to **frequency,** then **mass** must be related to **frequency**!" That's really a very logical argument. It's like saying "If **I'm** related to **my brother**, and **my brother** is related to **my sister,** then **I** must be related to **my sister**." Even though de Broglie's argument was logical, it led to a very illogical result. If mass is related to frequency, then an object with mass must also have frequency. In other words, an object with mass must have wave-like properties! This led de Broglie to propose the wave-particle duality of matter. But where were these so called matter waves? Why hadn't anybody seen them?

de Broglie Derived an Equation for the Wavelength of a Particle

Using Einstein's two equations, $E = mc^2$ and $E = hf$, along with the equation relating a wave's frequency and its wavelength, $c = \lambda f$, de Broglie was able to derive the following relationship between the wavelength of an object to the object's mass:



If you're good at math, you may be able to derive the exact same formula yourself. When de Broglie looked at his equation, though, he realized that something was wrong. Why should the wavelength of an object like an electron, or a baseball, depend on the speed of light? Neither baseballs nor electrons travel at the speed of light – only light travels at the speed of light! The problem, of course, was that de Broglie had derived his relationship using equations that applied to light, and not to matter. Luckily, the problem was easy to fix. All de Broglie needed to do was replace the speed of light, c, with some general speed, v.



That way, the de Broglie relationship between mass and wavelength could be applied to *any thing,* traveling at *any speed.* It could be applied to light, traveling at the speed $c = 3.00 \times 10^8$ m/s, it could be applied to a baseball, traveling at the speed $v = 45$ m/s, and it could be applied to a marathon runner traveling at the speed of $v = 3$ m/s. Let's try to find the wavelengths of a few common objects.

Figure 4: The wavelength for a typical baseball is far, far too small to be detectable, even in a laboratory!

(*Source:* http://www.flickr.com/photos/davehogg/129247229/.jpg, *License:* CC-BY-SA)

Example 1:

One of the fastest baseballs ever pitched traveled at a speed of 46.0 m/s. If the average baseball has a mass of 0.145 kg, what is the baseball's wavelength?

Planck's constant, $h = 6.63 \times 10^{-34}$ J.s

(Notice that you *always* know Planck's constant, even if the question doesn't give it to you)

speed, $v = 46.0$ m/s

mass, $m = 0.145$ kg

$$\lambda = \frac{h}{m \times v} = \frac{(6.63 \times 10^{-34}\ J{\cdot}s)}{(0.145\ kg)(46.0\ m/s)} = \frac{6.63 \times 10^{-34}\ J{\cdot}s}{6.67\ kg{\cdot}m/s} = 9.94 \times 10^{-35}\ \frac{J{\cdot}s}{kg{\cdot}m/s}$$

Dividing by a fraction is the same as multiplying by its reciprocal. This applies to units as well as numbers, so dividing by (kg/m·s) is the same as multiplying by (s/kg·m).

$$\lambda = 9.94 \times 10^{-35}\ \frac{J{\cdot}s{\cdot}s}{kg{\cdot}m}$$

In order to account for units, you have to substitute basic units for compound units. The definition of a Joule is, 1 J = 1 kg·m^2/s^2. Substituting these basic units into the equation in place of Joules yields:

$$\lambda = 9.94 \times 10^{-35}\ \frac{kg{\cdot}m^2}{s^2} \times \frac{s{\cdot}s}{kg{\cdot}m}$$

After cancelling units, the resultant unit is meters, the correct unit for wavelength.

$$\lambda = 9.94 \times 10^{-35}\ \text{m}$$

Figure 5: The wavelength for a typical stock car is far, far too small to be detectable.

(*Source:* http://en.wikipedia.org/wiki/Image:NASCAR_practice.jpg, *License:* Public Domain)

Example 2:

Stock cars typically race at around a speed of 77.0 m/s. If the average stock car has a mass of 1312 kg, what is the stock car's wavelength?

Planck's constant, $h = 6.63 \times 10^{-34}$ J.s

(Again, you *always* know Planck's constant, even if the question doesn't give it to you)

speed, $v = 77.0$ m/s

mass, $m = 1312$ kg

$$\lambda = \frac{h}{m \; x \; v} = \frac{(6.63 \; x \; 10^{-34} \; J{\cdot}s)}{(1310 \; kg)(77.0 \; m/s)} = \frac{6.63 \; x \; 10^{-34} \; J{\cdot}s}{100870 \; kg{\cdot}m/s} = 6.57 \text{ x } 10^{-39} \; \frac{J{\cdot}s}{kg{\cdot}m/s}$$

$$\lambda = 6.57 \text{ x } 10^{-39} \; \frac{kg{\cdot}m^2}{s^2} \times \frac{s{\cdot}s}{kg{\cdot}m}$$ When Joules is replaced with $kg{\cdot}m^2/s^2$.

After cancelling units, the resultant unit is meters, the correct unit for wavelength.

$\lambda = 6.57 \text{ x } 10^{-39}$ m

What do you notice about the wavelength of a typical baseball and the wavelength of a typical stock car? They're both extremely small, aren't they? In fact, even the strongest microscope in the world today can't see down to sizes like 9.94×10^{-35} m or 6.57×10^{-39} m. Well, that explains why we've never seen a matter wave – matter waves are just too small.

If matter waves are too small to see, then how did scientists *prove* that they exist? After all, the scientific method requires experimental evidence before a theory is accepted – and certainly before a scientist is awarded a Nobel Prize for that theory! Luckily, you can see matter waves. The only trick is to pick matter with waves that are big enough to see. Take another look at the two example questions that we just did. Notice how the *only* two factors influencing the **wavelength** of an object are the object's **mass** and the object's **speed.** (Of course, you also need to know the value of **Planck's constant, $h = 6.63 \times 10^{-34}$ J·s,** but since it's a constant, it doesn't change). In our two examples, the car was **more massive** than the baseball, and it was traveling at a **faster speed.** What do you notice about the car's wavelength compared to the baseball's wavelength? The car's wavelength was a lot smaller, wasn't it?

It turns out that the larger the mass of an object, and the faster the speed at which the object is traveling, the smaller the object's wavelength. Similarly, the smaller the mass of an object, and the slower the speed at which the object is traveling, the larger the object's wavelength. This is a direct consequence of de Broglie's equation for the wavelength – because both **mass, m,** and **speed, v,** appear in the denominator (the lower part of the fraction), they must both be big if you want a small wavelength, and small if you want a big wavelength.

Obviously, in order to see matter waves experimentally, it would be best to have a big wavelength. That means we need an object with a small mass and a slow speed. What's the smallest object that you know? It's an electron of course! Let's see if an electron wave is large enough to detect in a laboratory

Example 3:

What is the wavelength of an electron traveling at 1.25×10^{5} m/s if the mass of the electron is 9.11×10^{-31} kg?

Planck's constant, $h = 6.63 \times 10^{-34}$ J·s

(Remember, you *always* know Planck's constant, even if the question doesn't give it to you)

speed, $v = 1.25 \times 10^{5}$ m/s

mass, $m = 9.11 \times 10^{-31}$ kg

$$\lambda = \frac{h}{m \ x \ v} = \frac{(6.63 \ \text{x} \ 10^{-34} \ J{\cdot}s)}{(9.11 \ \text{x} \ 10^{-31} \ kg)(1.25 \ \text{x} \ 10^{5} \ m/s)} = \frac{6.63 \ \text{x} \ 10^{-34} \ J{\cdot}s}{1.14 \ \text{x} \ 10^{-25} \ kg{\cdot}m/s} = 5.82 \text{ x } 10^{-9} \ \frac{J{\cdot}s}{kg{\cdot}m/s}$$

$$\lambda = 5.82 \text{ x } 10^{-9} \ \frac{kg{\cdot}m^{2}}{s^{2}} \times \frac{s{\cdot}s}{kg{\cdot}m}$$

When Joules is replaced with kg·m^2/s^2.

After cancelling units, the resultant unit is meters, the correct unit for wavelength.

$\lambda = 5.82 \text{ x } 10^{-9}$ m

Now that wavelength is bigger! All right, it's still not huge, but it's big enough that, in the 1920s, scientists were able to find evidence of electron waves diffracting as electrons were forced through a thin metal film. But let's return to one of our initial questions – if electrons have wave-like properties, why didn't J. J. Thompson see electron diffraction in his cathode ray tube? The answer is simple – in that experiment, the hole that the electrons had to pass through was just too big to cause diffraction. Waves only diffract when their wavelengths are about the same size as the opening that they are forced through. Since electron waves are extremely small, there's no way that they will diffract unless they are forced through extremely small openings. As for your body when you walk through a door – well, if you're worried about your body diffracting, use your mass and the speed at which you walk through the door to figure out your wavelength. That should tell you about how narrow the door has to be to cause your body to diffract. From now on, you can avoid doors of that size! (If you do the calculation properly, you should get a number around 1×10^{-35} and, of course, you couldn't fit through a door of that size).

Lesson Summary

- At first electrons were thought to behave only as particles; de Broglie stated that all matter has wave properties and used Einstein's $E = mc^2$ formula and the formula $E = h f$ to derive the formula: $\lambda = h/(mv)$ to describe the wavelength λ of an object with mass m traveling at speed v.
- Matter waves are impossible to detect for ordinary objects, like baseballs and cars, because they are extremely small. The larger the mass, and the faster the speed of an object, the smaller its wavelength.

- Scientists found evidence of electrons diffracting when forced through a thin metal film.

Review Questions

1. In the last chapter you learned that light has wave-like properties and particle-like properties. Can you think of anything else that might have both wave-like properties and particle-like properties? **(Intermediate)**

2. Decide whether each of the following statements is true or false. **(Intermediate)**

a. Einstein was the first scientist to propose matter waves.

b. You can see baseballs diffract when you throw them.

c. The de Broglie's wave equation can only be applied to matter traveling at the speed of light.

d. Most matter waves are very small, and that is why scientists didn't realize matter had wave-like properties until the 1920s.

3. Choose the correct word in each of the following statements. **(Intermediate)**

a. The (*more/less*) massive an object is, the longer its wavelength is

b. The (*faster/slower*) an object is traveling, the shorter its wavelength is

c. A particle with a mass of 1.0 g has a (*longer/shorter*) wavelength than a particle with a mass of 3.0 g if both are traveling at the same speed

d. A baseball moving at 10 m/s has a (*longer/shorter*) wavelength than a baseball moving at 4 m/s

4. Choose the correct word in each of the following statements. **(Intermediate)**

a. An electron has a (*longer/shorter*) wavelength than a proton if both are traveling at the same speed.

b. An electron wave has a (*higher/lower*) frequency than a proton wave if both particles are traveling at the same speed.

c. If you want to increase the wavelength of an electron, you should (*slow the electron down/speed the electron up*).

5. Choose the correct statement from the options below. **(Intermediate)**

The factors that influence an object's wavelength are…

a. Only the speed of the object

b. Only the speed of light

c. The speed of light and the mass of the object

d. Only the mass of the object

e. The speed of the object and the mass of the object

6. Choose the correct statement from the options below. **(Intermediate)**

a. Light behaves only like a wave, and matter behaves only like a particle

b. Light behaves only like a wave, and matter behaves only like a wave

c. Light behaves only like a particle, and matter behaves only like a wave

d. Light behaves like a wave and like a particle, but matter only behaves like a particle

e. Light behaves only like a wave, but matter behaves like a wave and like a particle

f. Light behaves like a wave and like a particle, and matter behaves like a wave and like a particle as well

7. Fill in each of the following blanks. **(Intermediate)**

a. de Broglie used the equations ____________ and __________ to derive an equation for the wavelength of a matter wave.

b. Scientists first saw matter waves by looking for them in __________. This was a good idea, because _________ are small enough to have matter waves that can be observed in a laboratory.

8. What is the wavelength of a 5.0 kg bowling ball that rolls down the lane at 2.0 m/s? **(Challenging)**

9. If you walk through a door at 1.0 m/s, and you weight 120 lbs (or 54 kg), what is your wavelength? (This is also approximately the width of the door that would cause your body to diffract.) **(Intermediate)**

10. A car has a mass of 1250 kg. If the car's wavelength is 2.41×10^{-38} m, at what speed is the car traveling? **(Challenging)**

11. A bobsled sliding down the run at 14.8 m/s has a wavelength of 1.79×10^{-37} m. What is the total mass of the bobsled? **(Challenging)**

Further Reading / Supplemental Links

http://www.stockcarroadrace.com/compete2008.html

http://vergil.chemistry.gatech.edu/notes/quantrev/node6.html

http://www.colorado.edu/physics/2000/quantumzone/debroglie.html

http://www.launc.tased.edu.au/ONLINE/SCIENCES/physics/debroglie.html

http://my.morningside.edu/slaven/Physics/uncertainty/uncertainty3.html

http://physics.about.com/od/lightoptics/a/waveparticle.htm

http://nobelprize.org/nobel_prizes/physics/laureates/1929/broglie-bio.html

Vocabulary

wave-particle duality of matter	Matter exhibits both particle-like and wave-like properties.

Review Answers

1. (matter, but very few students will know this)

2.

(a) false (b) false (c) false (d) true

3.

(a) less (b) faster (c) longer (d) shorter

4.

(a) longer (b) lower (c) slow the electron down

5. e

6. f

7.

(a) ($E= mc^2$, $E = hf$)

(b) (electrons), (electrons)

8. (6.63×10^{-35} m)

9. (1.2×10^{-35} m)

10. (22.0 m/s)

11. (250 kg)

Schrodinger's Wave Functions

Lesson Objectives

- Distinguish between traveling and standing waves.
- Explain why electrons form standing waves, and what this means in terms of their energies.
- Define an electron wave function and electron density and relate these terms to the probability of finding an electron at any point in space.

Introduction

In the last lesson, you learned that electrons and, in fact, all objects with mass, have wave-like properties. It might be tempting to visualize matter waves as being just like ocean waves, or waves in a puddle, but it turns out that matter waves are special. Unlike ocean waves or puddle waves, matter waves are 'trapped' in space and, as a result, can never die out, escape, or disappear. If you think carefully, you'll realize that this isn't true of most other waves with which you are familiar. You can form waves in a puddle by stirring the puddle with a stick. When you do, what you'll notice is that the waves you create actually move from your stick out to the edge of the puddle, where they disappear. As long as you disturb the puddle with your stick, the puddle will have waves in it. But as soon as you leave the puddle alone, the surface of the puddle will become as calm as glass. Matter waves aren't like that. Unlike puddle waves, which eventually die out as they escape from the puddle, matter waves never do, because matter waves *don't move.* As a result, they are *forever* trapped in the matter that holds them. We'll talk more about these special matter waves in the next section.

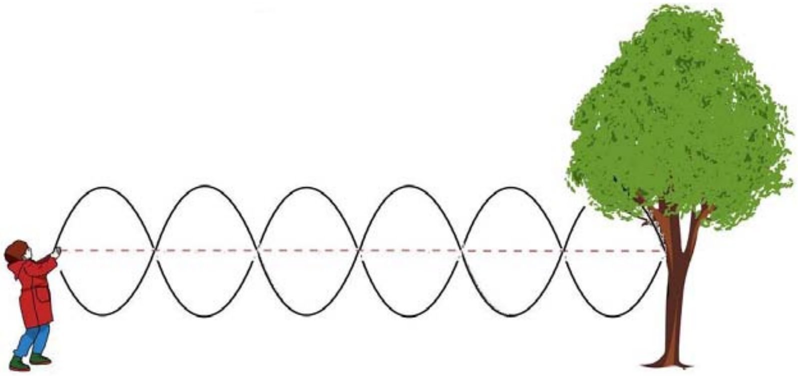
An Electron is Described as a Standing Wave

Most of the waves that you're probably familiar with are known as *traveling* waves, because they *travel* or *move.* When you're sitting on your surfboard, trying to catch a good wave, you'll often look out to sea in the hopes of spotting a 'big one'. When you finally do, you know that even though the big wave may be quite a distance off, it will eventually arrive at your surfboard and carry you in to shore. This, of course, implies that ocean waves are *traveling waves* because they actually *move* through the water. Similarly, if you're in the stands watching the Oakland A's play ball, you might find yourself jumping up and cheering as 'the wave' passes through the stadium. Again, this is an example of a *traveling* wave, because it *moves* from fans at one end of the stadium to fans at the other. There are, however, special waves that stay in one spot. Scientists call these waves *standing waves.*

Figure 1: When you're surfing, you wait for a good wave. Surfing is possible because ocean waves are traveling waves. In other words, ocean waves actually move through the water. (*Source:* http://en.wikipedia.org/wiki/Image:Surfer_above_the_wave.jpg, *License:* GNU-FDL)

Figure 2: Some fans getting ready for 'the wave' as it passes through the stadium. (*Source:* http://en.wikipedia.org/wiki/Image:Confed-Cup_2005_-_Laolawelle.jpg, *License:* GNU-FDL)

In an earlier part of this text, a wave was described in which a rope was tied to a tree and a person jerked the other end of the rope up and down to create a wave in the rope. When a wave travels down a rope and encounters an immoveable boundary (like a tree), the wave reflects off the boundary and travels back up the rope. This causes interference to occur between the wave traveling toward the tree and the reflected wave traveling back toward the person. If the person adjusts the rhythm of their hand just right, they can arrange for the crests and troughs of the wave moving toward the tree to exactly coincide with the crests and troughs of the reflected wave. When this occurs, the apparent horizontal motion of the wave ceases and the wave appears to "stand" in the same place in the rope. This is called a **standing wave**. In such a case, the crests and troughs will remain in the same places and nodes will appear between the crests and troughs where the rope does not appear to move at all.



In the standing wave shown above, the positions of the crests and troughs remain in the same positions. The crests and troughs appear to exchange places above and below the center line of the rope. The flat places where the rope crosses the center axis line are called **nodes** (positions of zero displacement). These nodal positions do not change.

Traveling waves appear to travel, and standing waves appear to stand still.

Even though standing waves don't move themselves, they are actually composed of traveling waves that *do.* Standing waves form when two traveling waves traveling in opposite directions at the same speed combine or run into each other. In today's lab, you'll learn how to create standing waves in a jump rope by feeding traveling waves into the jump rope from opposite directions. Even though a standing wave doesn't move, it can still 'die out'. As soon as the traveling waves that form a standing wave disappear, so does the standing wave itself. You'll see this first hand in the jump rope experiment. When you stop flicking the jump rope, the jump rope slackens and the standing waves are gone.

Why, then, are standing waves often associated with 'trapped' waves, or waves that never die out? The connection between standing waves and trapped waves isn't a misconception or a misunderstanding. It turns out that standing waves almost always form when traveling waves are 'trapped' in a small region of space. Imagine what would happen if you took a whole train of traveling waves, locked them up and threw them into jail. Those traveling waves would probably go crazy running around the jail cell trying to escape. No matter how hard they tried, though, they'd always end up hitting the jail cell walls. As a result, the poor waves would bounce back and forth and back and forth from one end of the jail cell to the other. Now, if there were several traveling waves trapped in the same jail cell at the same time, one set of waves would end up bouncing off of the left wall, at the same time (and speed) as another set of waves was bouncing off of the right wall. This, of course, is exactly what's required to set up a 'standing wave' (two waves traveling in opposite directions at the same speed).

The electron waves that you learned about in the last lesson form standing waves as a result of being trapped inside the atom. What do you think might imprison an electron wave inside an atom? The answer, of course, is that electrons are trapped because they are strongly attracted to the protons in the nucleus. Using the laws of physics to describe the forces of attraction between electrons and protons, scientists can figure out the size and shape of any electron's jail cell. Amazingly, by knowing the size and shape of an electron's jail cell, scientists can tell you what a particular electron standing wave will look like.

Frequently, rather than using words to describe an electron standing wave, scientists use what's known as an electron *wave function.* Wave functions for electrons, first developed by a man named Erwin Schrodinger, are mathematical expressions that describe the magnitude or 'height' of an electron standing wave at every point in space. Now, let's discuss electron energy, which is another important electron property that can be explained and predicted by electron standing waves and their associated wave functions.

Each Wave Function has an Allowed Energy Value

Electrons form standing waves whenever they're trapped inside an atom, and thus in order to understand and predict electron behavior, it's important to understand electron standing waves. One of the most important properties that electron standing waves can help to predict is electron energy. The energy of an electron in any atom depends on the size and shape of the electron's standing wave when it's trapped inside that atom. As a result, scientists can use the *wave function,* or the mathematical description of an electron's standing wave, to figure out how much energy that electron has.

While wave functions are helpful in predicting the amount of energy an electron *has,* they are also helpful in predicting the amount of energy an electron is *allowed* to have. In any confined space, like a box, a jail cell, or an atom, only certain standing waves are possible. Why? In order to exist, a standing wave must begin at one side of the box and end at the other. Waves that either don't begin where the box begins, or don't end where the box ends aren't allowed. Figure 5 shows several *allowed* standing waves and several *forbidden* standing waves. Notice that if the wave doesn't 'fit' perfectly inside the box, it isn't allowed.

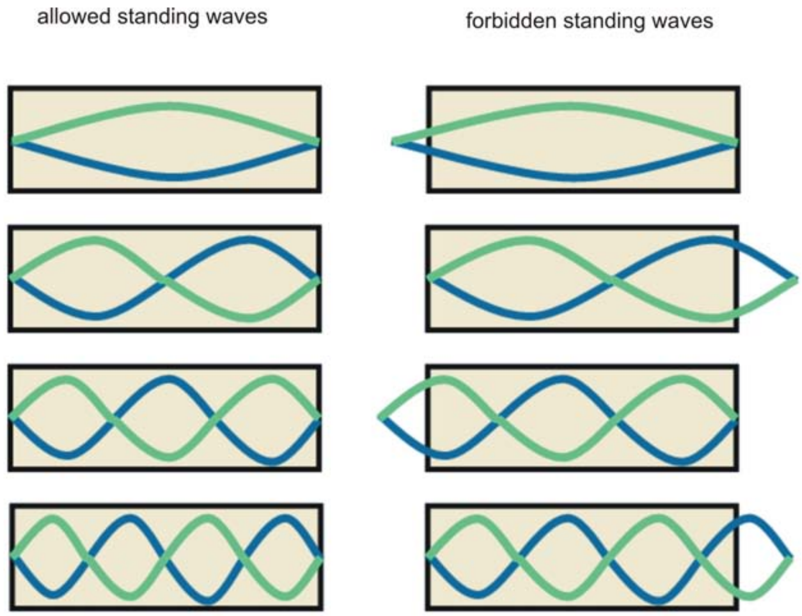
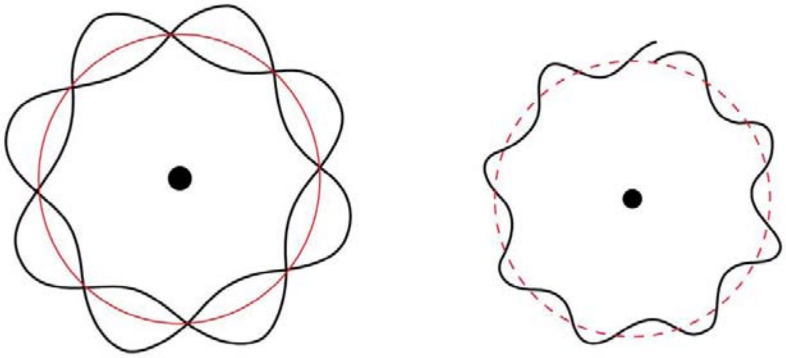


Figure 5: The standing waves on the left hand side of the figure are allowed to form in the brown box, because they fit perfectly inside the box. In contrast, the waves on the right hand side of the figure cannot form in the brown box because they do not fit perfectly inside the box.

Now here's the really strange thing about describing electrons as standing waves. Since only certain standing waves will fit perfectly inside an atom, electrons trapped in that atom can only have certain electron wave functions with certain electron energies. In other words, the standing wave picture accounts for the fact that some energy values are '*allowed*' (energy values associated with standing waves that 'fit' perfectly inside the atom) while others are '*forbidden*' energy values (energy values associated with standing waves that do not 'fit' perfectly inside the atom). That's *exactly* what Bohr said when he developed his model to explain atomic spectra! Bohr said that electrons could exist at specific '*allowed*' energy levels, but that they couldn't exist *between* those energy levels. Bohr, however, did not have an explanation for why only certain energy levels were allowed. Remarkably, the standing wave description of electrons predicts *quantized* electron energies just like the Bohr model!

When we represent electrons inside an atom, quantum mechanics requires that the wave must "fit" inside the atom so that the wave meets itself with no overlap; that is, the "electron wave" inside the atom must be a standing wave. If the wave is to be arranged in the form of a circle so that it attaches to itself, the waves can only occur if there is a whole number of waves in the circle.



The standing wave on the left in the sketch above exactly fits in the electron cloud and hence represents an "allowed" energy level whereas the standing wave on the right does not fit in the electron cloud and therefore is not an "allowed" energy level. There are only certain energies (frequencies) for which the wavelength fits exactly to form a standing wave. These are the same energy levels the Bohr model suggested but NOW there is a reason for why electrons may have ONLY these energies.

Max Born and Probability Patterns

There are very few scientists, if any, who can visualize the behavior of an electron during chemical bonding or chemical reactions as standing waves. When chemists are asked to describe the behavior of an electron during a chemical change, they do not describe the mathematical equations of quantum mechanics nor do they discuss standing waves. The behavior of electrons in chemical reactions is best understood in terms of a particle.

Erwin Schrodinger's wave equation for matter waves is similar to known equations for other wave motions in nature. The equation describes how a wave associated with an electron varies in space as the electron moves under various forces. Schrodinger worked out the solutions of his equation for the hydrogen atom and the results agreed with the Bohr values for the energy levels of these atoms. Furthermore, the equation could be applied to more complicated atoms. It was found that Schrodinger's equation gave a correct description of an electron's behavior in almost all cases. In spite of the overwhelming success of the wave equation in describing electron energies, the very meaning of the waves was vague.

A physicist named Max Born was able to attach some physical significance to the mathematics of quantum mechanics. Born used data from Schrodinger's equation to show the probability of finding the electron, as a particle, at the point in space for which Schrodinger's equation was solved. Born's ideas allowed chemists to visualize the results of the wave equation as probability patterns for electron positions.

Suppose we had a camera with such a fast shutter speed that it could take a photo of an electron in an electron cloud and show it frozen in position. We could then take a thousand pictures of this electron at different times and find it in many different positions in the atom. We could then plot all the different electron positions on one picture.

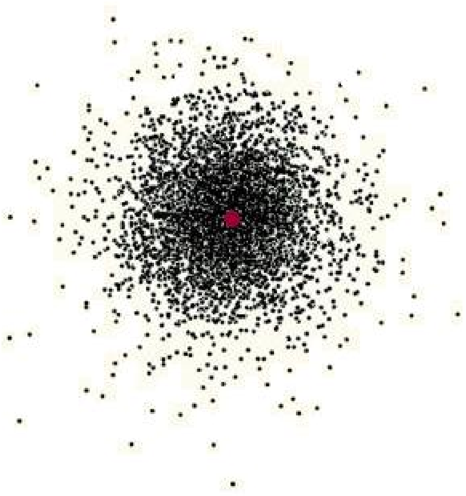


Figure 7: The probability pattern for a single electron atom.

(*Created by:* Richard Parsons, *License:* CC-BY-SA)

The sketch above shows the result of plotting many different positions of a single electron in the electron cloud of a hydrogen atom. One way of looking at this picture is as an indication of the probability of where you are likely to find the electron in this atom. You must recognize, of course, that the dots are not electrons; this atom has only one electron. The dots are positions where the electron can be found at different times. From this picture, it is clear that the electron spends more time near the nucleus than it does far away. As you move away from the nucleus, the probability of finding the electron becomes less and less. It is also important to note that there is no boundary for this electron cloud. That is, there is no distance from the nucleus where the probability becomes zero.

For much of the work we will be doing with atoms, it is convenient to have a boundary for the atom. Most often, chemists choose some distance from the nucleus beyond which the probability of finding the electron becomes very low and arbitrarily draw in a boundary for the atom. Frequently, the boundary is placed such that 90% or 95% of the probability for finding the electron is inside the boundary.

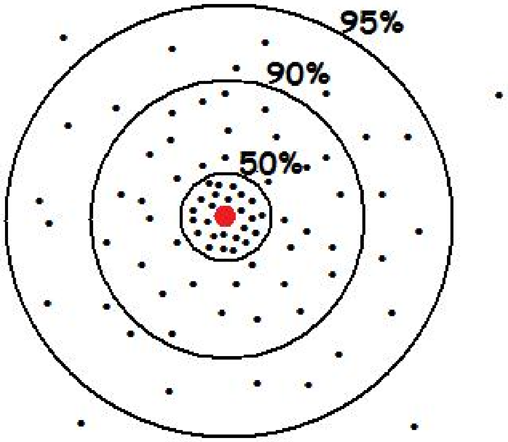


Figure 8: Artificial boundaries for an atom.

(*Created by:* Richard Parsons, *License:* CC-BY-SA)

Most of the time, we will be looking at drawings of atoms that show an outside boundary for the electron cloud. You should keep in mind, however, that the boundary is there for our convenience and there is no actual boundary on an atom; that is, the probability of finding the electron never becomes zero. This probability plot is very simple because it is for the first electron in an atom. As the atoms become more complicated (more energy levels and more electrons), the probability plots also become more complicated.

Lesson Summary

- There are two types of waves – traveling waves that move from one place to another, and standing waves that are stationary. Standing waves are formed when two traveling waves traveling in opposite directions at the same speed combine. Electrons in atoms form standing waves because they are trapped by the attractive forces that exist between their negative charges and the positive charges on the protons in the atom's nucleus. These attractive forces determine the shape and size of the electron's standing wave.
- Mathematical expressions called wave functions are used to describe an electrons standing wave in an atom. The energy of an electron in any atom depends on the size and shape of the electron's standing wave. The wave function can be used to determine the energy of an electron when it is trapped inside an atom.
- Electrons in atoms are only allowed to have certain energy levels (ie – those which correspond to standing waves that 'fit perfectly' inside the atom). All other electron energies are forbidden. The probability patterns for electrons (electron density) show the probability of finding the electron at a given point.

Review Questions

1. Choose the correct word in each of the following statements. **(Intermediate)**

a. The (*more/less*) electron density at a given location within the atom the more likely you are to find the electron there.

b. If there is no electron density at a particular point in space, there is (*no/a high*) chance of finding the electron there.

c. The higher the probability of finding an electron in a certain spot, the (*more/less*) electron density there will be at that spot.

2. The hydrogen ion, H^+ has no electrons. What is the total amount of electron density in a hydrogen atom? **(Intermediate)**

3. Decide whether each of the following statements is true or false. **(Intermediate)**

a. Only certain electron standing waves are allowed in any particular atom.

b. Only certain electron energies are allowed in any particular atom

4. The name for the mathematical expression used to describe an electron standing wave is ________. **(Intermediate)**

5. Choose the correct statement. **(Intermediate)**

a. Einstein first developed the method of describing electron standing waves with wave functions

b. Planck first developed the method of describing electron standing waves with wave functions

c. de Broglie first developed the method of describing electron standing waves with wave functions

d. Schrodinger first developed the method of describing electron standing waves with wave functions

6. Circle all of the statements below which are correct. **(Intermediate)**

a. The wave function description of electrons predicts that electrons orbit the nucleus just like planets orbit the sun.

b. The wave function description of electrons predicts that electron energies are quantized

c. The Bohr model of the atom suggests that electron energies are quantized.

7. Fill in the blanks. **(Intermediate)**

a. Since only certain values are allowed for the energy of an electron in an atom, we say that electron energies are _________.

b. Allowed electron energies correspond to ______________ that fit perfectly in the atom.

13. Forbidden electron energies correspond to electron standing waves that ________ in the atom. **(Intermediate)**

Further Reading / Supplemental Links

http://www.chemistry.ohio-state.edu/betha/qm

http://en.wikipedia.org/wiki/Many-worlds_interpretation

http://plato.stanford.edu/entries/qm-manyworlds

http://frombob.to/many.html

http://en.wikipedia.org

Vocabulary

traveling waves	Waves that travel, or move.
standing waves	Waves that do *not* travel, or move. They are formed when two traveling waves, moving in opposite directions at the same speed run into each other and combine.
electron wave function	A mathematical expression to describe the magnitude, or 'height' of an electron standing wave at every point in space.
electron density	The square of the wave function for the electron, it is related to the probability of finding an electron at a particular point in space.

Review Answers

1. (a) more (b) no (c) more

2. (there is no electron density in a hydrogen ion)

3. (a) true (b) true

4. (a wave function)

5. d

6. b, c

7.

(a) (quantized)

(b) (electron standing waves)

13. (do not fit perfectly)

Heisenberg's Contribution

Lesson Objectives

- Define the Heisenberg Uncertainty Principle.
- Explain what the Heisenberg Uncertainty Principle means in terms of the position and momentum of an electron.
- Explain why the Heisenberg Uncertainty Principle helps to justify the fact that a wave function can only predict the probable location of an electron and not its exact location.

Introduction

If you think back to the last lesson, you'll remember that scientists had a lot of difficulty understanding electron density and the wave function in terms of the wave properties and the particle properties of the electron. Max Born found a way to use the electron wave function to calculate electron density, and that electron density is actually equal to the *probability* of finding an electron at any point in space. This, however, leads to the question, why can't scientists predict where the electron will be with *certainty.* Why can they only predict the *probability* of finding an electron at any given point in space? Is there something wrong with the theory? Is it possible to improve the theory so that scientists *can* predict exactly where an electron is and where it's going?

Heisenberg Proposed the Uncertainty Principle for Behavior of Electrons

The Uncertainty Principle

When scientists first suggested that the wave function was related to the *probability* of an electron being at a specific point in space, it raised a lot of questions. Most importantly, scientists wondered why the wave function could *only* predict the *probability* of finding an electron at a given location, and not the *exact* location where the electron actually was. Some scientists suggested that the wave function couldn't make exact predictions because it wasn't complete. They believed that the wave function was actually missing information that was necessary to describe electron behavior with 'certainty'. Some early scientists thought that perhaps the wave function could only predict the probability of an electron being at a given location because the wave function was missing information. Many scientists spent time looking for 'hidden variables' that controlled electron behavior just like the spin controls the movement of a baseball. The assumption was that if the correct 'hidden variables' could be found and included in the wave function, then the exact movement, and the exact location of an electron could be predicted, just as easily as we can predict the movement of larger objects like baseballs, cars and planets. Everything changed, however, in 1926 when a man named Werner Heisenberg proposed what's known as the **Heisenberg Uncertainty Principle.** According to the Heisenberg Uncertainty Principle, it is impossible to measure certain properties, like momentum (speed multiplied by mass) and position at the same time without introducing uncertainty into the measurement. Of course, if you can't make accurate measurements, you can't make accurate prediction either.

Figure 2: Werner Heisenberg (*Source:* http://en.wikipedia.org/wiki/Image:Werner_Heisenberg.jpg, *License:* Public Domain)

What prevents scientists from making accurate predictions about small objects like atoms and electrons? Is it that the machinery used to make the measurements is simply not good enough? Could scientists design better machines and better measurements and *then* be able to predict electron behavior with certainty? According to Werner Heisenberg, the answer is 'no – when it comes to small objects, scientists will *never* be able to make accurate measurements and accurate predictions, no matter how good their machinery is'. If you find that statement strange, you're not alone. Many scientists, even today, are bothered by the Heisenberg Uncertainty Principle – it seems as if, with improved machines, we should be able to make better measurements and thus better predictions! To some extent, that's true. Better machines can help us to make better measurements and better predictions, but according to the Heisenberg Uncertainty Principle, there is a fundamental limit to how much we can know and how accurately we can know it. It's as if there is 'something' in the universe which prevents us from being able to make absolutely, one hundred percent accurate measurements and, as a result, we will always be plagued by some uncertainty. For large objects, like baseballs and planets, the uncertainty is just too small to matter, but for tiny things, like atoms and electrons, the uncertainty becomes important.

Impossible to Fix Both the Position of an Electron and Its Momentum

The Heisenberg Uncertainty Principle actually applies to a lot of different measurements, but often, scientists are concerned with two in particular – position and momentum. You probably know what position means, but momentum is a term that you don't hear a lot in everyday life. Momentum, p, is the quantity that you get when you multiply an object's mass by its speed (to be truly correct momentum is actually mass times velocity, but as in Chapter 1, we won't worry about the difference between speed and velocity).

In terms of the position and momentum, the Heisenberg Uncertainty Principle is as follows:

There is a fundamental limit to just how precisely we can measure both the position and the momentum of a particle at the same time.

So how does the Heisenberg Uncertainty Principle relate to the electron and all the problems scientists have interpreting the electron wave function? Well, if you think about it logically, the Heisenberg Uncertainty Principle basically means that it's impossible to predict **both** exactly what the electron will do or exactly where the electron will be found. Suppose, for instance, that you know the electron's precise position, then according to the Heisenberg Uncertainty Principle, you can't know its precise momentum as well. In other words, **when you know where the electron is, you don't know where it's going** (since where it's going is determined by the velocity component of its moment). Suppose, on the other hand, that you know the electron's precise momentum. According to the Heisenberg Uncertainty Principle, you can't know its precise position as well. In other words, **when you know where the electron is going, you don't know where it is.**

Obviously, there is always some uncertainty when it comes to electrons. You either don't know where they are, or else you don't know where they're going. As a result, any theory that claimed to predict exactly *where* the electron was, or exactly which path it would take as it traveled around inside the atom would go against the Heisenberg Uncertainty Principle. Luckily, the wave function description *doesn't* claim to predict the precise behavior of the electron. Instead, it only makes statements about the probability of finding the electron at one place or another.

In other words, the wave function model is consistent with the Heisenberg Uncertainty Principle. Moreover, the Heisenberg Uncertainty Principle suggests that the electron wave function equation is as complete as it can possibly be. It may not entirely predict electron behavior, but that isn't because the model is wrong, or faulty. It's because, in our universe, there is a limit to how accurately we can actually *know* what tiny objects like electrons are doing.

The Problem of Making Very Small Measurements

When you use a thermometer to measure the temperature of a volume of water, you place the thermometer into the water and leave it there until the water and the thermometer have adjusted to the same temperature. Almost all solids and liquids expand when they are heated and contract when they are cooled. Each substance, however, expands and contracts by different amounts. In the case of the mercury and glass in a thermometer, the mercury expands and contracts faster than the glass and so as a thermometer is heated, the mercury expands faster that the glass tube and the mercury runs up the tube. The glass has been marked (calibrated) for each temperature so that you can read the correct temperature from the markings on the tube. In the process of measuring the temperature of hot water, the thermometer is placed in the water and the thermometer **absorbs** heat from the water so that its temperature becomes the same as the water and you can read the temperature of the water from the temperature of the thermometer.

You should see, at least theoretically, that when the thermometer absorbs heat from the water, the water is cooled down; that is, the temperature of the water decreases because of the heat lost to the thermometer. Therefore, the temperature you get when you measure the temperature is not the same temperature of the water that was present before you introduced the thermometer. **The act of measuring the temperature of the water changed the temperature.** When the volume of the water is reasonably large, the magnitude of the change caused by introducing the thermometer is not significant so we don't bother to consider it. What about if the volume of the water is very small? If the volume of water is 200 mL and the thermometer absorbs 20 Joules of heat, the introduction of the thermometer might change the temperature of the water by approximately 0.03^{o}C. Which is certainly not a significant change. But what if the volume of water whose temperature we were measuring was only 2 mL? Introducing the same thermometer into this small volume might change the temperature of the water 3^{o}C, which would certainly be a significant change. The point is that when we measure very small things, the act of making the measurement may change what we are observing.

Consider the method that humans use to see objects. We arrange for photons (quanta) of light to strike the object and we see the object by the directions, angles, and colors of the photons that bounce off the object and strike us in the eye or other light measuring instrument. If only red photons bounce back, we say the object is red. If no photons bounce back, we say there is no object present. Suppose for a moment that humans were gigantic stone creatures and we used golf balls to "see" with. That is, we would fire off golf balls at our surroundings and the balls would bounce off objects and come back and enter our eyes so we could see the object. If this were true, we could see mountains successfully and large buildings and trees . . . but could we see butterflies or small flowers? Obviously, the answer is no. The golf balls would simply knock small objects out of the way and continue on . . . they would not bounce back to our eyes.

In the case of humans trying to look at electrons, the photons we use to see them with are of significant energy compared to electrons and when the photons collide with the electrons, the motion and/or position of the electron would be changed by the collision. Heisenberg's Uncertainty principle tells us we cannot be sure of both the location of the electron and the motion (path) of an electron at the same time. As a consequence, **scientists had to give up the idea of knowing the path the electron follows inside an atom**.

Lesson Summary

- The Heisenberg Uncertainty Principle states that it is impossible to measure certain pairs of properties like momentum (mass multiplied by velocity) and position at the same time without introducing uncertainty into one or both of the measurements. In other words, it is *impossible* to know both the exact momentum and the exact position of a particle at the same time.
- The Heisenberg Uncertainty Principle suggests that the electron wave function is complete and that it does not predict the exact behavior of an electron because it is actually impossible to do so.
- The uncertainty that Heisenberg spoke of is not due to the failure or inadequacies of the measuring equipment, but rather a fundamental limit imposed by our universe.

Review Questions

1. What types of things in everyday life are impossible to predict with absolute certainty? **(Intermediate)**

2. Why is it impossible to predict the future with absolute certainty? **(Intermediate)**

3. Fill in the blank.

According to the _________ Uncertainty Principle, it is impossible to know both an electron’s _________ and momentum at the same time. **(Beginning)**

4. Decide whether each of the following statements is true or false:

a. According to the Heisenberg Uncertainty Principle, we will eventually be able to measure both an electron’s exact position and its exact location at the same time.

b. The problem that we have when we try to measure an electron’s position and its location at the same time is that our measuring equipment is not as good as it could be.

c. According to the Heisenberg Uncertainty Principle, we cannot know both the exact position and the exact location of a car at the same time. **(Challenging)**

5. Circle the correct statement

The Heisenberg Uncertainty Principle… **(Beginning)**

a. applies only to very small objects like protons and electrons

b. applies only to very big objects like cars and airplanes

c. applies to both very small objects like protons and electrons and very big objects like cars and airplanes

Further Reading / Supplemental Links

http://zebu.uoregon.edu/~imamura/208/jan27/hup.html

http://www.aip.org/history/heisenberg/p08.htm

http://scienceworld.wolfram.com/physics/UncertaintyPrinciple.html

http://plato.stanford.edu/entries/qt-uncertainty

http://en.wikipedia.org/wiki

Vocabulary

momentum (p)	The quantity you get when you multiply an object's mass by it’s velocity (which as far as you’re concerned is the same as its speed).
Heisenberg’s Uncertainty Principle	Specific pairs of properties, such as momentum and position, are impossible to measure simultaneously without introducing some uncertainty.

Review Answers

1. (whether or not it will rain, what cards you’ll get when you’re dealt a hand in a game of poker, whether or not you’ll pass your next chemistry test… actually, practically everything!)

2. (We don’t have enough information, there are too many variables to consider, certain processes in the natural world are inherently random, etc.)

3. (Heisenberg), (position or location)

4.

(a) false

(b) false

(c) true

5. c (Although the Heisenberg Uncertainty Principle applies to objects of all sizes, it is more important for small objects, because the uncertainty is too small to matter for bigger objects.)

Quantum Numbers

Lesson objectives

- Explain the meaning of the principal quantum number, n.
- Explain the meaning of the azimuthal quantum number, ℓ .

- Explain the meaning of the magnetic quantum number, m_l.

Introduction

We've spent a lot of Chapter 6 talking about waves, and electron waves in particular. While most of us know what normal water waves look like, very few people have an understanding of what electron waves look like. In the last lesson, we talked about electron density, and how an electron wave could be thought of as representing the thickness or thinness of the electron density 'fog' at any point in space within the atom. We considered the probability pattern for the electron in a hydrogen atom. Now let's consider some more complicated atoms.

Schrodinger's Equation Provides Three Integers Used to Define the Energy States and Orbital for an Electron

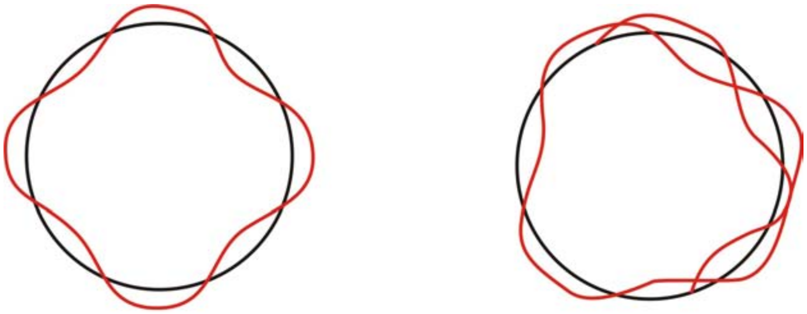
You should remember that electrons form standing waves whenever they are trapped within an atom. You should also remember that only certain standing waves are allowed in any confined space because only certain standing waves can fit perfectly inside that space (remember, a perfect fit requires that a wave begin and end where its box begins and ends). In a one-dimensional box, it's easy to picture all of the possible waves that fit perfectly inside. In three dimensions, it's a little harder. Unfortunately when it comes to electrons in an atom, there's an additional complication *on top* of the fact that electron waves are three-dimensional! It turns out that the electrons in an atom aren't confined to nice square or rectangular boxes. Instead, they're confined to spherical boxes (which should make sense, since atoms are, after all, tiny little spheres). In other words, electron waves inside an atom must begin and end on the surface of a sphere. You may have a really good imagination, and an amazing ability to picture objects in three-dimensions, but for most people, trying to figure out what these spherical three-dimensional waves look like can be quite a challenge.

Luckily, that's how electron wave functions can help. Electron wave functions basically describe the possible shapes that electron waves can take. We won't actually worry about the wave functions. Instead, we'll only worry about specific numbers, called *quantum numbers.* Quantum numbers are always part of an electron wave function and are extremely important when it comes to determining the shape of a probability pattern.

When electron wave functions were first developed by a man named Erwin Schrodinger, his goal was to show how a wave-like description of the electron could be used to understand the behavior of an electron in a hydrogen atom. In order to do this, Schrodinger first defined the size and spherical shape of the hydrogen atom itself. Schrodinger then assumed an electron trapped within a hydrogen atom formed a standing wave that fit perfectly inside without 'spilling out' or 'doubling over' on itself (it turns out that in circular or spherical boxes, misfit waves don't 'spill out' so much as they 'double over', as shown in Figure 2). Finally, Schrodinger supposed that an electron wave had to be continuous (remember, something that is continuous has no gaps, holes or jumps).

Figure 1: A photograph of Erwin Schrodinger

(*Source:* http://en.wikipedia.org/wiki/Image:Erwin_Schr%C3%B6dinger.jpg, *License:* Public Domain)



This wave fits perfectly on the circle

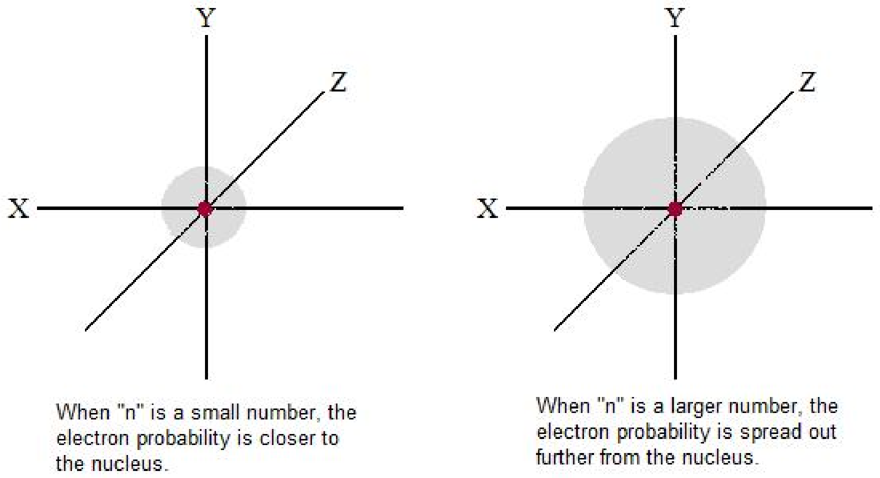
This wave, however, doubles over on itself

Figure 2: When waves fit perfectly on a circle (or a sphere) they meet up with themselves and form a closed loop. When waves *don't* fit perfectly on a circle, though, they end up 'doubling over' on themselves.

Amazingly, what Schrodinger discovered was that in order to satisfy his basic assumptions about the electron wave both fitting inside the atom and being continuous, certain quantities in the electron wave function had to be 'whole number integers'. Whenever Schrodinger assigned a whole number to these quantities, he ended up with a wave that fit perfectly inside the hydrogen atom. However, whenever he assigned a decimal number to these quantities, he ended up with a wave function that either 'doubled over' on itself, or was discontinuous! The quantities that had to be assigned whole numbers soon became known as *quantum numbers.* In the wave function for a hydrogen electron **there** are always three quantum numbers. The first quantum number, n , is called the principal quantum number, the second quantum number, ℓ , is called the azimuthal quantum number, and the third quantum number, m_l , is called the magnetic quantum number. Together these three quantum numbers define the energy state and orbital of an electron, but we'll talk more about exactly what that means in the next section.

n = Principal Quantum Number (Energy Level)

The first quantum number, known as the principal quantum number, is given the symbol n. In order to describe a valid standing wave, n has to have integer values, but there's an additional restriction on n as well. The value of n must be a *positive* integer value (***n*** = 1, 2, 3,...). In other words, ***n*** can never equal a negative integer. In fact, ***n*** can never even equal 0! The principal quantum number gives you two different clues as to what an electron wave looks like. First, it tells you how the electron density spreads out as you move away from the center of the atom. For electron waves with low principal numbers, like ***n*** = 1, the electron density is very thick right in close to the center of the atom, but then becomes rapidly thinner as you move out. In contrast, for electron waves with high principal quantum numbers, like ***n*** = 6, the electron density isn't as thick near the center of the atom, but is spread quite a bit further out. In general, the higher the principal quantum number, the further away from the nucleus you'll be able to detect a significant amount of electron density.



When "n" is a small number, the electron probability is closer to the nucleus.

When "n" is a larger number, the electron probability is spread out further from the nucleus.

Figure 3: When the principal quantum number, ***n*** , is small, most of the electron density is found close to the nucleus of the atom. When the principal quantum number is large, though, the electron density spreads further out.

(*Source: Created by:* Richard Parsons, *License:* CC-BY-SA)

Sometimes, you will hear people say that the principal quantum number determines the 'size' of the electron wave function. When people say this, they don't actually mean the absolute or total 'size' of the electron wave. What they mean is how big or small the electron wave *appears* to be based on where most (usually about 90%) of the electron density is concentrated. In an electron wave with a low principal quantum number, the electron density is mostly found close to the center of the atom. Even though there is a tiny bit of electron density at distances far away from the atom's nucleus, there's so little that you can't really tell it's there. As a result, electron waves with low principal quantum numbers appear small. On the other hand, in an electron waves with a high principal quantum number, the electron density is much more spread out, and thus much thicker at distances far from the center of the atom. Therefore, electron waves with high principal quantum numbers appear big.

The principal quantum number also describes the total number of *nodes* that the electron wave contains. What are nodes? Nodes are places where the electron wave has absolutely no amplitude, or 'height'. Take a look at the one-dimensional waves in Figure 4 a. Can you spot the nodes? Now take a look at the two-dimensional waves in Figure 4 b. Can you spot the nodes? A three-dimensional wave with nodes is something like an onion. Think of how the onion has layers and how in between the different layers there's always an empty space or a break. If the onion was a three-dimensional wave, the breaks in between the onion layers would be like the nodes. The higher the principal quantum number, ***n*** , the more nodes an electron wave has.

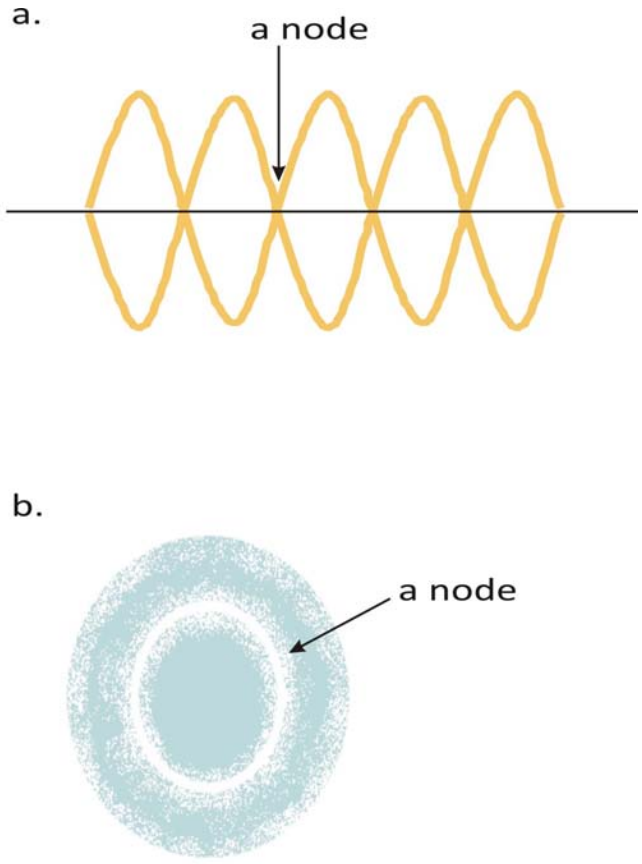


Figure 4: A node is any place where a wave has zero amplitude, or zero height. Both a. and b. illustrate different ways of representing waves. In a. the amplitude corresponds to the height of the yellow line above (or below) the black axis. When the yellow wave crosses the black axis, the wave has zero amplitude and thus a node. In b., the amplitude of the wave corresponds to the thickness of the blue cloud. When there is no blue cloud, the wave has zero amplitude and thus a node.

The principal quantum number is extremely important, not only because it tells you something about the ‘size’ of an electron wave and the number of nodes in an electron wave, but also because it tells you something about the energy of that wave. If you think back to Chapter 4, you’ll remember that negative electrons like to be close to the positive nucleus because the energy of an electron is lower the closer it is to a positive charge. What does that mean in terms of the principal quantum number? It means that an electron wave with a **lower principal quantum number**, and electron density centered **close** to the **nucleus** of the atom, will have a **lower energy**, while an electron wave with a **higher principal quantum number**, and electron density spread **further away** from the nucleus of the atom, will have a **higher energy**.

Similarly, as the number of nodes in an electron wave increases, the energy of the wave increases as well. Think about the jump rope experiment. Do you remember how you created standing waves in a jump rope? Did it take more or less energy on your part to get multiple waves to form along the rope? It should have taken you more energy to create more waves. That’s because in the process of creating more waves, you also created more nodes and nodes are always associated with an increase in energy. Again, let’s take a look at what his means in terms of the principal quantum number. An electron wave with a **lower principal quantum number** has **fewer nodes,** and thus will also have a **lower energy**. On the other hand, an electron wave with a **higher principal quantum number** has **more nodes** and thus will have a **higher energy**.

Notice that as n increases, both the ‘size’ of the electron wave and the number of nodes it has increase as well. As a result, the energy of an electron wave *always* increases with n .

1. The bigger value of the n , the higher the energy.

2. The smaller the value of n, the lower the energy.

Since the principal quantum number determines the energy of a particular electron wave, n is often thought of as referring to the 'energy level' of the electron. The term 'energy level' actually comes from Bohr's old solar system model of the atom. Thanks to Schrodinger, and his wave equation, though, we now know that the energy level doesn't correspond to a particular orbit around the nucleus, but rather, to a particular electron wave adopted by the electron when it becomes trapped inside the atom.

ℓ

= Angular Momentum Quantum Number (Sub-levels, s, p, d, f)

The second quantum number, known as the azimuthal quantum number, is given the symbol ℓ . While the principal quantum number told you about the 'size' of an electron wave and the number of nodes in an electron wave, the azimuthal quantum number tells you more about the 'shape' of an electron wave. In other words, the shape that the electron wave appears to have as a result of its electron density being 'thicker' in one place than it is in another. You might be tempted to think that the shape of an electron wave is always spherical because the atom itself is spherical. It turns out, however, that while there are spherical electron waves, there are *also* waves that look like dumb-bells and waves that look like butterflies, and waves that look so crazy it's almost impossible to describe them! Some of the different possible shapes for electron waves are shown in Figure 5.

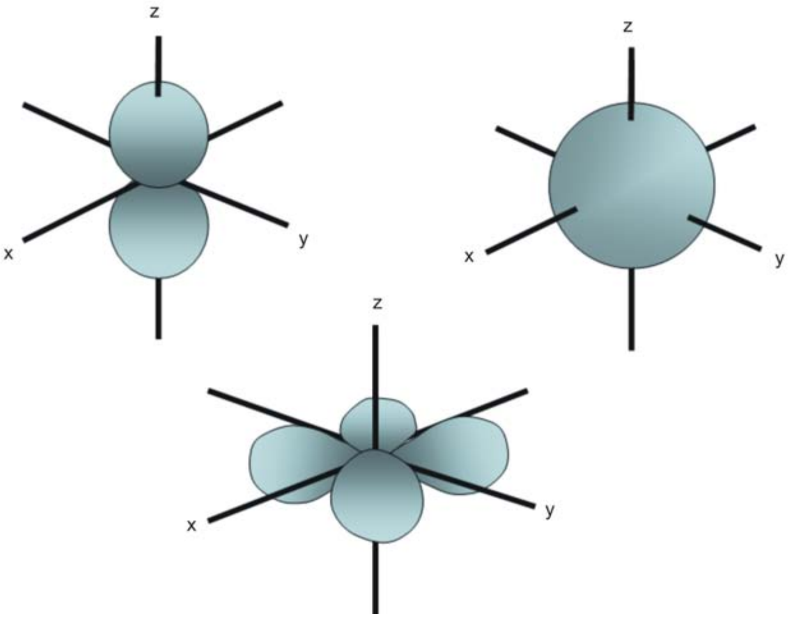


Figure 5: Several examples of the different possible shapes for an electron wave.

You might wonder about the various balloon-like shapes in Figure 5. One difficulty with using drawings to represent electron waves is that the electron density itself is actually spread over a *huge* region of space surrounding the center of the atom. As you learned earlier, though, for many electron waves, almost *all* of the electron density is in close to the nucleus of the atom, with only a tiny bit of electron density further out. Over the years, scientists have developed a standard way of drawing electron waves. Rather than trying to account for *all* of the electron density in an electron wave, scientists usually just draw 'balloons' around the region of space that contains about 90% of the electron wave's total electron density. Figure 6 shows how scientists convert a cloud of electron density into a balloon. Even though there is a little bit of electron density outside of the cartoon balloons (and thus a small probability of finding the electron outside of its balloon), most electron behavior can be understood by ignoring the tiny bit of electron density that the cartoon balloon doesn't capture.

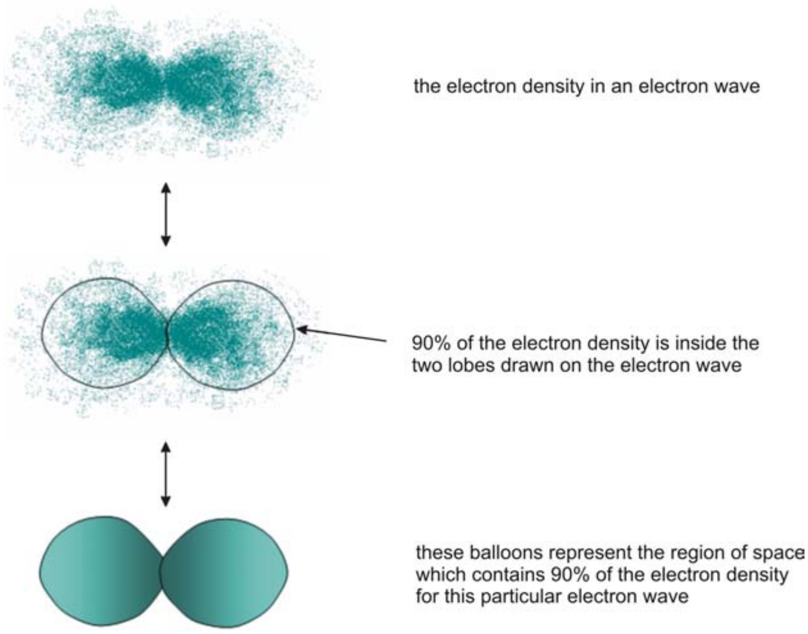


Figure 6: How scientists convert the electron density from an electron wave into cartoon 'balloons.'

The exact shape of the cartoon balloon representing an electron wave is determined by the value of ℓ. In other words, the dumb-bell shaped balloon in Figure 5 has one value of ℓ, while the butterfly-shaped balloon in Figure 5 has another value of ℓ. Of course, scientists would get pretty tired of saying things like 'the dumb-bell shaped wave,' or 'the butterfly shaped wave,' so instead, they name the different waves using letters from the alphabet. The most common shapes for waves are called s, p, d and f. (You would probably find it a lot easier to remember what the different waves looked like if scientists had given them nice descriptive names, like the 'dumb-bell wave' or the 'butterfly wave,' but boring names like s, p, d and f turn out to be much more convenient).

In the next lesson, we'll take a closer look at exactly what some of the common wave shapes look like. First, though, we have to consider the relationship between n and ℓ. Remember that a wave function for an electron always has *three* quantum numbers. In order to fully describe an electron wave, then, you have to know the values of *all three* of these numbers (n, ℓ and m_l). Now you might think that as long as n, ℓ and m_l are all integers, the wave that they describe will be a perfectly good electron wave. But that's NOT the way it works. It turns out that for a particular value of n, only certain values of ℓ are allowed.

Warning! For a particular value of n, only certain values of ℓ are allowed.

For wave functions that actually describe electrons in an atom, ℓ is always no less than 0, but also no more than n-1 (ℓ = 0, 1, 2,... n-1). The following examples should help to clarify the restriction on ℓ.

Example 1:

What are the allowable values of ℓ for an electron wave with $n = 3$?

$n = 3$

1. Find the minimum value of ℓ.

*The minimum value of ℓ is **always** 0.*

2. Find the maximum value of ℓ .

The maximum value of ℓ *is always n – 1*

maximum $\ell = n - 1$

maximum $\ell = 3 - 1$

maximum $\ell = 2$

3. List *all* of the integers (no decimals!) starting from the minimum value of ℓ and ending with the maximum value of ℓ .

$\ell = 0, 1, 2$

Example 2:

What are the allowable values of ℓ for an electron wave with n = 1

n = 1

1. Find the minimum value of ℓ .

The minimum value of ℓ *is* ***always*** *0*.

2. Find the maximum value of ℓ .

The maximum value of ℓ *is always 1 – 1*

maximum $\ell = 1 - 1$

maximum $\ell = 0$

3. List *all* of the integers (no decimals!) starting from the minimum value of ℓ and ending with the maximum value of ℓ .

$\ell = 0$

Often, scientists will refer the different values of ℓ as *electron sublevels*. In a hydrogen atom with one electron, the value of ℓ has *no* effect on the energy of the electron. However, in an atom with *more* than one electron, the value of ℓ does have a *small* effect on the electron's energy. In other words, the principle quantum number, n , always determines the overall energy level of an electron, but that energy level is actually divided into multiple sublevels based on the value of ℓ . All of these sublevels have equal energy in a hydrogen atom, because the hydrogen atom only has one electron. For atoms with more than one electron, though, the different sublevels split apart, and some of them end up having more energy than others.

m_l = Magnetic Quantum Number (Identifies Orbital)

The third, and final quantum number, known as the magnetic quantum number, is given the symbol m_l . Remember, the principal quantum number told you about the 'size' of an electron wave and the number of nodes in an electron wave, while the azimuthal quantum number told you more about the 'shape' of an electron wave. The magnetic quantum number, though, gives you even more information about what the electron wave looks like. The magnetic quantum number tells you how the electron wave is orientated in space.

Orientation in space basically means *where* the electron wave *points*. Take a look at the two dumb-bell shaped electron waves shown in Figure 8 (in the next lesson, you'll learn that these are actually 'p' orbitals). In the first electron wave, lobes of the wave point 'up-and-down' along the z-axis, while in the second electron wave, the lobes of the wave point 'in-and-out' along the x-axis. These two electron waves have different orientations in space, and thus different values for the quantum number m_l .

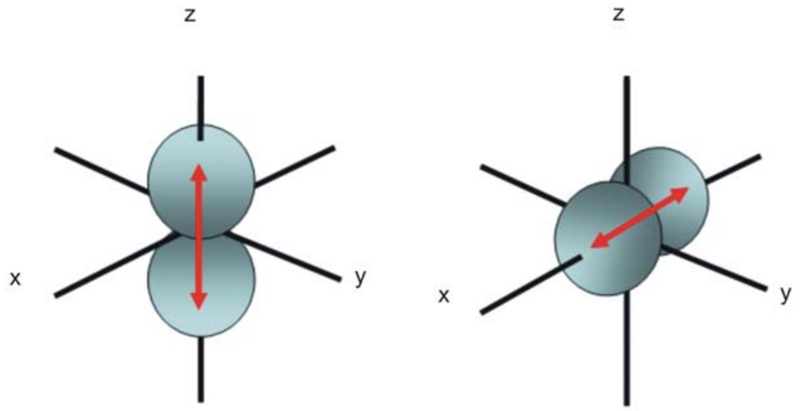


Figure 8: Two possible orientations for an electron wave with a dumb-bell shape.

Now compare Figure 8 with Figure 9. In both figures, the electron wave has a different orientation in space, as indicated by the red arrow. But what do you notice about the orientations of the electron wave in Figure 9? They look the same, don't they? Obviously, orientation *doesn't matter* for the spherical electron wave. In other words, because the spherical electron wave looks the same no matter how you rotate it, there's really just *one* orientation. So how many different m_l values should an electron wave with a spherical shape have (remember, m_l values are used to describe orientation)? Clearly, an electron wave with a spherical shape should only have one m_l value, because it only has *one* possible orientation. What about an orbital with a dumb-bell shape? Should it have a single m_l value, or should it have several different m_l values? Well, since different orientations of the dumb-bell shaped wave actually *look* different, you'd probably expect the dumb-bell shaped wave to have several different m_l values, one for each possible orientation. In fact, the dumb-bell shaped wave actually has three possible values for m_l , and so it has three possible orientations. (Don't worry about why there are *exactly* three orientations for the dumb-bell shaped wave. We'll talk a little bit about that in the next lesson, but the full explanation requires a lot of math that you'll learn about if you decide to study quantum physics or quantum chemistry). Hopefully, by comparing Figures 8 and 9, you should be convinced that the *shape* of the wave (which depends on ℓ) is important when it comes to determining the number of possible orientations (or the number of possible m_l values). It shouldn't be surprising, then, that for any given value of ℓ , only certain m_l values are allowed if you want to end up with a wave function that makes sense and actually describes electrons in a hydrogen atom.

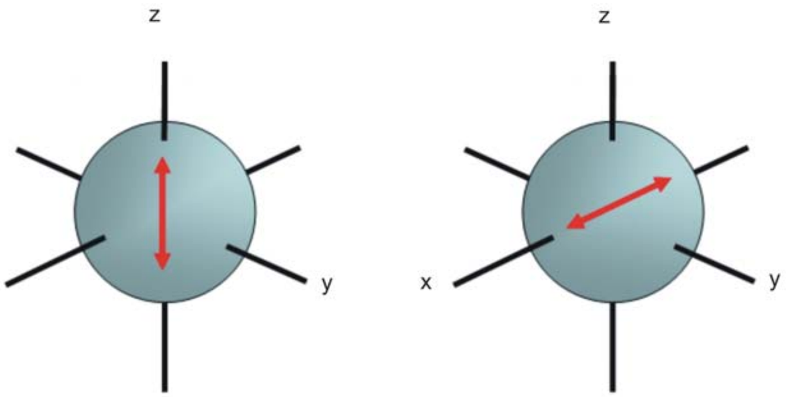


Figure 9: Two possible orientations for an electron wave with a spherical shape. Notice that there isn't a noticeable difference between these orientations.

Warning!

For a particular value of ℓ , only certain values of m_l are allowed.

The rule for m_l is that for any value of ℓ , m_l can be any integer starting from $-\ell$ and ending at $+\ell$. m_l = $-\ell$,..., $+\ell$). The following examples should help to clarify the restriction on m_l .

Example 3:

What are the allowable values of m_l for an electron wave with $\ell = 2$?

$$\ell = 2$$

1. Find the minimum value of m_l .

The minimum value of m_l *is* ***always*** $-\ell$.

minimum **m_l** = *-2*

2. Find the maximum value of m_l .

The maximum value of m_l *is* ***always*** $+\ell$

maximum **m_l** = *+2*

3. List *all* of the integers (no decimals!) starting from the minimum value of m_l and ending with the maximum value of m_l

m_l = *-2, -1, 0, 1, 2*

Example 4:

What are the allowable values of m_l for an electron wave with $\ell = 0$?

$\ell = 0$

1. Find the minimum value of m_l

The minimum value of m_l *is* ***always*** $-\ell$.

minimum m_l *= 0*

2. Find the maximum value of m_l .

The maximum value of m_l *is always* $+\ell$

maximum m_l *= 0*

3. List *all* of the integers (no decimals!) starting from the minimum value of m_l and ending with the maximum value of m_l

m_l *= 0*

Now that we've talked about all three of the different quantum numbers, you should have a good understanding of how different electron waves can be described. You can describe the 'size' of an electron wave, and the number of nodes in an electron wave using the principal quantum number, n. You can describe the shape of an electron wave using the azimuthal quantum number, ℓ . Finally, you can describe the orientation of the electron wave using the magnetic quantum number, m_l . Since you know how to describe a general electron wave, it's time to look at several examples of specific electron waves. That's what we'll talk about in the next lesson.

Lesson Summary

- Schrodinger discovered that in order for a wave function to describe a standing wave that was continuous, and that didn't 'doubled back' on itself, certain quantities in his wave function had to have integer values.
- The quantities in the wave function which must have integer values are known as quantum numbers.
- In the wave function for hydrogen, there are three quantum numbers. They are called the principal quantum number (n), the azimuthal quantum number (ℓ), and the magnetic quantum number (m_l).
- The principal quantum number can only have positive integer values, (n = 1, 2, 3...).
- The principal quantum number determines how far the bulk of the electron density extends from the center of the atom. The higher the value of n , the further away from the nucleus you will be able to detect a significant amount of electron density.
- The principal quantum number also determines the number of nodes in an electron standing wave. The higher the value of n , the more nodes there are in the electron wave.
- The higher the principal quantum number, the greater the energy of the electron. Therefore the principal quantum number is determines the *energy level* of the electron.
- The azimuthal quantum number, ℓ , determines the shape of the electron wave. The values of ℓ are also called the *electron sublevels.* They are labeled with the letters s, p, d, f, g, h, etc.
- For a wave function that actually describes an electron in an atom, ℓ is always no less than zero, but also no more than n - 1 (ℓ = 0, 1, 2... n - 1).

- In atoms with more than one electron, ℓ has a small effect on the electron's energy.
- The magnetic quantum number, m_l, determines how the electron wave is orientated in space. For any given value of ℓ, m_l can be any integer from $-\ell$ to $+\ell$ ($m_l = -\ell, \ldots, +\ell$).

Review Questions

1. Match each quantum number with the property that they describe. **(Beginning)**

a. n i. shape
b. ℓ ii. orientation in space
c. m_l iii. number of nodes

2. A point in an electron wave where there is zero electron density is called a _________. **(Beginning)**

3. Choose the correct word in each of the following statements. **(Intermediate)**

a. The (*higher/lower*) the value of n, the more nodes there are in the electron standing wave.

b. The (*higher/lower*) the value of n, the less energy the electron has.

c. The (*more/less*) energy the electron has, the more nodes there are in its electron standing wave.

4. Fill in the blank. For lower values of n, the electron density is typically found ________ the nucleus of the atom, while for higher values of n, the electron density is typically found __________the nucleus of the atom. **(Intermediate)**

5. Circle all of the statements that make sense: **(Intermediate)**

Schrodinger discovered that certain quantities in the electron wave equation had to be integers, because when they weren't, the wave equation described waves which…

a. were discontinuous

b. were too small

c. were too long and narrow

d. were too short and fat

e. 'doubled back' on themselves

6. What are the allowed values of ℓ for an electron standing wave with $n = 4$? **(Intermediate)**

7. How many values of ℓ are possible for an electron standing wave with $n = 9$? **(Intermediate)**

8. What are the allowed values of m_l for an electron standing wave with $\ell = 3$? **(Intermediate)**

9. How many different orientations are possible for an electron standing wave with $\ell = 4$? **(Intermediate)**

10. What are the allowed values of m_l for n = 2? **(Intermediate)**

Further Reading / Supplemental Links

http://www.colorado.edu/physics/2000/elements_as_atoms/quantum_numbers.html

http://dbhs.wvusd.k12.ca.us/webdocs/Electrons/QuantumNumbers.html

http://www.wwnorton.com/college/chemistry/gilbert/concepts/chapter3/ch3_2.htm

http://www.sparknotes.com/testprep/books/sat2/chemistry/chapter4section4.rhtml

Vocabulary

quantum numbers	Integer numbers assigned to certain quantities in the electron wave function. Because electron standing waves must be continuous and must not 'double over' on themselves, quantum numbers are restricted to integer values.
principal quantum number (n)	Defines the energy level of the wave function for an electron, the size of the electron's standing wave, and the number of nodes in that wave.
node	A place where the electron wave has zero height. In other words, it is a place where there is no electron density.
azimuthal quantum number (ℓ)	Defines the electron sublevel, and determines the shape of the electron wave.
magnetic quantum number (m_l)	Determines the orientation of the electron standing wave in space.

Review Answers

1. a. iii., b. i., c. ii

2. node

3.

(a) higher

(b) lower

(c) more

4. (closer to), (further from)

5. a. and e

6. ℓ = 0, 1, 2, 3

7. 9 (they are ℓ = 0, 1, 2, 3, 4, 5, 6, 7, 8)

8. m_l = -3, -2, -1, 0, 1, 2, 3

9. 9 (they are m_l = -4, -3, -2, -1, 0, 1, 2, 3, 4)

10. m_l = 0 (from ℓ = 0) and m_l = -1, 0, 1 (from ℓ = 1)

Shapes of Atomic Orbitals

Learning Objectives

- Define an electron orbital.
- Be able to recognize s orbitals by their shape.
- Be able to recognize p orbitals by their shape.

Introduction

In the last lesson, we learned how the principal quantum number determines the size of an electron wave (and the number of nodes), ℓ determines the shape of an electron wave, and m_l determines the orientation of an electron wave. Now the effects of n are probably easy to visualize. For bigger values of n, the electron wave gets bigger, and it ends up with more nodes. Similarly, the effects of m_l are easy to visualize as well. For different values of m_l, the electron wave gets rotated into different orientations. In other words, the electron wave points in different directions. What about the effects of ℓ? You know that ℓ tells you something about the shape of the electron wave. You also know that certain waves are spherical while others are dumbbell shaped, or butterfly shaped or just plain crazy shaped! But how do you know which value of ℓ corresponds to *which* shape?

Unless you have a lot of training in mathematics, and can understand the wave function, there's really no way for you to predict what the shape of a wave with a particular value of ℓ will look like. Really, you just have to know, or be told – so that's what we'll do in the next few sections. We'll *tell* you what an ℓ = 0 wave looks like, and what an ℓ = 1 wave looks like.

When the Azimuthal Quantum Number is 0, The Electron Occupies an s Orbital

In the last lesson, you learned that different electron wave shapes have different names, and that these names are always letters of the alphabet like s, p, d and f. [These letters were chosen on the basis of observations of line spectra. Certain lines were observed as a "sharp" series; others were classified as " principal," "diffuse" or "fundamental series, thus s, p, d, f.] These letters correspond to the shape of the electron wave, or at least the shape that the electron wave appears to take as a result of its electron density being thicker in one place than it is in the other. Now this can get a little confusing, but remember, electron waves describe electron density, or electron 'fog' which comes from interpreting the wave-like properties of the electron. Nevertheless, we always have to be careful that we don't forget about the particle-like properties of the electron as well. As a result, once scientists know the shape of a particular electron wave, they will often switch and start describing the electron as a *particle* again. To do this, they use the name for the shape of the wave, but rather than saying 'the **electron wave** has an **s shape**', or 'the **electron wave** has a **p shape**', they will say 'the **electron** is **in an s orbital**', or 'the **electron** is **in a p orbital'**. This makes it sound as if the electron is a particle again, and as if the orbital is some sort of box that the particle is confined to, or at least some sort of territory that the particle patrols.

This switching back and forth between the wave-like description of the electron and the particle-like description of the electron may seem confusing, or annoying, or just plain strange, but scientists do it to remind themselves that electrons are *both* particles *and* waves. So exactly what *is* an **orbital?** Technically speaking, an orbital is a wave function for an electron defined by the three quantum numbers, n, ℓ and m_l. What the wave function describes, though, is a region in space with a particular shape, where you are likely to find an electron. In terms of waves, the orbital describes the region in space where the electron density is very thick. In terms of particles, the orbital describes the region in space where there is a high probability of finding the electron (which should make sense, because wherever the electron density is thick, there is also a high probability of finding the electron).

So far we've decided that ℓ describes the shape of an orbital, which in turn describes where the electron density is thick (and there is a high probability of finding the electron) and where the electron density is thin (and there is a low probability of finding the electron). We're still, however, working towards a description of what these waves with regions of thick and thin electron density actually look like. Let's begin with the simplest wave shape. The simplest wave shape occurs for ℓ = 0. Whenever an electron wave is described by the quantum number ℓ = 0, we say that the wave function describes what's known as an s wave and thus the electron is in an s orbital. s waves can be big or small, depending on the value of n. s waves can also have a huge number of nodes, or no nodes at all, again depending on the value of n. What all s waves have in common, though, is their shape. That's what we'll talk about in the next section.

s Sublevels are Spherically Shaped

All ℓ = 0 electron waves are s waves, or waves from the s sublevel, and they all describe electrons in s orbitals. As suggested in the previous section, all electron waves from the s sublevel have the same overall shape, regardless of the value of n, regardless of their size, and regardless of the number of nodes they contain. s orbitals always correspond to spherical waves. The quantum numbers n = 1 and ℓ = 0 describe a small spherical wave with no nodes, the quantum numbers n = 2 and ℓ = 0 describe a larger spherical wave with a single node, and the quantum numbers n = 3 and ℓ = 0 describe an even larger spherical wave with two nodes. These waves all look slightly different, as shown in Figure 1.

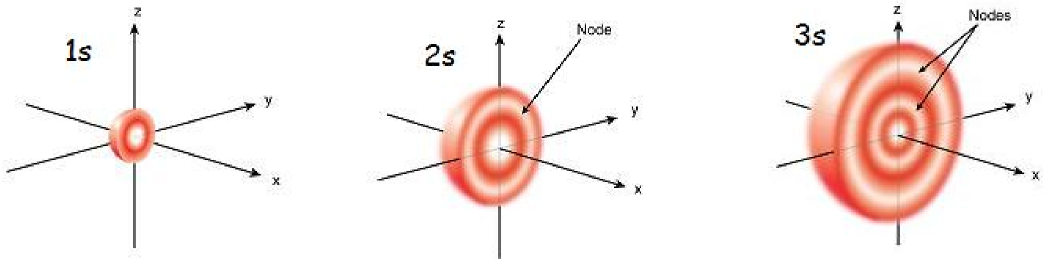


Figure 1: Various s orbitals. All of these orbitals have ℓ = 0, but they have different values for n. The first orbital has n = 1, and thus is small and has no nodes. The second orbital has n = 2, and thus is larger and has one node. The third orbital has n = 3, and thus is even larger and has two nodes.

(*Source:* CK-12 Foundation, *License:* CC-BY-SA)

Nevertheless, they are all spherical, because they all have ℓ = 0. Their shapes don't change – only their sizes and the number of nodes that they contain.

Now if you think back to an earlier lesson, you might remember something special about the different orientations of a spherical wave. Do you remember what happened when we rotated the spherical wave so that it pointed in different directions? It ended up looking the same, didn't it! No matter which way you rotate a sphere, it always looks the same. So how many different m_l values do you expect for a spherical wave? One, of course! Now that you know spherical waves all have ℓ = 0, you can use your rules for m_l to figure out exactly how many different m_l are allowed. If you look back to Example 4 in the previous lesson, you'll see that we actually did that calculation. It turned out that there was only **one** allowable value for m_l, and that was m_l = 0. In other words, there is only **one** orientation of a spherical wave. It all makes sense!

So what does a spherical wave really mean? It means that your probability of finding an electron at any particular distance from the center of the atom *only* depends on the distance, and *not* on the direction. You can see this in Figure 2.

Figure 2: Notice that the amount of electron density (here represented by the intensity of the blue color) doesn't depend on direction. It does, however, depend on distance from the center of the atom.

Notice how it doesn't matter which direction you move as you travel from the center of the atom out, your probability of finding the electron is the same whether you head straight up, or straight down, or straight to the right, or straight to the left! The fact that electron density, and the probability of finding an electron is independent of direction is a special property of s orbitals, as you'll see shortly when we begin discussing some of the other possible electron orbitals like those for ℓ = 1.

When the Azimuthal Quantum Number is 1, then m_l *Can Only Be -1, 0 or +1*

All ℓ = 1 electron waves are p waves, or waves from the p sublevel, and they describe electrons in what are known as p orbitals. Unlike s orbitals, p orbitals are not spherical, so they *can* have different orientations in space. Now that you know all p orbitals have ℓ = 1, you should be able to figure out exactly *how many* different p orbital orientations exist by using your rules for m_l . (m_l is the quantum number associated with the orientation of a particular orbital). Let's figure it out.

Example 1:

How many different p orbital orientations are possible?

$\ell = 1$ From now on, whenever you're told an electron is in a p orbital, you're expected to know that electron has the quantum number ℓ = 1

The question how many p orbital orientations are possible, but what it's *really* asking is how many different m_l values are allowed when ℓ = 1. We've already done this type of problem.

1. Find the minimum value of m_l .

The minimum value of m_l *is* ***always*** $-\ell$.

minimum m_l *= -1*

2. Find the maximum value of m_l .

The maximum value of m_l *is always* $+\ell$

maximum $m_l = +1$

3. List all of the integers (no decimals!) starting from the minimum value of m_l and ending with the maximum value of m_l .

$m_l = -1, 0, 1$

In this case m_l can equal -1, 0 or 1, so there are a total of 3 allowed values for m_l , and thus 3 possible p orbital orientations.

The p Orbitals are Often Described as Dumb-bell Shaped

Even though you know that there are three possible orientations for p orbitals, you can't really predict their shape unless you know a lot more about mathematics, physics and wave functions. When scientists use the wave function to draw the shape of an electron's p orbital, though, they always end up with is something that looks a lot like a dumb-bell. Not only that, the three different p orbitals (one with $m_l = -1$, another with $m_l = 0$, and the third with $m_l = 1$) turn out to be perpendicular to each other. In other words, if one p orbital points along the x-axis, another p orbital points along the y-axis, and the third points along the z-axis. Scientists typically label these three orbitals p_x, p_y and p_z respectively. Figure 3 shows each of the three p orbitals separately, and then all three together on the same atom.

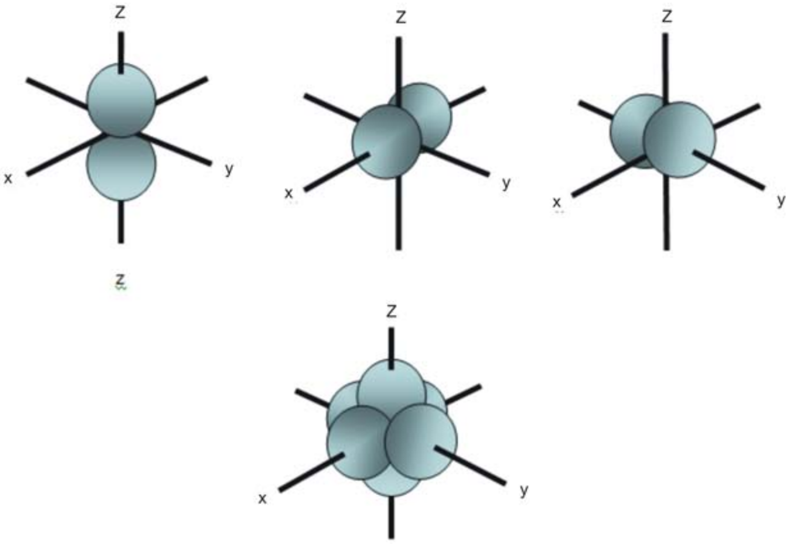


Figure 3: The three possible orientations for the p orbitals. Notice how when all three orbitals put on the same axis, the overall shape is actually fairly spherical, even though each individual orbital looks like a dumb-bell. That shouldn't surprise you, given that atoms themselves are spherical.

Sometimes we get so caught up thinking about electron wave functions, and electron orbitals, that we forget entirely about the atom itself. Remember, electron standing waves form because electrons get trapped inside an atom by the positive charge on the atom's nucleus. As a result, s orbitals, and p orbitals and even d and f orbitals always extend out from the atom's nucleus. Don't get so caught up in orbitals that you forget where they are and why they exist.

As with s orbitals, p orbitals can be big or small, depending on the value of n, and they can also have more or less nodes, also depending on the value of n. Notice, however, that unlike the s orbital, which can have no nodes at *all*, p orbital always have *at least one node*. Take a look at Figure 3 again. Can you spot the node in each of the p orbitals? Since all p orbitals have at least one node, there are no p orbitals with n = 1. In fact, the first principal quantum number, n, for which p orbitals are allowed is n = 2. Of course you could have figured that out for yourself, right? No? Well, here's a hint – remember the rules for predicting which values of ℓ are allowed for any given value of n. In the last lesson, you learned that ℓ must be no less than 0, but also, no greater than n - 1. For the n = 1 energy level, then, the maximum allowed value for ℓ is

maximum $\ell = n - 1$

maximum $\ell = 1 - 1$

maximum $\ell = 0$

As a result, only s orbitals ($\ell = 0$) are allowed. For the n = 2 energy level, though, the maximum allowed value for ℓ is

maximum $\ell = n - 1$

maximum $\ell = 2 - 1$

maximum $\ell = 1$

which means p orbitals ($\ell = 1$) are allowed as well. So now you see that the restrictions on ℓ are actually there to make sure that all n = 1 wave functions have no nodes, all n = 2 wave functions have 1 node, all n = 3 wave functions have 2 nodes, all... well, you get the picture.

One interesting property of p orbitals that is different from s orbitals is that the total amount of electron density changes with *both* the distance from the center of the atom *and* the direction. Take a look at Figure 4. Notice how the electron density is different depending on which direction you travel from the center of the atom out. In the particular p orbital shown in Figure 4, the probability of finding the electron is greater as you head straight up from the center of the atom than it is as you head straight to the left or to the right of the atom. It turns out that this dependence on direction is very important when it comes to studying how different atoms interact and form bonds. We'll talk more about that in a later chapter.

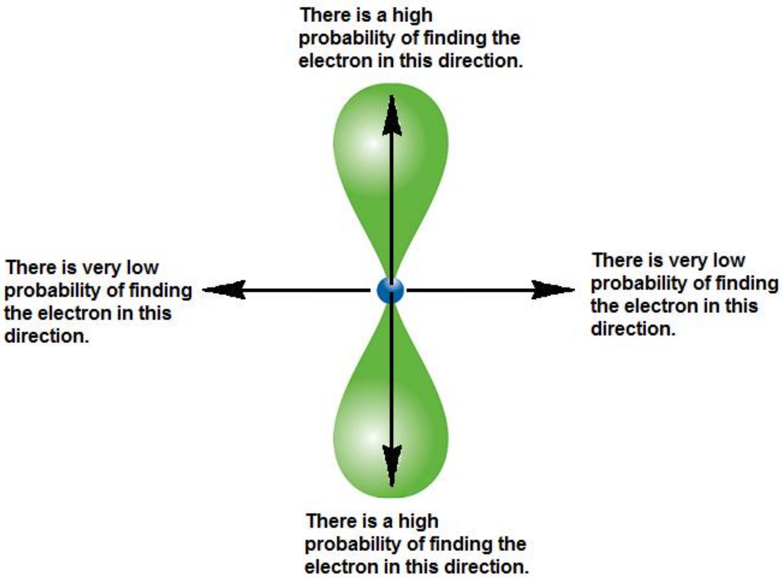


Figure 4: For p orbitals, the amount of electron density, and thus the probability of finding an electron, depends on both the distance from the center of the atom *and* the direction.

(*Source:* CK-12 Foundation, *License:* CC-BY-SA)

The d Orbitals and f Orbitals are Not Easily Visualized

Did you notice how the p orbitals looked a lot fancier than the simple spherical s orbitals? Well, you can imagine that if p orbitals with ℓ = 1 are fancy, then d orbitals, with ℓ = 2 are even fancier, and f orbitals, with ℓ = 3 are just plain crazy! Most people can visualize p orbitals, but d orbitals and f orbitals are actually rather difficult to imagine. Most d-orbitals are butterfly shaped, although one has an unusual shape that looks like a donut surrounding a Q-tip! The 5 possible d orbitals are shown in Figure 5 (and you could have figured out that there were 5, right?). Don't worry too much about why one of the d orbitals is different. Again, it takes a lot of complex math to understand where the different d orbital pictures came from, and you won't have to worry about that unless you decide to go on and study quantum chemistry at the university level. As for f orbitals, they are even hard to draw, not to mention the fact that there are a total of 7 of them! We won't be too concerned with d orbitals in this course, although they do become very important if you want to study certain metals like those found in the center of the periodic table. Similarly, f orbitals aren't all that important when it comes to common chemicals like hydrogen, or oxygen, or even copper. They do become important, though when you want to study some of the most important radioactive elements like uranium and plutonium!

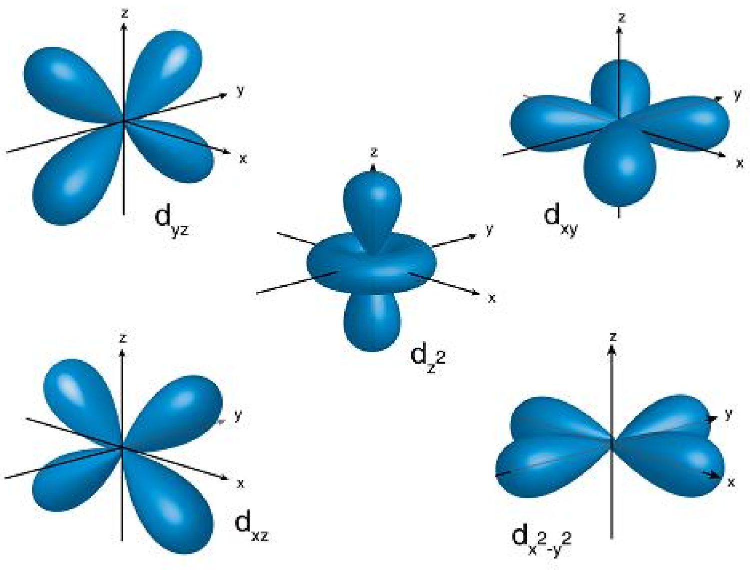


Figure 5: The probability patterns for the **d** orbitals.

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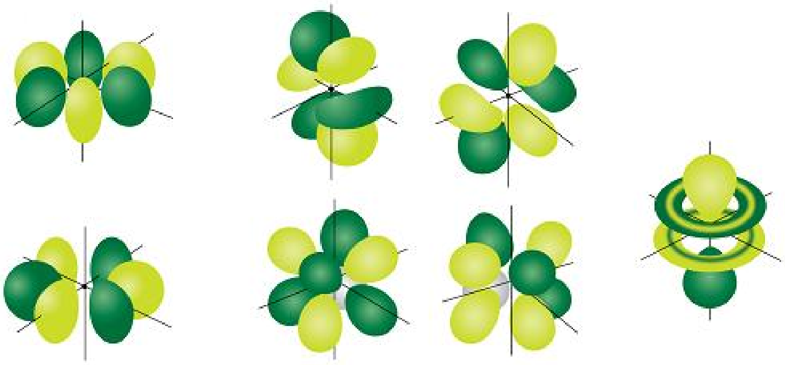

Figure 6: The probability patterns for the **f** orbitals.

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Information About the Quantum Theory

General Information

You should keep in mind that the theories scientists eventually accept are those that are in agreement with observations on nature and offer explanations for those observations. Theories about science that are the result of only mathematical development usually are not accepted until supportive observations are made. Such was certainly the case with Einstein's theory of relativity.

In the case of quantum theory, even though it was developed primarily from observations on black-body radiation and light emissions from atoms, its application is much broader. The primary tenet of quantum theory is that energy comes in small packages called quanta. It doesn't say only light energy comes in packages, it says all energy comes in packages. One of these packets of energy is called a quantum (plural = quanta). In the specific case of light, a packet of energy can also be called a **photon**. Quantum theory says that all energy is quantized (comes in little bundles). That means that even the kinetic energy of a moving baseball must increase or decrease in steps. That is, a baseball may not have "any" possible energy but rather must have stepwise increases or decreases in energy. This stepwise change in energy is not possible to observe in baseballs, of course, because the change in the velocity of a baseball with the increase or decrease of one quantum of energy would be much too small for us to detect. In order for us to actually see the stepwise changes in energy of an object, the object must be extremely small so that a change in energy of a single quantum would be measureable. Of course, such observations are made in the gain or loss of energy by the electrons in the electron cloud of an atom when precise frequencies of light (corresponding to individual photons) are absorbed or emitted when electrons change energy levels.

But, the stepwise change in energy is also detectable in the behavior of other very small objects. Molecules, in addition to their linear motion, also rotate. This rotational motion requires very small levels of energy and shows a stepwise increases and decreases in rotation. That is, certain molecules can be observed to rotate at 3 revolutions per second or 6 revolutions per second, or 9 revolutions per second, but cannot be observed to rotate at speeds in between those observed values. Molecules also have vibrational motion in their chemical bonds. This vibrational motion is also observed to be stepwise in nature. These are just some of the observations that are supportive of the quantum theory.

Quantum Numbers and Electron Arrangement

Quantum theory in general and specifically solutions to Schrodinger's equation gives us a great deal of information about the arrangement of electrons in the electron clouds of atoms. When we interpret this information, it is quite apparent that it came from a mathematical development. Keep in mind, however, that eventually you will see laboratory observations that have no explanation without quantum theory, just as the spectra of elements were observed 100 years before anyone could explain why it occurred.

The principal quantum number, n , that comes from solutions to Schrodinger's equation indicates the major energy level that contains that electron. These energy levels are numbered 1, 2, 3, . . . etc. *(The energy levels were originally named K, L, M, N, . . . etc, but later they were re-named 1, 2, 3, ... and so on. Sometimes, in older text material, you will see references to the K energy level.)* Since Schrodinger's equation is a theoretical statement, an infinite number of energy levels exist. However, when we place the electrons for our known atoms into the energy level structure, the electrons from even the largest known atom all fit in just 7 energy levels. There might be some theoretical discussion of an 8th or higher energy level but we never actually use any above 7.

These energy levels also contain sub-levels. The sub-levels also have been named. The names of the sub-levels are s, p, d, and f. Mathematically, the number of sub-levels that an energy level can have is equal to the principal energy level number. That is, the 1st energy level can have 1 sub-level, the 2nd energy level can have 2 sub-levels, and so on. Obviously, if the number of sub-levels possible is equal to the energy level number, then energy level 6 could theoretically have 6 sub-energy levels. Therefore, some people list the sub-energy levels as s, p, d, f, g, h, i, ... etc. Again, however, we find that our largest atom with the greatest number of electrons never uses any sub-level beyond f. Therefore, it is often said that the largest number of sub-levels used by atoms is 4.

The sub-energy levels have the probability patterns for electrons that you saw in the last section. The s sub-energy level produces spherical probability patters, the p sub-levels produce the dumbbell shaped probability patterns, the d sub-energy levels produce the butterfly probability patterns, and the f sub-levels produce the probability patterns with no verbal description - but they do have a mathematical description. The n quantum number identifies the sub-level that contains the electron. When ℓ = 0, the electron is in an s-orbital, when ℓ = 1, the electron is in a p-orbital, when ℓ = 2, the electron is in a d-orbital, and when ℓ = 3, the electron is in an f-orbital. For all our known atoms, ℓ never gets larger than 3.

The sub-energy levels contain various spatial orientations of probability patterns called **orbitals**. This word is a carryover from the Bohr theory where an orbital was a circular path the electron followed around the nucleus but that is not the meaning of the word in modern chemistry. In modern chemistry, an orbital is a specifically designated volume inside the electron cloud where the probability of finding the electron is high. As mentioned earlier, the first energy level, n = 1, has only one sub-energy level because ℓ must equal 0 and that sub-level is an s sub-level. The number of orbitals in the s sub-levels was calculated in the last section. Sub-energy level s has a single orbital that is spherical in shape. Sub-energy level p has three dumbbell shaped orbitals, while sub-energy level d has five orbitals, and sub-energy level f has seven orbitals.

Summary of Energy Levels, Sub-Levels, and Orbitals

Energy Level Number	Sub-Energy Levels	Number of Orbitals
1	s	1
2	s	1
2	p	3
3	s	1
3	p	3
3	d	5
4	s	1
4	p	3
4	d	5
4	f	7
5	s	1
5	p	3
5	d	5

5	f	7

For actual atoms, all the energy levels after 4 are repetitions of 4. That is, they have the same sub-energy levels and orbitals as energy level 4. In theory, of course, energy level 5 could have five sub-energy levels and the fifth sub-energy level would be named g and have 9 orbitals. We don't normally discuss that sub-energy level or any beyond it because they are never used. You might note the mathematical tone in this data, in that the total number of orbitals in any energy level is equal to the energy level number squared, n^2. You probably also noticed that the number of orbitals in each succeeding sub-level increases by 2.

Lesson Summary

- An orbital is a wave function for an electron defined by the three quantum numbers, n, ℓ and m_l. Orbitals define regions in space where you are likely to find electrons.
- s orbitals ($\ell = 0$) are spherical shaped.
- p orbitals ($\ell = 1$) are dumb-bell shaped.
- The three possible p orbitals are always perpendicular to each other.

Review Questions

1. Fill in the blanks. **(Intermediate)**

When $\ell = 0$, the electron orbital is _________ and when $\ell = 1$, the electron orbital is _________ shaped.

2. The n = 1 s orbital has _____ nodes. **(Intermediate)**

3. The n = 2 s orbital has _____ nodes. **(Intermediate)**

4. The n = 2 p orbital has _____ nodes. **(Intermediate)**

5. The n = 1 p orbital has _____ nodes. **(Intermediate)**

6. There are ____ different p orbitals. **(Beginning)**

7. What energy level (or value of n) has s, p and d orbitals, but no f orbitals? **(Intermediate)**

8. How many different d orbital orientations are there? **(Intermediate)**

9. How many f orbital orientations are there? **(Intermediate)**

10. How many different orbitals are there in the n = 3 energy level? **(Challenging)**

Vocabulary

orbital A wave function for an electron defined by all three quantum numbers, n, l, and m_l. Orbitals define regions in space where there is a high probability of finding the electron.

Review Answers

1. spherical, dumb-bell

2. 0

3. 1

4. 1

5. the n = 1 p orbital DOES NOT EXIST!

6. 3

7. n = 3

8. 5, they are m_l = -2, -1, 0, 1, 2

9. 7, they are m_l = -3, -2, -1, 0, 1, 2, 3

10. 9 – they are (ℓ , m_l) = (0, 0), (1, -1), (1,0), (1, 1), (2, -2), (2, -1), (2, 0), (2, 1), (2, 2)

7. Electron Configurations for Atoms

The Electron Spin Quantum Number

Lesson Objectives

- Explain what is meant by the spin quantum number, ms.
- Explain how the spin quantum number affects the number of electrons in an orbital.
- Explain the difference between diamagnetic atoms and paramagnetic atoms.

Introduction

In the last chapter, you learned about quantum numbers. Remember, quantum numbers actually come from the wave function. Even though you've never seen a mathematical equation for a wave function (and you'd probably think it was pretty scary if you did!) you can still understand what the different quantum numbers mean, because they all control different aspects of what the electron standing wave looks like. The principal quantum number, n, determines the 'size' and the number of nodes in the electron wave, the azimuthal quantum number, ℓ, determines the 'shape' of the electron wave, and the magnetic quantum number, m_l, determines the 'orientation' of the electron wave. Now suppose that you were told the exact size, the exact shape and the exact orientation of an electron orbital. Could you draw that object without being told anything else? You should be able to – what could you possibly need to know about an electron wave other than its size, shape and orientation? It seems as if the first three quantum numbers tell us all the information necessary to picture what an electron's probability pattern looks like – but it turns out that there's *fourth* quantum number! What! How could there be another quantum number? What property could it possibly describe? There's nothing left after size, shape, and orientation. That's exactly what scientists thought until they discovered *spin*.

m_s = +1/2 or -1/2

In the early days, when scientists were just beginning to learn about *quantum* physics, most of what they knew about *quantization* involved atomic spectra. Remember, in Chapter 5 you learned that atomic spectra were discontinuous, and that this led Bohr to propose the existence of *quantized energy levels*. To explain these quantized energy levels, Bohr suggested that electrons in an atom were restricted to specific orbits and that they moved around the nucleus in these orbits just like the planets move around the sun. It turned out that Bohr's model wasn't entirely correct because electrons don't orbit the nucleus. In fact, based on what scientists know of the wave-particle duality and the Heisenberg Uncertainty Principle, scientists now think that electrons can be anywhere inside the atom, although the probability of finding them at any one particular location over another depends on the relative amount of electron density at those locations. Even though Bohr's model had some problems, Bohr was right in his prediction that electrons could only exist at specific 'allowed' energy levels, and that all other energies were 'forbidden'.

In the last chapter, you learned how the 'allowed' and 'forbidden' energy levels could be explained in terms of electron standing waves. Only certain electron standing waves will fit perfectly inside the atom without 'doubling over' on themselves, or containing discontinuous jumps. Therefore, just like the Bohr Theory of the atom, the wave function theory of the electron explains the existence of *discontinuous* atomic spectra. Actually, wave functions themselves are pretty good at predicting exactly what the atomic spectra of different atoms will look like (In other words, at which wavelengths lines of light will appear – if you have forgotten about atomic spectra, go back and read Chapter Four!) Remember, Bohr's model could only predict the atomic spectrum of hydrogen. With a little bit of work, though, scientists could get electron wave functions to predict many different atomic spectra for many different types of atoms. It seemed perfect… but there was a still a slight problem. Every so often when scientists looked carefully at atomic spectra, they would find *two* separate lines of light at a wavelength where the wave function had only predicted one. The two separate lines were always really close together, so if you didn't look carefully, you'd think it was just one line and you'd think that the wave function was doing a great job. But the fact remained that frequently the wave function was missing some of the finer details of the atomic spectra.

Now if you think back to what we discussed in Chapter Five, you'll remember that the lines of light in an atomic spectrum result when an electron 'falls' from one energy level to another and releases its extra energy in the form of light. Even though we learned about this process in terms of the Bohr model, the same principle applies to the wave function theory as well. Remember, in terms of wave functions, the energy level of an electron is determined by the principal quantum number, n, while the azimuthal quantum number, ℓ, defines the sublevel and also affects electron energy in atoms with more than one electron.

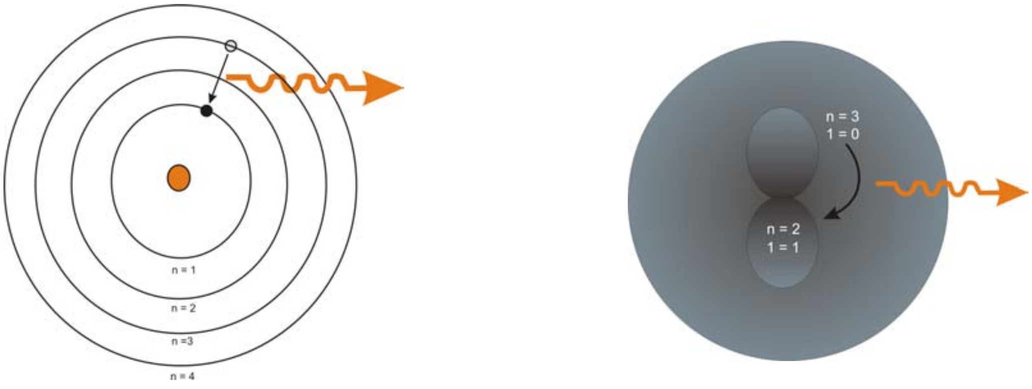

Figure 1: a. Electrons don't circle the nucleus like planets in a solar system b. Nevertheless, when they fall from a higher energy level electron standing wave to a lower energy electron standing wave they release light in much the same way.

When an electron begins at one energy (one value of n and ℓ) and then falls to a lower energy (with a different value of n and ℓ), it releases its extra energy in the form of light. Therefore, if there are two very closely spaced lines of light in an atomic spectrum, it must mean that there are two very closely spaced energy states from which (or to which) an electron can 'fall'. In terms of predicting the finer details of an atomic spectrum, then, it's clear that the problem with the wave function was that in certain situations it would only find one allowed energy state where there should have been two!

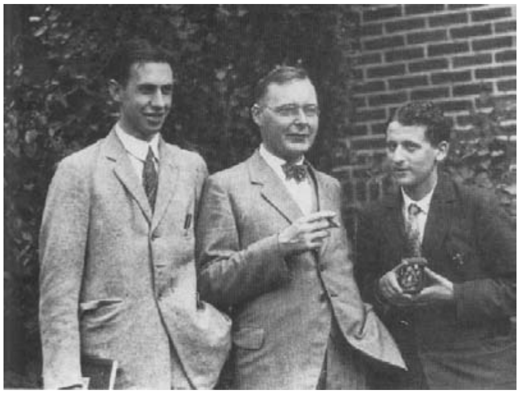

Figure 2: George Uhlenbeck (on the far left) and Samuel Goudsmit (on the far right), the two scientists who first proposed the existence of the spin quantum number. (*Source:* http://en.wikipedia.org/wiki/Image:Uhlenbeck-KramersGoudsmit.jpg, *License:* Public Domain)

The story got even stranger when scientists put magnets around different atoms and looked at what happened to their atomic spectra as a result. All of those pairs of closely spaced spectral lines that the wave function couldn't predict actually split apart *even further*! In other words, magnetic fields affected the two different energy levels differently. It made the low energy level drop even lower, and it made the high energy level rise even higher. After the magnet experiments, scientists came to the realization that their wave function description was not as complete as they had hoped. There was some other property that had to be included – but what? In 1925, two scientists by the names of Samuel Goudsmit and George Uhlenbeck suggested extending the wave function equation so that it included a fourth quantum number, called the 'spin' quantum number. When any charged object (like, for example, a negatively charged electron) spins in a magnetic field, its energy is determined by the direction in which it rotates. In other words, if the object rotates clockwise, it will have a different amount of energy than it would have if it had rotated counterclockwise. Goudsmit and Uhlenbeck argued that if the electron was spinning, then it was easy to explain why those two closely spaced spectral lines split further apart in the presence of a magnetic field.

One line corresponded to the energy level for the electron spinning clockwise, and the other corresponded to the energy level for the electron spinning counterclockwise. (If you're really clever, you might wonder why these two energy levels were different and could be seen in atomic spectra even when there weren't any external magnets around. It turns out that there are *always* tiny internal magnetic fields created by matter itself. Usually, though, these internal magnetic fields are very small, so their effect is very small as well).

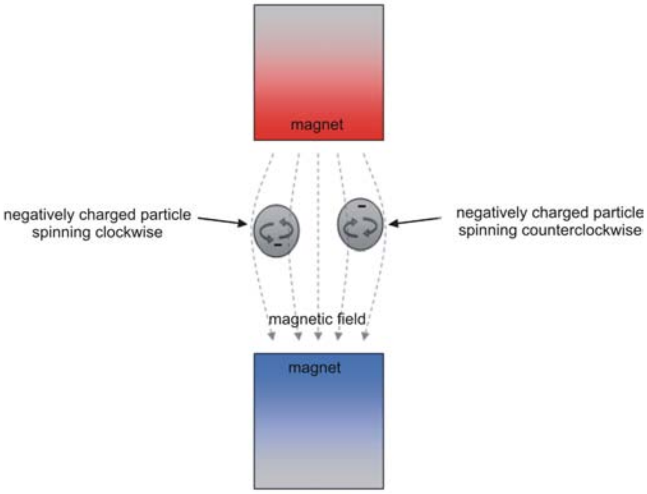

Figure 3: Two negatively charged particles spinning in a magnetic field. The left particle will have a different energy than the right particle, because they are spinning in different directions.

By incorporating electron spin into the electron wave function, scientists found that the fourth quantum number, also known as the spin quantum number, m_s, could take on two different values – they were $m_s = +1/2$ and $m_s = -1/2$. Notice that unlike n, ℓ and m_l, which can only be integers, m_s can be *half-integers*. The value of m_s will never be some crazy decimal like $m_s = 0.943895$, but it *can* be the decimal $m_s = 0.5$, because that corresponds to *one-half*, or a *half-integer*.

Now it's tempting to think of $m_s = +1/2$ as the electron spinning in one direction, and $m_s = -1/2$ as the electron spinning in the other direction. When you do that, though, how are you picturing the electron? You're picturing it as a particle, aren't you? And how do you explain the wave-like nature of an electron in terms of rotation clockwise or counterclockwise? Well, you can't. So despite the fact that the idea for including electron spin in the wave function came from picturing electrons as tiny little spinning objects, scientists try not to make any direct comparisons between the spin quantum number and a particle rotating clockwise or counterclockwise. Instead, scientists usually make vague statements like 'spin can only *truly* be understood as a *quantum* property. There is no directly comparable macroscopic (large scale) property'. Rather than saying anything about a clockwise rotation, or a counterclockwise rotation, scientists call electrons with **$m_s = +1/2$ 'spin-up'** and electrons with **$m_s = -1/2$ 'spin down'**.

When Two Electrons Occupy the Same Orbital, They Will Have Opposite Spins

Do you remember what an orbital is? An orbital is a wave function for an electron with a specific set of quantum numbers, n, ℓ, and m_l. For example, the numbers $n = 1$, $\ell = 0$ and $m_l = 0$ define one particular orbital, while the numbers $n = 2$, $\ell = 1$ and $m_l = -1$ define another orbital, and the numbers n

= 2, ℓ = 1 and m_l = 0 define a different orbital again. Orbitals are very important because any time you know the values of the first three quantum numbers n, ℓ and m_l, you know the region in space where there is a high probability of finding the electron. In other words, if you know which orbital an electron is in, you know exactly what its 'box', or 'territory' looks. The orbital is really just a description of *where* the electron spends most of its time.

For example, if you're told that the electron is in an orbital with n = 1, ℓ = 0, m_l = 0, you automatically know that the electron is probably going to be found in a spherical shaped 'territory' that's pretty close to the nucleus of the atom. On the other hand, if you're told that the electron is in an orbital with n = 5, ℓ = 1 and m_l = 0 you know that the electron is probably going to be found in a dumb-bell shaped 'territory' that extends quite far from the nucleus of the atom, along the y axis (technically speaking m_l = 0 could be the orbital along the x-axis, the orbital along the y-axis or the orbital along the z-axis, but whichever axis you choose for the m_l = 0 orbital, the m_l = 1 and m_l = -1 orbitals will automatically point along the other two axes).

The spin quantum number doesn't tell you anything about the region in space where you're likely to find the electron. Therefore, if you want to know which orbital an electron is in, *all* you need to know is the values of the first three quantum numbers – you don't need to know the value of the fourth. So why is the value of the fourth quantum number important? Well, the spin quantum number determines whether or not an electron is *allowed* to share an orbital with another electron that's already there. It turns out that each region of the atom (or each orbital) can actually be shared by *two* electrons.

Two electrons can share their territory, or their orbital, provided each electron does something different. This means that sharing an orbital is *only* possible for electrons which have *different spin quantum numbers*. An electron that has a spin quantum number of m_s = +1/2 can share an orbital with an electron that has a spin quantum number of m_s = -1/2. However, an electron that has a spin quantum number of m_s = +1/2 *cannot* share an orbital with another electron that also has a spin quantum number of m_s = +1/2. Similarly, an electron that has a spin quantum number of m_s = -1/2 *cannot* share an orbital with another electron that has a spin quantum number of m_s = -1/2.

When Electrons are Paired, They are Diamagnetic i.e. No Magnetic Attraction

In the last section, you learned that any time two electrons share the same orbital, their spin quantum numbers have to be different. In other words, one of the electrons has to be 'spin-up', with m_s = +1/2, while the other electron is 'spin-down', with m_s = -1/2. This is important when it comes to determining the *total spin* in an electron orbital. Technically speaking, an electron's *spin* isn't exactly the same as its *spin quantum number*, but the difference isn't important when it comes to figuring out whether or not two electron spins cancel out. In order to decide whether or not electron spins cancel all you need to do is add their spin quantum numbers together. If the **total is 0**, then the **spins cancel** each other out. If the **total is greater than 0, or less than 0**, then the **spins do not cancel** each other out. Let's take a look at two examples:

Example 1:

Electron A has m_s = +1/2 while electron B has m_s = -1/2. Do the spins of these two electrons cancel each other out?

m_s for A = +1/2

m_s for B = -1/2

Total m_s = m_s for A + m_s for B

Total m_s = (+1/2) + (-1/2)

Total m_s = 1/2 - 1/2

Total m_s = 0

In this case, the spins of electron A and electron B *do* cancel each other out.

Example 2:

Electron A has m_s = -1/2 while electron B has m_s = -1/2. Do the spins of these two electrons cancel each other out?

m_s for A = -1/2

m_s for B = -1/2

Total m_s = m_s for A + m_s for B

Total m_s = (-1/2) + (-1/2)

Total m_s = -1/2 - 1/2

Total m_s = -1

In this case, the spins of electron A and electron B *do not* cancel each other out.

The idea of 'canceling out' should make sense to you. If one spin is 'up', and the other is 'down', then the 'up' spin cancels the 'down' spin and there is no leftover spin at all. The same logic applies if we think of spins as 'clockwise' and 'counterclockwise'. If one spin is 'clockwise' and the other is 'counterclockwise', then the two spin directions balance each other out and there is no leftover rotation at all. Notice what all of this means in terms of electrons sharing an orbital. Since electrons in the same orbital *always* have opposite values for their spin quantum numbers, m_s, they will *always* end up canceling each other out! In other words, there is no leftover (or 'net') spin in an orbital that contains two electrons. Whenever two **electrons are paired** together in an orbital, we call them ***diamagnetic*** electrons. On the other hand, an orbital containing only one electron will have a total spin equal to the spin of the electron that it contains.

Even though electron spin can only be *truly* understood using quantum physics, it does produces effects that we can actually see in our everyday lives. Electron spin is very important in determining the magnetic properties of an atom. If all of the electrons in an atom are paired up and share their orbital with another electron, then the total spin in each orbital is zero and, by extension, the total spin in the *entire atom* is zero as well! When this happens, we say that the atom is diamagnetic because it contains **only** diamagnetic electrons. Diamagnetic atoms are NOT attracted to a magnetic field. In fact, diamagnetic atoms are slightly repelled by magnetic fields.

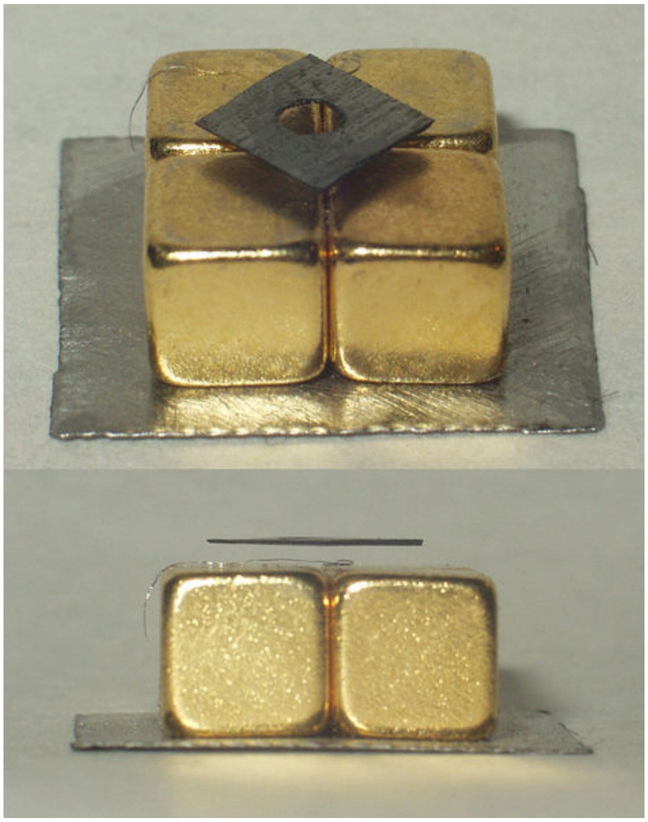

Figure 6: Since diamagnetic atoms are slightly repelled by a magnetic field, it is actually possible to make certain diamagnetic materials float! Here, you can see a thin black sheet of pyrolytic graphite floating above the gold magnets.

(*Source:* http://en.wikipedia.org/wiki/Image:Diamagnetic_graphite_levitation.jpg, *License:* Public Domain)

When an Electron is Unpaired, Paramagnetism will be Observed

If atoms that contain *only paired electrons* are slightly *repelled* by a magnetic field, what do you think is true of atoms that contain *unpaired electrons*? If you guessed that atoms with unpaired electrons are slightly attracted to a magnetic field, then you guessed right! Whenever **electrons are alone** in an orbital, we call them ***paramagnetic*** electrons. Remember, if an electron is all by itself in an orbital, the orbital has a 'net' spin, because the spin of the lone electron doesn't get canceled out. If even *one* orbital has a 'net' spin, the entire atom will have a 'net' spin as well. Therefore, we say an **atom is paramagnetic** when it **contains at least one paramagnetic electron.** Notice that the definition of diamagnetism and the definition of paramagnetism are subtly different. This can be confusing if you aren't careful. Be sure to note: In order for an atom to be diamagnetic, *all* of its electrons must be paired up in orbitals. In order for an atom to be paramagnetic, *at least one* of its electrons must be unpaired.

In other words, an atom could have 10 paired (diamagnetic) electrons, but as long as it *also* has 1 unpaired (paramagnetic) electron, it's still considered a 'paramagnetic atom'. In order to be a 'diamagnetic atom', the atom would have to have 10 paired (diamagnetic) electrons and *no* unpaired (paramagnetic) electrons. Just as **diamagnetic atoms** are slightly **repelled from a magnetic field**, **paramagnetic atoms** are slightly **attracted to a magnetic field**.

Lesson Summary

- If you only consider the first three quantum numbers, the wave function model for the electron will sometimes predict one spectral line where there are actually two closely spaced spectral lines.
- This led to the proposal of a fourth quantum number, the spin quantum number m_s.

- m_s can have two possible values for an electron. It can be 'spin-up' with $m_s = +1/2$ or 'spin-down' with $m_s = -1/2$
- When two electrons occupy the same orbital, they must have different spin quantum numbers.
- An orbital containing two electrons will have no net spin. When this is the case, the two electrons are called diamagnetic electrons.
- An orbital containing only one electron will have a total spin equal to the spin of the electron that it contains. When this is the case, the electron is called a paramagnetic electron.
- Electron spin helps to determine the magnetic properties of an atom.
- If all electrons in an atom are diamagnetic, the entire atom has no net spin, and is termed a 'diamagnetic atom'. Diamagnetic atoms are slightly repelled from a magnetic field.
- If an atom contains even one paramagnetic electron, the entire atom has a net spin and is termed a paramagnetic atom. Paramagnetic atoms are slightly attracted to a magnetic field.

Review Questions

1. The principal quantum number describes the size of an electron energy level, the azimuthal quantum number describes the shape of an electron energy level, and the magnetic quantum number describes the orientation of the electron energy level. If there was another quantum number, what do you think it might describe about the electron? **(Challenging)**

2. There is, in fact, a fourth quantum number that we'll learn about in this lesson. The fourth quantum number is called the spin quantum number. Now can you guess what the final quantum number might describe? **(Beginning)**

3. Choose the correct statement. **(Beginning)**

a. The spin quantum number for an electron can only have the values $m_s = +1$ and $m_s = -1$

b. The spin quantum number for an electron can only have the value $m_s = 0$

c. The spin quantum number for an electron can have any integer value between $-\ell$ and $+\ell$

d. The spin quantum number for an electron can only have the values $m_s = +1/2$ and $m_s = -1/2$

e. The spin quantum number does not apply to electrons

4. Choose the correct statement. **(Beginning)**

a. When two electrons share an orbital, they always have the same spin quantum numbers

b. When two electrons share an orbital, they always have opposite spin quantum numbers

c. Two electrons cannot share the same orbital

d. When two electrons share an orbital there is no way to predict whether or not they will have the same spin quantum numbers

5. Fill in the blanks in the following statement using numbers. **(Challenging)**

When scientists used the Schrodinger equation with only __ quantum numbers, they found that the Schrodinger equation was pretty good at predicting atomic spectra, except that there were occasionally __ closely spaced lines of light where the Schrodinger equation predicted only __. This led scientists to suggest that a complete description of an electron, which required ___ quantum numbers.

6. In many atomic spectra, there are two very closely spaced lines of light which can only be predicted by including the spin quantum number into the Schrodinger equation. Decide whether the following statements about these two lines are true or false. **(Beginning)**

a. the two lines spread further apart when the atom is placed in a magnetic field

b. the two lines move closer together when the atom is placed in a magnetic field

c. the two lines are the result of an experimental error. If scientists are careful, they find that there is really just one line.

d. the two lines actually result from the fact that there are two very closely spaced energy states

7. Goudsmit and Uhlenbeck proposed the existence of **(Beginning)**

a. the principal quantum number

b. the azimuthal quantum number

c. the spin quantum number

d. the magnetic quantum number

8. Circle all of the quantum numbers that tell you about the region in space where you're most likely to find the electron. **(Intermediate)**

a. the spin quantum number

b. the magnetic quantum number

c. the principal quantum number

d. the azimuthal quantum number

9. Select the correct statement from the list below. An electron with a spin quantum number of $m_s = -1/2$ **(Beginning)**

a. cannot share an orbital with an electron that has a spin quantum number of $m_s = +1/2$

b. prefers to share an orbital with an electron that has a spin quantum number of $m_s = -1/2$

c. cannot share an orbital with an electron that has a spin quantum number of $m_s = -1/2$

d. cannot share an orbital with another electron

10. What is the total spin in an electron orbital if **(Intermediate)**

a. the orbital contains one 'spin-up' electron

b. the orbital contains one 'spin-down' electron

c. the orbital contains two 'spin-up' the orbital contains one 'spin-up' electron and one 'spin-down' electron

Further Reading / Supplemental Links

http://www.ethbib.ethz.ch/exhibit/pauli/elektronenspin_e.html http://www.lorentz.leidenuniv.nl/history/spin/goudsmit.html

http://en.wikipedia.org/wiki

Vocabulary

spin quantum number, m_s	The fourth quantum number that must be included in the wave function of an electron in an atom in order to completely describe the electron.
spin-up	The term applied to electrons with spin quantum number $m_s = +1/2$.
spin down	The term applied to electrons with spin quantum number $m_s = -1/2$.
diamagnetic electrons	Two electrons with opposite spins, paired together in an orbital.
diamagnetic atom	An atom with no net spin; an atom with *only* diamagnetic electrons.
paramagnetic electron	An electron alone in an orbital.
paramagnetic atom	An atom with a net spin; an atom with *at least one* paramagnetic electron.

Review Answers

1. (spin, although students probably won't know this)

2. (clockwise/counterclockwise rotation, etc…)

3. d

4. b

5. 3, 2, 1, 4

6.

(a) true

(b) false

(c) false

(d) true

7. c

8. b, c and d

9. c

10.

(a) +1/2

(b) -1/2

(c) electrons an orbital *cannot have* two 'spin-up' electrons

(d) 0

Pauli Exclusion Principle

Lesson Objectives

- Explain the meaning of the Pauli Exclusion Principle.
- Determine whether or not two electrons can coexist in the same atom based on their quantum numbers.
- State the maximum number of electrons that can be found in any orbital.

Introduction

When electrons are found inside an atom, they're restricted to specific areas, or regions within the atom which can be described by orbitals. Let's see what this means in terms of quantum numbers.

No Two Electrons in an Atom Can Have the Same Four Quantum Numbers

How do you know that two electrons are in the same orbital? In order to fully specify an orbital, you need to know the principal quantum number, n, the azimuthal quantum number, ℓ, and the magnetic quantum number, m_l. The values of first three quantum numbers for an electron determine exactly which orbital the electron in. Clearly, then, in order to be in the same orbital, two electrons have to have exactly the same values for n, ℓ, and m_l. Now when two electrons have exactly the same values for n, ℓ, and m_l, they share the same region of space within the atom, and in the last lesson, you learned that that had important consequences in terms of their spins. If you remember back to an earlier section, electrons in the same orbital, sharing the same region of space, had to have different values of m_s. If one electron had m_s = +1/2, then the other had to have m_s = -1/2 and vice versa. Let's take a look at several examples.

Example 1:

An electron with n = 2, ℓ = 1, m_l = -1 and m_s = +1/2 is found in the same atom as a second electron with n = 2, ℓ = 1, and m_l = -1. What is the spin quantum number for the second electron?

First electron: n = 1, ℓ = 1, m_l = -1, m_s = + 1/2

Second electron: n = 1, ℓ = 1, m_l = -1, m_s = ?

Since the first three quantum numbers are identical for these two electrons, we know that they are in the same orbital. As a result, the spin quantum number for the second electron *cannot* be the same as the spin quantum number for the first electron. This means that the spin quantum number for the second electron must be m_s = -1/2.

Example 2:

An electron with n = 5, ℓ = 4, m_l = 3 and m_s = -1/2 is found in the same atom as a second electron with n = 5, ℓ = 4, and m_l = 3. What is the spin quantum number for the second electron?

First electron: n = 5, ℓ = 4, m_l = 3, m_s = - 1/2

Second electron: n = 5, ℓ = 4, m_l = 3, m_s = ?

Since the first three quantum numbers are identical for these two electrons, we know that they are in the same orbital. As a result, the spin quantum number for the second electron *cannot* be the same as the spin quantum number for the first electron. This means that the spin quantum number for the second electron must be m_s = +1/2.

Notice that whenever the two electron's first three quantum numbers are the same, the fourth is different. Let's take a look at a few more examples…

Example 3:

Can an electron with n = 1, ℓ = 0, m_l = 0 and m_s = +1/2 exist in the same atom as a second electron with n = 2, ℓ = 0, m_l = 0 and m_s = +1/2?

First electron: n = 1, ℓ = 0, m_l = 0, m_s = + 1/2

Second electron: n = 2, ℓ = 0, m_l = 0, m_s = + 1/2

Since these two electrons are in different orbitals, they occupy different regions of space within the atom. As a result, their spin quantum numbers *can* be the same, and thus these two electrons *can* exist in the same atom.

Example 4:

Can an electron with n = 3, ℓ = 1, m_l = -1 and m_s = -1/2 exist in the same atom as a second electron with n = 3, ℓ = 2, m_l = -1 and m_s = -1/2?

First electron: n = 3, ℓ = 1, m_l = -1, m_s = - 1/2

Second electron: n = 3, ℓ = 2, m_l = -1, m_s = - 1/2

Since these two electrons are in different orbitals, they occupy different regions of space within the atom. As a result, their spin quantum numbers *can* be the same, and thus these two electrons *can* exist in the same atom.

Example 5:

Can an electron with n = 1, ℓ = 0, m_l = 0 and m_s = +1/2 exist in the same atom as a second electron with n = 2, ℓ = 1, m_l = 0 and m_s = +1/2?

First electron: n = 1, ℓ = 0, m_l = 0, m_s = + 1/2

Second electron: n = 2, ℓ = 1, m_l = 0, m_s = + 1/2

Since these two electrons are in different orbitals, they occupy different regions of space within the atom. As a result, their spin quantum numbers *can* be the same, and thus these two electrons *can* exist in the same atom.

Notice that whenever the two electrons have different values of n, or different values of ℓ, or different values of m_l, they can have the same spin quantum number m_s, because they are not in the same orbital, and thus they are not sharing the same region of space within the atom. Let's take a look at one final example

Example 6:

Can an electron with $n = 1$, $\ell = 0$, $m_l = 0$ and $m_s = +1/2$ exist in the same atom as a second electron with $n = 1$, $\ell = 0$, $m_l = 0$ and $m_s = +1/2$?

First electron: $n = 1$, $\ell = 0$, $m_l = 0$, $m_s = +1/2$

Second electron: $n = 2$, $\ell = 1$, $m_l = 0$, $m_s = +1/2$

Since these two electrons are in the same orbital, they occupy the same region of space within the atom. As a result, their spin quantum numbers *cannot* be the same, and thus these two electrons *cannot exist* in the same atom.

Hopefully after having looked at seven different examples, it should be obvious to you that electrons in the same atom with the same spin must be in different orbitals, while electrons in the same orbital of the same atom must have different spins. As a result, no two electrons in the same atom can have exactly the same four quantum numbers. If two electrons have the same n, the same ℓ, and the same m_l, then they are in the same orbital. If they also have the same m_s, then they also have the same spin, and that is impossible.

The first scientist to realize that two electrons in the same atom couldn't have the same four quantum numbers was a man name Wolfgang Pauli. In 1925, Pauli stated what has come to be known as the **Pauli Exclusion Principle.** The Pauli Exclusion Principle states that no two identical fermions (a fancy word for electrons and other subatomic particles like electrons) may occupy the same quantum state in an atom simultaneously. In other words, no two electrons in the same atom can have the same four quantum numbers. If n, ℓ, and m_l are the same, m_s must be different such that the electrons have opposite spins.

Figure 1: Wolfgang Pauli, the scientist who first proposed the Pauli Exclusion Principle.

(*Source:* http://en.wikipedia.org/wiki/Image:Wolfgang_Pauli2.jpg, *License:* Public Domain)

No Atomic Orbital Can Contain More than Two Electrons

An electron can share its territory, or its orbital, with another electron, but *only* if the other electron is slightly different – in other words, only if the other electron has a different spin.

There's a limit to the number of different electrons that can share an orbital, because there's a limit to the number of different spins that those electrons can have. When it comes to spins, though, there are *only two* possibilities. An electron can either be 'spin-up', with m_s = +1/2, or 'spin-down', with m_s = -1/2. Therefore, if an orbital has one electron that is 'spin-up', and a second electron that is 'spin-down', the orbital is full. What if a third electron tried to enter the orbital? Well, if the third electron was 'spin-up' it would have trouble sharing the orbital, with the 'spin-up' electron that's already there. Similarly, if the third electron was 'spin-down', it would have trouble sharing the orbital with the 'spin-down' electron that's already there. Since the only two options for the third electron are 'spin-up' and 'spin-down', there's really nothing that third electron can do – it just has to move on and find a new orbital! To summarize, then, because there are only two possibilities for the spin quantum number of an electron,

NO ATOMIC ORBITAL CAN CONTAIN MORE THAN TWO ELECTRONS!

Lesson Summary

- The Pauli Exclusion Principle states that 'no two identical fermions may occupy the same quantum state in an atom simultaneously'. That is, no two electrons in an atom can have n, ℓ, m_l and m_s all the same.
- No atomic orbital can contain more than two electrons.

Review Questions

1. Electrons in the same orbital must have different spin quantum numbers. What is true of the other three quantum numbers for two electrons in the same orbital? **(Intermediate)**

2. Electrons in different orbitals can have the same spin quantum numbers. What is true of the other three quantum numbers for two electrons in different orbitals? **(Beginning)**

3. Fill in the blank using either the word 'can', or 'cannot'. **(Beginning)**

a. An electron with the quantum numbers n = 1, ℓ = 0, m_l = 0 and m_s = +1/2 _____ exist in the same atom as an electron with the quantum numbers n = 2, ℓ = 0, m_l = 0 and m_s = +1/2

b. An electron with the quantum numbers n = 1, ℓ = 0, m_l = 0 and m_s = +1/2 _____ exist in the same atom as an electron with the quantum numbers n = 1, ℓ = 0, m_l = 0 and m_s = -1/2

4. Fill in the blanks using numbers. **(Intermediate)**

a. There is only 1 orbital at the n = 1 energy level. Therefore the n = 1 energy level can hold a maximum of __ electrons

b. There are 4 orbitals at the n = 2 energy level. Therefore the n = 2 energy level can hold a maximum of __ electrons

c. There are 9 orbitals at the n = 3 energy level. Therefore the n = 3 energy level can hold a maximum of __ electrons

d. There are 16 orbitals at the $n = 4$ energy level. Therefore the $n = 4$ energy level can hold a maximum of __ electrons

5. What is the maximum number of electrons that can exist in p orbitals at energy levels with $n < 3$. **(Intermediate)**

6. What is the maximum number of electrons that can exist in p orbitals at energy levels with $n < 5$. **(Intermediate)**

Further Reading / Supplemental Links

http://theory.uwinnipeg.ca/mod_tech/node168.html

http://en.wikipedia.org/wiki

Vocabulary

Pauli Exclusion Principle	No two fermions may occupy the same quantum state in an atom simultaneously; no two electrons in an atom can have the same four quantum numbers.

Review Answers

1. (they are the same)

2. (they differ in at least one of the three quantum numbers n, ℓ or m_l)

3.

(a) can

(b) can

4.

(a) 2

(b) 8

(c) 18

(d) 32

5. 6

6. 18

Aufbau Principle

Lesson Objectives

- Explain the Aufbau Principle.

- Given two different orbitals, predict which the electron will *choose* to go into.

Introduction

Everything in the universe is driven to *minimize* its potential energy. Previously we learned that heavy objects fall when they're dropped, because their total potential energy is lower on the ground than it is when they're hovering in the air. That's why Wile E. Coyote could drop an anvil on Road Runner – he knew that the anvil would fall, because falling would lower its potential energy. It's the same with a bowling ball placed on a hill. At the top of the hill, the bowling ball has more potential energy than it does at the bottom, so you can always bet on the bowling ball rolling down the hill rather than up the hill, because the bowling ball will always try to minimize its energy. In this chapter, we won't look at heavy objects like bowling balls and anvils. Instead, we'll look at tiny objects – we'll look at electrons. Even though electrons are much, much smaller than anvils and bowling balls, the same principle applies. An electron will do anything that it can to lower its potential energy.

Electrons are Found in Energy Levels with Increasingly Higher Energy

Whenever an electron is found inside an atom, it exists in what's known as an orbital. By now, you should know what an orbital is. An orbital describes a particular region of space within the atom where the electron is most likely to be found. While orbitals are important when it comes to figuring out an electron's probable location, they are equally important when it comes to figuring out an electron's energy. Electrons in different orbitals frequently have different energies. Of course, an electron is *never* going to "choose" to be in an orbital that has a higher energy if there's space available in an orbital that has a lower energy. It's a lot like you riding the bus. You would *never* choose to waste energy walking 20 miles to school provided there was space for you on the bus. If there wasn't any space on the bus, though, you may be *forced* to walk. It's the same with electrons.

Figure 2: If there's no room on the bus, you may be forced to walk. It's the same with electrons. If there's no room in a low energy orbital, they may be forced into a higher energy orbital. (*Source:* http://en.wikipedia.org/wiki/Image:HDaumierOmnibus.JPG, *License:* Public Domain)

If there isn't any space in a low energy orbital, an electron may be *forced* into a higher energy orbital. The fact that electrons always fill up lower energy orbitals first has important consequences when it comes to determining *which* orbitals contain electrons in any given atom.

Remember that the principal quantum number, n, is associated with the 'energy level' of the electron. Electrons with standing waves described by bigger values of n had higher energies, while electrons with standing waves described by smaller values of n had lower energies. If you were an electron, then, and you had the choice of being in an orbital with n = 1 or an orbital with n = 2, which would you choose? Obviously you'd choose to be in the orbital with n = 1, because it has a smaller value of n, and thus a lower energy (remember, both people and electrons prefer to be in states with lower energy).

Naturally, there is a limit to the total number of electrons that can exist in the same atom at the n = 1 energy level. In fact, it turns out that there can be at most two electrons with n = 1 in any given atom. That's because there is only one n = 1 orbital per atom. Of course, there are many atoms with more than two electrons. Lithium, for instance, has three. What happens to the electrons in an atom like lithium? Obviously, the first two electrons are going to occupy the single orbital that exists at the n = 1 energy level. Since this orbital only has room for two electrons, though, the third electron has to move up to the n = 2 energy level. In other words, electrons will fill up orbitals in order of increasing energy. If there's space at the n = 1 energy level, that space will be filled before any electrons move into the n = 2 energy level. Similarly, if there's space at the n = 2 energy level, that space will be filled before any electrons move into the n = 3 energy level.

In an Energy Level Electrons are Assigned to Sublevels with Increasingly Higher Energy

So far you know that an electron will always be found occupying the orbital in the first energy level, rather than the second energy level, provided that there is space available. Similarly, an electron will be found occupying the second energy level, rather than the third energy level, provided that there is space available. But what about electron sublevels? Among the orbitals with the same value of ***n*** , the s orbital will always be filled first, followed by the p orbitals (and then the d orbitals).

We can summarize these rules with the following statement: Electrons will fill available orbitals starting with those at the lowest energies before moving to those at higher energies. This statement is known as the **Aufbau Principle.** That may sound like a funny name, but 'aufbau' is actually the German word for 'construction', and the Aufbau Principle describes how the orbitals are 'constructed' by progressively adding electrons to higher and higher energy levels.

Before we move on and consider exactly how many electrons go into each energy level, and sublevel, it's important to point out how the energies of the electrons in an atom relate to the energy of the entire atom itself. If each electron tries to minimize its energy by going into the lowest energy orbital available, then the *total* energy of *all* the electrons in the atom is also as low as possible.

Let's compare electrons minimizing their energy in an atom to your relatives minimizing their energy consumption in your family. If you do your best to turn off the lights and save as much energy as possible, and your brother does his best to turn off the lights and save as much energy as possible, and your sister does her best to turn off the lights and save as much energy as possible, and your parents also do their best to turn off the lights and save as much energy as possible, then collectively, your entire family is saving as much energy as possible as well. It's the same with electrons. If the first electron fills the lowest energy orbital available to it, and the second electron fills the lowest energy orbital available to it, and the third electron fills the lowest energy orbital available to it, and the fourth electron also fills the lowest energy orbital available to it, then collectively, the entire atom is in the lowest energy state possible as well.

Just as you would prefer to minimize your energy by sleeping, or riding a bus, electrons minimize their energy by occupying the lowest energy orbital available to them and atoms minimize their energy by having all of their electrons in the lowest energy 'configuration' (arrangement) possible. Later, you will learn that practically all chemical processes rely on this same principle of energy minimization.

Lesson Summary

- In an atom, electrons will fill up orbitals in order of increasing energy.
- The principle quantum number determines the 'energy level' of the orbital. Orbitals with lower values of n are usually associated with lower energy and will be filled first.
- The azimuthal quantum number determines the 'sublevel' of the orbital.
- Orbitals with lower values of l (but the same value of n) are *always* associated with lower energy and will be filled first.
- The Aufbau Principle states that electrons will fill available orbitals starting with those at the lowest energies before moving to those at higher energies.
- Since each electron in an atom minimizes its energy, the energy of the entire atom is a minimum as well.

Review Questions

1. While we have talked about emission spectra, another type of spectra is known as absorption spectra. In emission spectra, the atom emits lines of light like those you saw in the examples of atomic spectra. In absorption spectra, the atom absorbs lines of light, rather than emitting them. Can you explain this in terms

of electrons and orbitals? What do you think the relationship between absorption spectra and emission spectra might be? **(Intermediate)**

2. If an electron has a ”choice” between going into an orbital in the n = 1 energy level or an orbital in the n = 2 energy level, which do you think it chooses? **(Beginning)**

3. If an electron in the n = 3 energy level has a “choice” between going into an orbital with ℓ = 0 or an orbital with ℓ = 1, which do you think it chooses? **(Beginning)**

4. Select the correct statement. **(Intermediate)**

According to the Aufbau Principle

a. orbitals with higher values of n fill up first

b. orbitals in the same energy level, but with higher values of l fill up first

c. orbitals with lower values of n fill up first

d. it is impossible to predict which orbitals will fill up first

5. Decide whether each of the following statements is true or false. **(Intermediate)**

a. Electrons in different orbitals have different energies.

b. An electron will enter an orbital of higher energy when a lower energy orbital is already filled.

c. For some atoms the first energy level can contain more than two electrons.

6. Does the electron in the hydrogen atom absorb or emit energy when it makes a transition between the following energy levels: **(Intermediate)**

a. n = 2 to n = 4

b. n = 6 to n = 5

c. n = 3 to n = 6

7. Fill in the blanks. There is one s orbital, three p orbitals, and five d orbitals in the n = 3 energy level of an atom. If a particular atom has a total of 5 electrons in the n = 3 energy level, then there are… **(Intermediate)**

a. ___ electrons in the s orbital

b. ___ electrons in p orbitals

c. ___ electrons in d orbitals

8. Fill in the blanks. There is one s orbital, three p orbitals, five d orbitals and 7 f orbitals in the n = 4 energy level of an atom. If a particular atom has a total of 7 electrons in the n = 4 energy level, then there are… **(Intermediate)**

a. ___ electrons in the s orbital

b. ___ electrons in p orbitals

c. ___ electrons in d orbitals

d. ___ electrons in f orbitals

Further Reading / Supplemental Links

http://www.iun.edu/~cpanhd/C101webnotes/modern-atomic-theory/aufbau-principle.html

http://www.avogadro.co.uk/light/aufbau/aufbau.htm

http://en.wikipedia.org/wiki

Vocabulary

Aufbau principle	Electrons will fill available orbitals starting with those at the lowest energy before moving to those at higher energies.

Review Answers

1. For emission spectra, electrons emit energy as they drop to lower levels; for absorption spectra, the electrons absorb energy as the go up to higher energy levels. The emission spectra is a black background with lines of light where quanta are emitted and absorption spectra are full spectrums with black lines where have been absorbed..

2. (n = 1, minimizes energy)

3. (l = 0, minimizes energy)

4. c

5. (a) true (b) true (c) false

6. (a) absorb (b) emit (c) absorb

7. (a) 2 (b) 3 (c) 0

8.

(a) 2

(b) 5

(c) 0

(d) 0

Writing Electron Configurations

Lesson Objectives

- Figure out how many electrons can exist at any given sublevel.
- Figure out how many different sublevels can exist at any given energy level.
- Be able to write electron configuration of any element given the total number of electrons in that element.

- Be able to write either orbital representations or electron configuration codes.

Introduction

It's pretty easy to say 'electrons will fill the lowest available energy orbital'. Figuring out what that lowest available energy orbital is, though, can be quite a challenge. In this lesson, we're going to try to decide *exactly which* orbitals get filled, and when. Most people who are just beginning to learn about quantum chemistry tend to find orbital filling problems very confusing, so we'll take it slowly, and show you how diagrams and rules can help you to remember the ways in which different orbitals are organized and filled

Electron Configurations

How do electrons fill the different energy levels, energy sublevels, and orbitals? To understand that question, it helps a lot to look at a diagram. Figure 1 shows the first three energy levels (marked by the large differently colored blocks), and the sublevels (separated by dotted lines) that are present in any atom. In Figure 1, each of the circles represents an orbital and, of course, each can hold a total of two electrons. Notice the red n = 1 block contains only an s orbital. That orbital will hold the first two electrons in the atom. Once the red n = 1 block is entirely filled, electrons will start filling the orange n = 2 block. In the orange n = 2 block, there are four different orbitals. The first orbital is an s orbital and the other three are p orbitals. Once all four orbitals in the orange n = 2 block have been filled, electrons will start filling the yellow n = 3 block. In the yellow n = 3 block, there are nine different orbitals. The first orbital is an s orbital, the next three are p orbitals, and the last five are d orbitals. When filling the n = 3 block, the s sublevel will always be filled first, since it is lowest in energy. Again, it can hold at most 2 electrons. After that, the next six will fill the three p orbitals

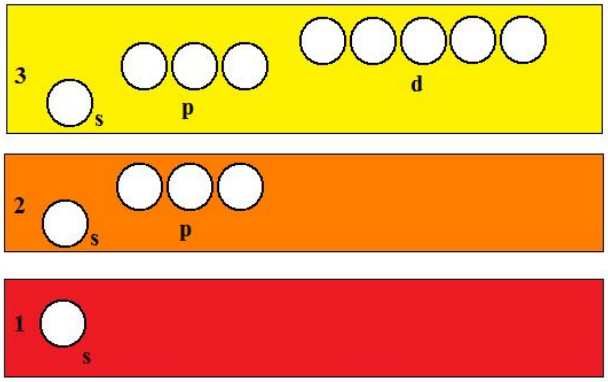

Figure 1: These are the first three energy levels with their sub-levels.

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So far we've talked about filling the orbitals in Figure 1 up to the 3p orbitals. That's a total of 18 electrons. The first 18 electrons are 'nice and easy', because they fill the orbitals in order. First, all of the n = 1 orbitals get filled, then all of the n = 2 orbitals get filled, then the n = 3 orbitals get filled. From the 19th electron on, though, things get a little crazy! Before we move on to the that region beyond 18 electrons, let's take a brief look at a shorthand notation that scientists use to signify the electron orbital filling of a given atom.

Since orbitals are filled in order of increasing n and, within each energy level, in order of increasing ℓ , scientists can use a short hand, known as the electron configuration code, to represent filled orbitals. To write the electron configuration code for an atom, you write the symbol for the type of orbital present at a particular sublevel (1s, 2s, 2p, etc.) followed by a superscript to indicate how many electrons are actually in that sublevel in the atom you are describing. Let's take a look at a few examples.

Example 1:

Nitrogen has 7 electrons. Write the electron configuration for nitrogen.

Take a close look at Figure 1, and use it to figure out how many electrons go into each sublevel, and also the order in which the different sublevels get filled.

1. Begin by **filling up the 1s sublevel.** This gives **$1s^2$** . Now all of the orbitals in the red n = 1 block are filled.

Since we used 2 electrons, there are 7 – 2 = 5 electrons left

2. Next, **fill the 2s sublevel.** This gives **$1s^22s^2$** . Now all of the orbitals in the s sublevel of the orange n = 2 block are filled.

Since we used another 2 electrons, there are 5 – 2 = 3 electrons left

3. Notice that we haven't filled the entire n = 2 block yet… there are still the p orbitals! The final 3 electrons **go into the 2p sublevel.** This gives **$1s^22s^22p^3$**

The overall electron configuration is: $1s^22s^22p^3$.

Overlapping Energy Levels

If you had to guess, which orbital do you think would be filled after the 3p orbitals? Most likely you'd guess that the 3d orbitals would come next – and that guess makes a lot of sense. Unfortunately, that guess is also wrong! It turns out that the **4s orbitals are filled *before* the 3d orbitals,** even though the 4s orbitals have n = 4 and the 3d orbitals only have n = 3.

How is that possible? Does it mean that electrons go into higher energy orbitals before completely filling the lower energy orbitals? Is there something wrong with those electrons? Are certain electrons prevented from entering low energy orbitals? What's going on?

It turns out that there's nothing wrong with those 4s electrons at all. They're still behaving like normal electrons and they're still going into the lowest energy orbital available. The only difference is that **the 4s orbital is a *lower in energy* than the 3d orbitals**. Sometimes, we get tricked into thinking that the principal quantum number determines which orbitals will get filled first. When it comes to the order in which orbitals are filled, though, the principal quantum number isn't the only factor – what also matters is the energy of the orbital. Usually orbitals with lower principal quantum numbers have lower energies, but that isn't the case when you compare the energies of the 3d orbitals and the energies of the 4s orbitals. In this case, the 4s orbitals are lower in energy than the 3d orbitals *even though* they have higher principal quantum numbers. Figure 2 shows is a modified version of Figure 1, which shows the n = 4 orbital positions. Let's take a look at an example of an electron where some n = 4 orbitals are filled.

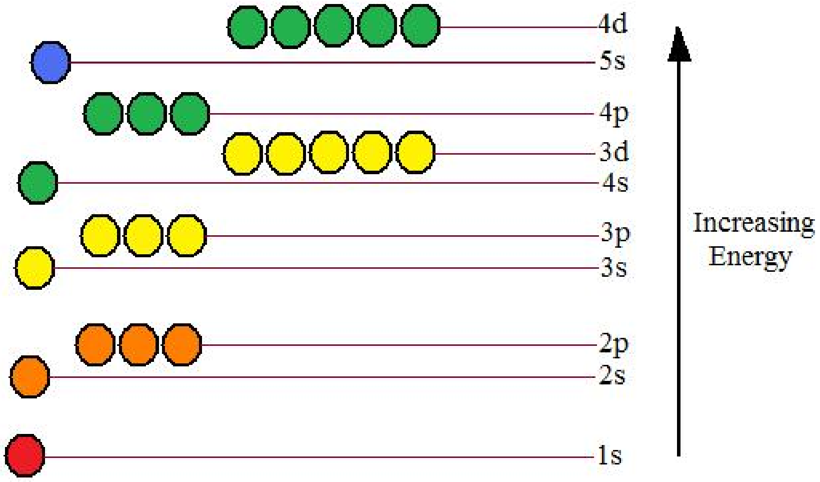


Figure 2: Notice that the s orbital from the next higher energy level has slightly lower energy than the d orbitals in the lower energy level.

(*Source: Created by:* Richard Parsons, *License:* CC-BY-SA)

Example 2:

Potassium has 19 electrons. Write the electron configuration code for potassium.

This time, take a close look at Figure 2.

1. Begin by **filling up the 1s sublevel.** This gives **$1s^2$** . Now the n = 1 level is filled. Since we used 2 electrons, there are 19 – 2 = 17 electrons left

2. Next, **fill the 2s sublevel.** This gives **$1s^2 2s^2$**

Since we used another 2 electrons, there are 17 – 2 = 15 electrons left

3. Next, **fill the 2p sublevel.** This gives **$1s^2 2s^2 2p^6$.** Now the n = 2 level is filled. Since we used another 6 electrons, there are 15 – 6 = 9 electrons left

4. Next, **fill the 3s sublevel**. This gives **$1s^2 2s^2 2p^6 3s^2$**

Since we used another 2 electrons, there are 9 – 2 = 7 electrons left

5. Next, **fill the 3p sublevel.** This gives **$1s^2 2s^2 2p^6 3s^2 3p^6$**

Since we used another 6 electrons, there are 7 – 6 = 1 electron left

Here's where we have to be careful – right after $3p^6$!

Remember, 4s comes before 3d!

6. The final electron **goes into the 4s sublevel**. This gives **$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$**

The overall electron configuration code is: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$.

The Diagonal Rule

Unfortunately, 4s orbitals aren't the only ones that get filled earlier than you'd expect based on their principal quantum number. The same turns out to be true of the 5s orbitals as well. Even though 5s orbitals have a higher principal quantum number than 4d orbitals, (n = 5 compared to n = 4), they're actually *lower* in energy. As a result, 5s orbitals are always filled *before* 4d orbitals. Similarly, 6s orbitals are lower in energy than 5d orbitals, so 6s orbitals are always filled first. The story gets even stranger when you consider f orbitals. 5s, 5p *and* 6s orbitals are *all* lower than 4f orbitals. In other words, before you can get an electron into a 4f orbital, you must first fill up the 5s orbitals, *and* the 5p orbitals *and* the 6s orbitals!

Filling up orbitals and writing electron configurations was so easy for atoms with less than 18 electrons! But for atoms with more than 18 electrons, it seems hopeless to memorize all of the different rules. How will you ever get straight whether the 5s orbital is higher or lower than the 4d orbital or the 4f orbital? Thankfully, there's a simple rule known as the diagonal rule. The diagonal rule states that: Electrons fill orbitals in order of increasing 'quantum number sum' ($n + \ell$). When two orbitals share the same quantum number sum, they will be filled in order of increasing n.

Luckily, the diagonal rule also has a diagram that's easy to remember, and that allows you to easily figure out the order in which electron orbitals are filled. Figure 1 shows the diagram. In order to use it, you must follow the arrows from tail-to-tip, starting with the first arrow in the upper left-hand corner, and working your way down through the arrows to the lower right-hand corner of the diagram. To see how this works, let's take a look at an example.

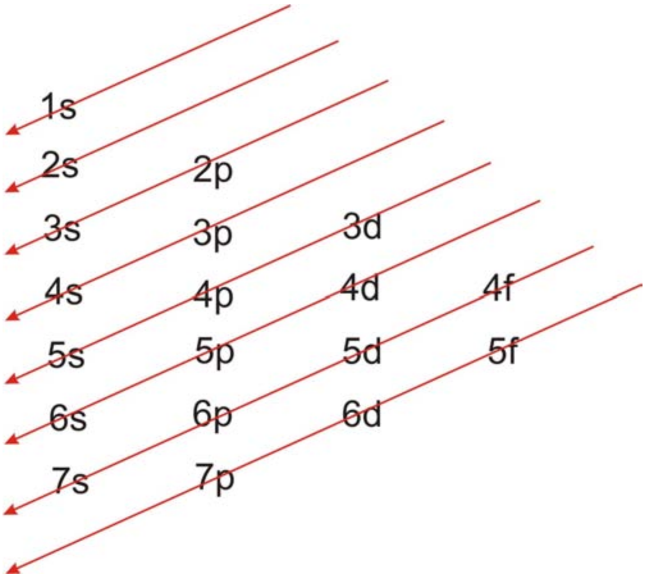


Figure 1: The diagonal rule.

Example 3:

Hafnium has 72 electrons. Write the electron configuration for hafnium.

We can follow the arrows in the diagram (as shown below), until we have assigned all 72 electrons.

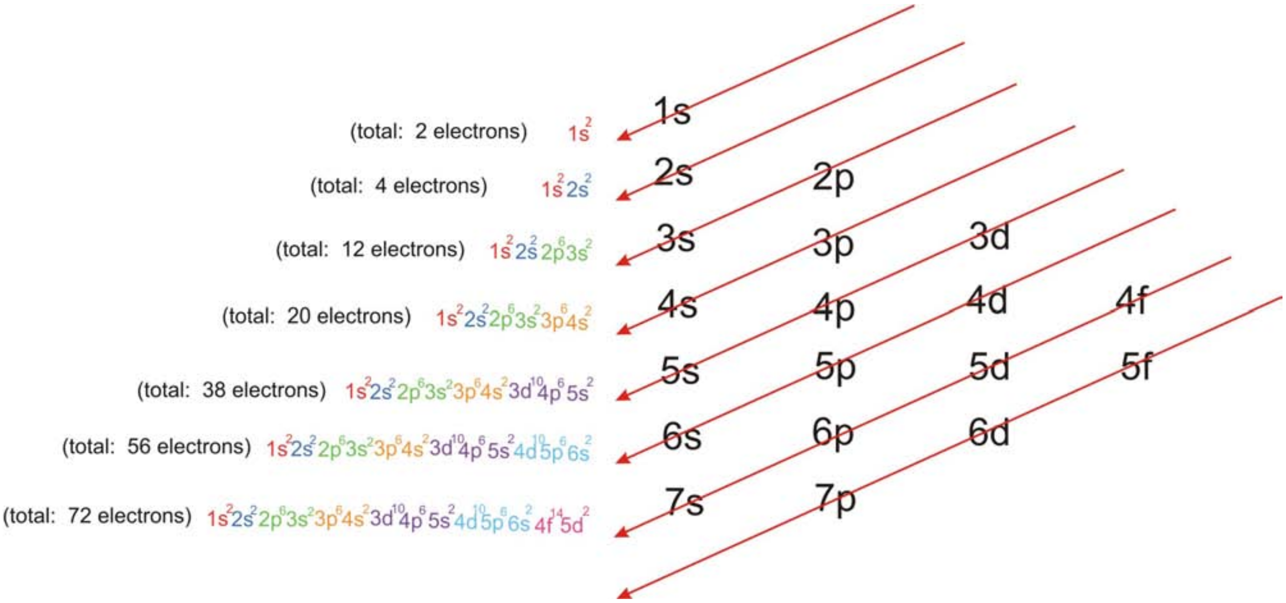


Figure 2: Notice how you fill orbitals as you progress along the arrows, starting from the top arrow and moving down. Remember to stop once you hit 72. At that point, you have finished writing the electron configuration for Hafnium.

Now that we know how electrons are assigned to orbitals, we can start to talk about how different orbitals, and different electron configurations actually affect the chemical properties of different atoms. In other words, we can actually start to talk about chemistry! Sometimes it seems that quantum physics and quantum chemistry are very far removed from the real world chemistry that we see and use in every day life. How are orbitals important when it comes to developing new drugs to treat cancer? How are energy levels important when it comes to inventing different kinds of superconductors or plastics? How are electron standing waves important when it comes to testing for toxins in your food? All of these processes are determined by chemical properties which are, themselves, a direct result of how electrons are arranged, and interact within different atoms and molecules. Sometimes it is easy to forget about the electrons, and some of the strange quantum properties of subatomic particles. Nevertheless, we will never be able to fully understand chemistry, if we don't understand its smallest components – components like electrons, protons, neutrons and, of course, the atom.

Lesson Summary

- For any atom with less than 18 electrons, orbitals are filled in order of increasing n and, for any given n, in order of increasing ℓ .
- Electron configurations are a shorthand notation for representing the filled orbitals in a given atom. They are written using the principal quantum number, n, for the energy level, the letter (s, p, d or f) for the sublevel, and a superscript for the number of electrons in that sublevel.
- For atoms with more than 18 electrons, the orbitals are filled in order of increasing n (and in order of increasing ℓ for a given n) *up to* the 18th electron; however *after* the 18th electron the 4s orbital are filled before the 3d orbitals. This is because the 4s orbital has lower energy than the 3d orbital.
- The diagonal rule states that electrons fill orbitals in order of increasing 'quantum number sum' ($n + \ell$). When two orbitals share the same 'quantum number sum', they will be filled in order of increasing n .

Review Questions

1. Write the electron configuration for beryllium. Beryllium has 4 electrons. **(Intermediate)**

2. Write the electron configuration for silicon. Silicon has 4 electrons. **(Intermediate)**

3. Write the electron configuration for nitrogen. Nitrogen has 7 electrons. **(Intermediate)**

4. Write the electron configuration for chromium. Chromium has 24 electrons. **(Challenging)**

5. Write the electron configuration for silver. Silver has 47 electrons. **(Challenging)**

Further Reading / Supplemental Links

Website with lessons, worksheets, and quizzes on various high school chemistry topics.

- Lesson 3-1 is on the Development of the Atomic Theory.
- Lesson 3-2 is on the Development of the Atomic Model.
- Lesson 3-3 is on Atomic Structure.
- Lesson 3-4 is on the Periodic Table.
- Lesson 3.6 is on Electron Configuration.

http://www.fordhamprep.org/gcurran/sho/sho/lessons/lesson31.htm

Vocabulary

electron configuration	A short hand notation to indicate the electron orbitals which are filled in a particular atom.
diagonal rule	The electrons fill orbitals in order of increasing ‘quantum number sum’ (**n** + ℓ). When two orbitals share the same ‘quantum number sum’, they will be filled in order of increasing n.
quantum number sum	The sum of the principal quantum number, n, and the azimuthal quantum number, l, for an electron. That is n + l.

Review Answers

1. $1s^2 2s^2$

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

3. $1s^2 2s^2 2p^3$

4. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^4$

5. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^9$

8. Electron Configurations and the Periodic Table

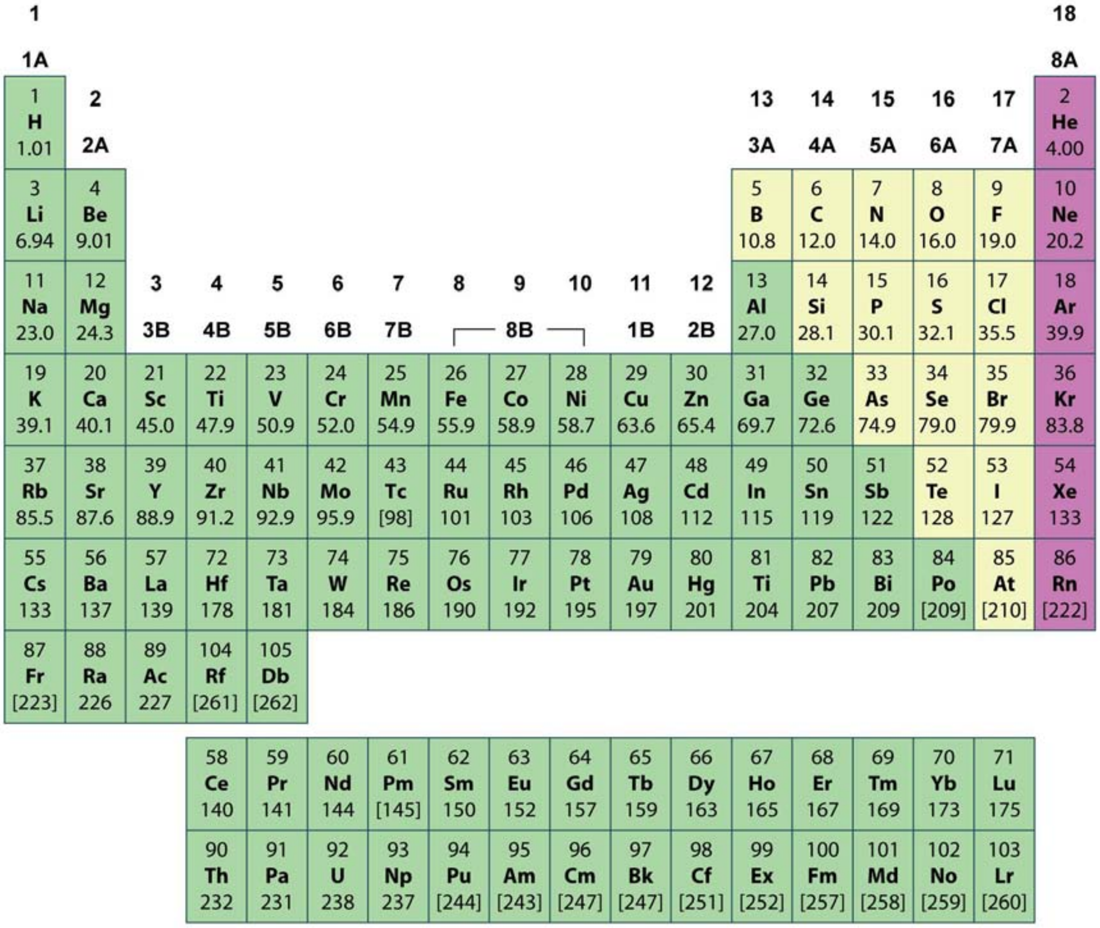
Electron Configurations of Main Group Elements

Lesson Objectives

- Explain how the elements in the Periodic Table are organized into rows and columns.
- Explain how the electron configurations within a column are similar to each other.

Introduction

It probably seems like all we've been spending a lot of time learning about protons… and neutrons… and electrons… and electrons… and more electrons… so you might be wondering – when do we actually get to study *chemistry*? When do we get to study *reactions*? When do we get to study *explosions*? When do we get to study plastics, and medicines that can be made by combining different kinds of *chemicals*? The answer is *now*. We're finally ready to discuss the chemical properties of the simplest chemicals out there – we're finally ready to discuss the elements. Remember, you have learned that there were 117 different kinds of atoms, and that each was known as an element. And you have learned that atoms of different elements have different numbers of protons. Hydrogen has 1 proton (and 1 electron if it's neutral), helium has 2 protons (and 2 electrons, if it's neutral), and lithium has 3 protons (and 3 electrons, if it's neutral). Finally, you have seen examples of the Periodic Table. Scientists use the Periodic Table to summarize information about all of the known elements that exist in our world.



1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8	9 8B	10	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1 **H** 1.01																	2 **He** 4.00
3 **Li** 6.94	4 **Be** 9.01											5 **B** 10.8	6 **C** 12.0	7 **N** 14.0	8 **O** 16.0	9 **F** 19.0	10 **Ne** 20.2
11 **Na** 23.0	12 **Mg** 24.3											13 **Al** 27.0	14 **Si** 28.1	15 **P** 30.1	16 **S** 32.1	17 **Cl** 35.5	18 **Ar** 39.9
19 **K** 39.1	20 **Ca** 40.1	21 **Sc** 45.0	22 **Ti** 47.9	23 **V** 50.9	24 **Cr** 52.0	25 **Mn** 54.9	26 **Fe** 55.9	27 **Co** 58.9	28 **Ni** 58.7	29 **Cu** 63.6	30 **Zn** 65.4	31 **Ga** 69.7	32 **Ge** 72.6	33 **As** 74.9	34 **Se** 79.0	35 **Br** 79.9	36 **Kr** 83.8
37 **Rb** 85.5	38 **Sr** 87.6	39 **Y** 88.9	40 **Zr** 91.2	41 **Nb** 92.9	42 **Mo** 95.9	43 **Tc** [98]	44 **Ru** 101	45 **Rh** 103	46 **Pd** 106	47 **Ag** 108	48 **Cd** 112	49 **In** 115	50 **Sn** 119	51 **Sb** 122	52 **Te** 128	53 **I** 127	54 **Xe** 133
55 **Cs** 133	56 **Ba** 137	57 **La** 139	72 **Hf** 178	73 **Ta** 181	74 **W** 184	75 **Re** 186	76 **Os** 190	77 **Ir** 192	78 **Pt** 195	79 **Au** 197	80 **Hg** 201	81 **Ti** 204	82 **Pb** 207	83 **Bi** 209	84 **Po** [209]	85 **At** [210]	86 **Rn** [222]
87 **Fr** [223]	88 **Ra** 226	89 **Ac** 227	104 **Rf** [261]	105 **Db** [262]													

58 **Ce** 140	59 **Pr** 141	60 **Nd** 144	61 **Pm** [145]	62 **Sm** 150	63 **Eu** 152	64 **Gd** 157	65 **Tb** 159	66 **Dy** 163	67 **Ho** 165	68 **Er** 167	69 **Tm** 169	70 **Yb** 173	71 **Lu** 175
90 **Th** 232	91 **Pa** 231	92 **U** 238	93 **Np** 237	94 **Pu** [244]	95 **Am** [243]	96 **Cm** [247]	97 **Bk** [247]	98 **Cf** [251]	99 **Ex** [252]	100 **Fm** [257]	101 **Md** [258]	102 **No** [259]	103 **Lr** [260]

Figure 1: The Periodic Table – in this lesson, you will learn why the Periodic Table has such an unusual shape.

(*Source:* CK-12 Foundation, *License:* Public Domain)

Now, what's the first thing you thought when you saw the Periodic Table? If you're like most people, the first thing you thought was probably something like, 'Wow – that's a funny shape! Why is the Periodic Table shaped like that? Why is it lower in the middle? Why is it higher on either end? Why is there that odd-looking disconnected piece at the bottom? The Periodic *Table* doesn't look like a *table* at all!' In this chapter, you'll begin to see why the Periodic Table has such a funny shape. It turns out that the shape of the Periodic Table actually helps to tell us about the chemical properties of the different elements that exist in our world. In this section, for example, you'll learn that elements in the same column of the Periodic Table have similar chemical properties. Later we'll take a look at how elements in the same row are related.

Group 1A Elements Have One s Electron

Remember that according to the *Aufbau* principle electrons are added to low energy orbitals first and then, as the low energy orbitals are filled up, electrons go into higher and higher energy orbitals. When one atom reacts with another atom in a chemical reaction, it's the high-energy electrons that are involved.

Since it's only the high-energy electrons that participate in a chemical reaction, it's only the high-energy electrons that we will concern us when we want to determine the chemical properties of a particular element. Just how 'high' in energy does an electron need to be to participate in a chemical reaction? Well, in most chemical reactions, the only electrons involved are the electrons in the *highest energy level.* In other words, the electrons with the highest value of n (the principal quantum number), participate in chemical reactions, while the electrons with lower values of n are called "core electrons", are closer to the nucleus and, as a result, don't get involved. The electrons with the highest value of n are known as *valence* electrons. Core electrons are also referred as *non-valence electrons.* Two **different elements** have **similar chemical properties** when they have the **same number of valence electrons** in their outermost energy level.

Elements in the same *column* of the Periodic Table have similar chemical properties. So what does that mean about their valence electrons? You guessed it! Elements in the same *column* of the Periodic Table have the same number of valence electrons – that's *why* they have similar chemical properties. Let's see if this is true for some of the elements in the first column of the Periodic Table.

Example 1:

Write the electron configuration for hydrogen (H).

First, you need to find hydrogen on the Periodic Table. Take a look at the Periodic Table in Figure 1. You know that hydrogen is in the first column, and if you look carefully, you'll see that hydrogen also happens to be at the top of the first column. The Periodic Table tells you that the atomic number for hydrogen is Z = 1, thus hydrogen has 1 proton. Neutral hydrogen will also have 1 electron. You need to write the electron configuration for an atom with 1 electron.

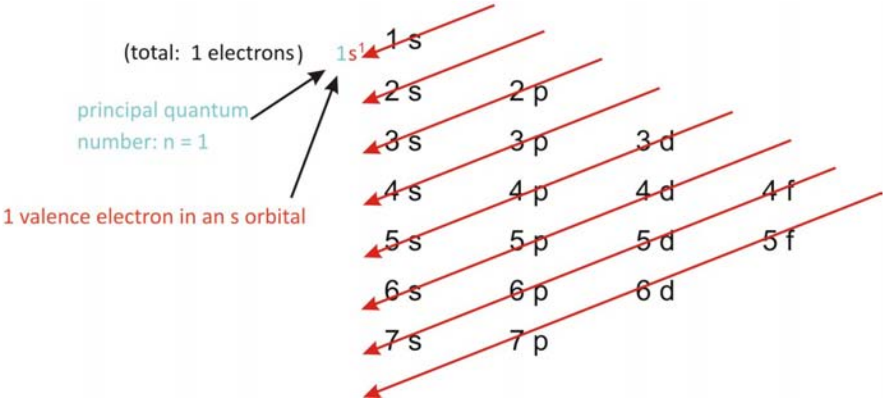


Figure 2: The diagonal rule applied to hydrogen (H).

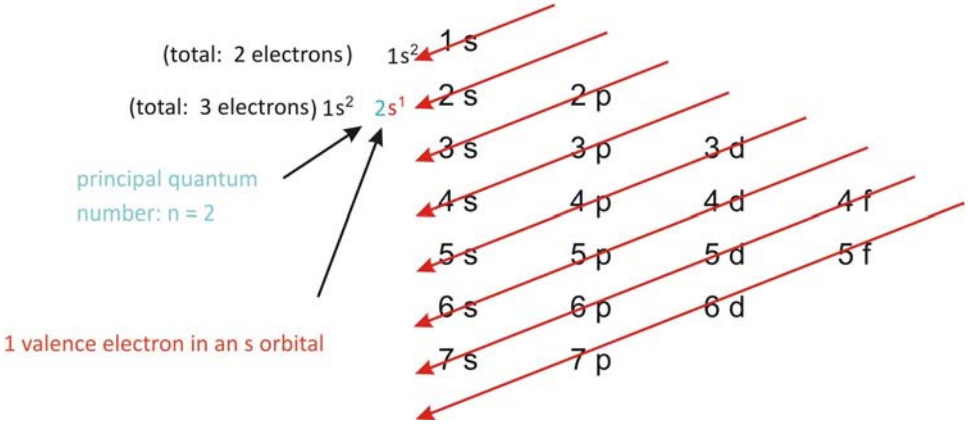
Therefore we write the electron configuration for H: $1s^1$.

Remember, when you write electron configurations, the number out in front always indicates the principal quantum number, ***n***, of a particular orbital, thus $1s^2$ has n = 1, while $3s^1$ has ***n*** = 3. What is the *highest* principal quantum number that you see in hydrogen's electron configuration? It's ***n*** = 1, so all electrons with ***n*** = 1 are valence electrons. ***Hydrogen has 1 valence electron in an s orbital.***

Example 2:

Write the electron configuration for lithium (Li).

First, you find lithium on the Periodic Table. The Periodic Table tells you that the atomic number for lithium is Z = 3, thus lithium has 3 protons. Neutral lithium will also have 3 electrons. You need to write the electron configuration for an atom with 3 electrons.



non-valence electrons: $1s^2$

Figure 3: The diagonal rule applied to lithium (Li).

Therefore we write the electron configuration for Li: $1s^2\ 2s^1$.

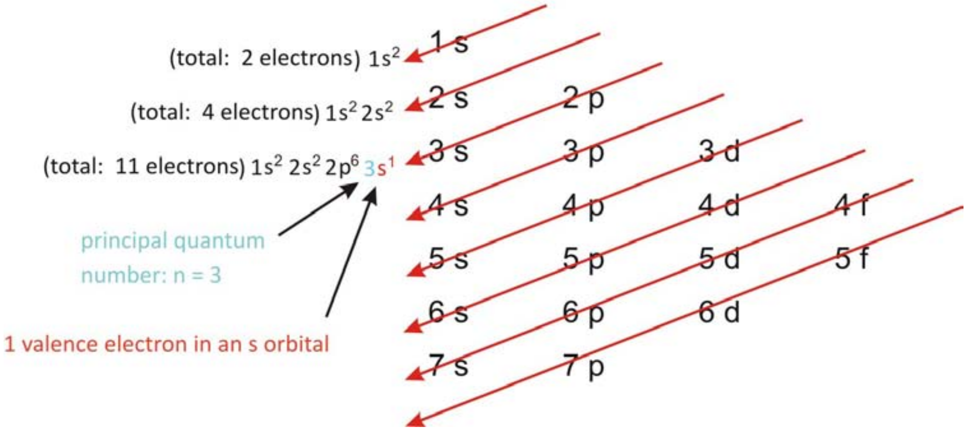
What is the *highest* principal quantum number that you see in lithium's electron configuration?

It's ***n = 2***, so all electrons with ***n*** = 2 are valence electrons, and all electrons with n < 2 are non-valence electrons. ***Lithium has 1 valence electron in an s orbital.***

Example 3:

Write the electron configuration for sodium (Na).

First, you find sodium on the Periodic Table. The Periodic Table tells you that the atomic number for sodium is Z = 11, thus sodium has 11 protons. Neutral sodium will also have 11 electrons. You need to write the electron configuration for an atom with 11 electrons.



non-valence electrons: $1s^2 2s^2 2p^6$

Figure 4: The diagonal rule applied to sodium (Na).

Therefore we write the electron configuration for Na: $1s^2\ 2s^2\ 2p^6\ 3s^1$.

What is the *highest* principal quantum number that you see in sodium's electron configuration?

It's ***n*** = 3, so all electrons with ***n*** = 3 are valence electrons, and all electrons with n < 3 are non-valence electrons. (Don't be fooled by the $2p^6$ orbitals. Even though they are p orbitals, not s orbitals, they have ***n*** = 2, so they are **non-valence** electrons!) ***Sodium has 1 valence electron in an s orbital.***

If you look at the last line in Example 1, Example 2, Example 3 you should notice a pattern.

Hydrogen ***has 1 valence electron in an s orbital***
Lithium ***has 1 valence electron in an s orbital***
Sodium ***has 1 valence electron in an s orbital***

In fact, all elements in the **first column** of the Periodic Table have ***1 valence electron in an s orbital.*** Therefore, we would expect all of these elements to have similar chemical properties – and they do. (Hydrogen is special because it is the *first* element in the Periodic Table. As a result, hydrogen has only *one* proton and *one* electron, which give it special chemical properties. Sometimes scientists don't include hydrogen in the first column of the Periodic Table, but instead give it its own 'special' column to reflect its special properties – we won't do that here, but you should realize that hydrogen does *not* have all the same chemical properties as the rest of the elements in its column).

The elements in the first column of the Periodic Table (other than hydrogen) are known as **Group 1A metals,** or **Alkali Metals.** When you compare the chemical properties of these elements (lithium, sodium, potassium, rubidium, cesium and francium), what you'll notice is that they are all remarkably similar. Group 1A elements are metals, silver-colored and soft. These elements are *extremely* reactive. Several of them explode if you put them in water.

Figure 5: Notice how the elements lithium (Li), sodium (Na) and potassium (K) all look alike. They are all soft, silver metals. Since Li, Na and K are all Group 1A metals, they all share similar chemical properties.

(*Sources:* http://en.wikipedia.org/wiki/Image:Limetal.jpg, *License:* CC-SA; http://en.wikipedia.org/wiki/Image:Nametal.jpg, *License:* CC-SA; http://en.wikipedia.org/wiki/Image:Kmetal.jpg, *License:* CC-SA)

And finally, because they are so reactive, Group 1A elements are not found in their elemental form in nature – in other words, you don't find *pure* sodium or *pure* potassium in nature.

non-valence electrons: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$

Figure 6: The diagonal rule applied to rubidium (Rb).

Group 2A Elements Have Two s Electrons

All of the elements in the first column of the periodic table have 1 valence electron in an s sublevel. How do you think the elements in the second column of the periodic table differ? Let's find out by taking a look at a few examples.

Example 4:

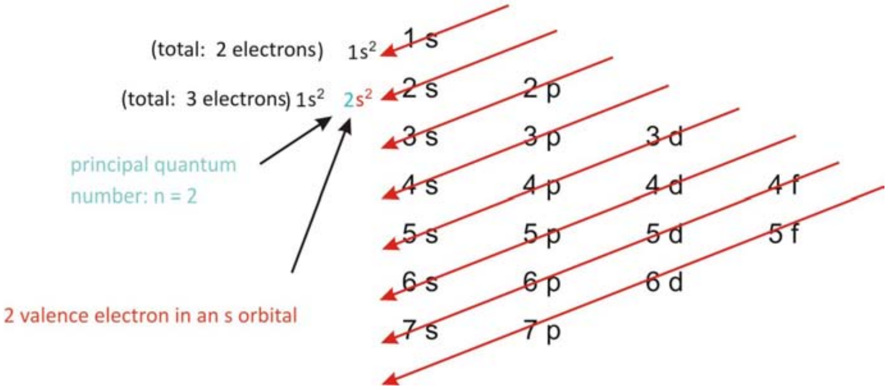
Write the electron configuration for beryllium (Be).

First, you find beryllium on the Periodic Table. The Periodic Table tells you that the atomic number for beryllium is Z = 4, thus beryllium has 4 protons. Neutral beryllium will also have 4 electrons. You need to write the electron configuration for an atom with 4 electrons.

Therefore we write the electron configuration for Be: $1s^2\ 2s^2$

What is the *highest* principal quantum number that you see in beryllium's electron configuration?

It's n = 2, so all electrons with n = 2 are valence electrons, and all electrons with n < 2 are non-valence electrons. ***Beryllium has 2 valence electrons in an s orbital.***



non-valence electrons: $1s^2$

Figure 7: The diagonal rule applied to beryllium (Be).

Example 5:

Write the electron configuration for magnesium (Mg).

First, you find magnesium on the Periodic Table. The Periodic Table tells you that the atomic number for magnesium is Z = 12, thus magnesium has 12 protons. Neutral magnesium will also have 12 electrons. You need to write the electron configuration for an atom with 12 electrons.

Therefore the electron configuration for Mg: $1s^2\ 2s^2 2p^6\ 3s^2$.

What is the *highest* principal quantum number that you see in strontium's electron configuration?

It's n = 3, so all electrons with n = 3 are valence electrons, and all electrons with n < 3 are non-valence electrons. ***Magnesium has 2 valence electrons in an s orbital.***

Notice that:

Beryllium ***has 2 valence electrons in an s orbital***
Magnesium ***has 2 valence electrons in an s orbital***

You can probably guess the number and type of valence electrons in an atom of calcium (Ca), strontium (Sr), barium (Ba) or radium (Ra). If you guessed 2 electrons in an s orbital, then you guessed right! *All* elements in the **second column** of the Periodic Table have ***2 valence electrons in an s orbital.*** The elements in the second column of the Periodic Table are known as **Group 2A metals,** or **Alkaline Earth Metals.** As you might expect, because all Group 2A metals have 2 valence electrons in an s orbital, they all share similar chemical properties. Group 2A elements are metals, silver colored and are quite reactive though they are not nearly as reactive as the Group 1A elements.

Figure 9: Sports drinks frequently contain the electrolyte calcium chloride. (*Source:* CK-12 Foundation, *License:* SA-BY-CC)

Group 3A Elements Have 2 s and 1 p Electrons

All of the elements in the first column of the periodic table have 1 valence electron in an s sublevel and all of the elements in the second column of the periodic table have 2 valence electrons in an s sublevel. Can you make any prediction about the valence electrons in the third column of the periodic table? Where is the third column of the periodic table? It turns out that there are really two different ‘third columns’ in the Periodic Table. Take a close look at Figure 1. Can you spot the column labeled ‘3A’? Can you spot the column labeled ‘3B’? Notice that the smallest atom in the ‘3B’ column has Z = 21 (Scandium, Sc), while the smallest atom in the ‘3A’ column has Z = 5 (Boron, B). [You need to note that there is an alternate way to name 3A elements; the can also be referred to as group 13 since these elements are in the 13th column of the periodic table]. Therefore, it obviously makes sense to discuss the 3A column first. Let’s figure out how many valence electrons atoms in the 3A column have:

Example 6:

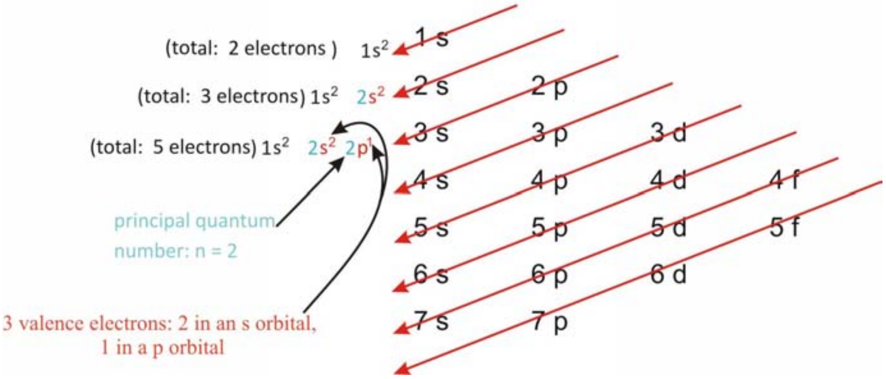
Write the electron configuration for boron (B).

The Periodic Table tells you that the atomic number for boron is Z = 5, thus boron has 5 protons. Neutral boron will also have 5 electrons. You need to write the electron configuration for an atom with 5 electrons.

Therefore the electron configuration for B: $1s^2\ 2s^2\ 2p^1$

What is the *highest* principal quantum number that you see in boron’s electron configuration?

It’s n = 2, so all electrons with n = 2 are valence electrons, and all electrons with n < 2 are non-valence electrons. Both the electron in the 2p orbital *and* the electrons in the 2s orbital are valence electrons. ***Boron has 2 valence electrons in an s orbital, and 1 valence electron in a p orbital, for a total of 3 valence electrons.***



non-valence electrons: $1s^2$

Figure 10: The diagonal rule applied to boron (B).

Example 7:

Write the electron configuration for aluminum (Al).

The Periodic Table tells you that the atomic number for aluminum is Z = 13; thus neutral aluminum has 13 protons and 13 electrons. You need to write the electron configuration for an atom with 13 electrons.

Therefore the electron configuration for Al: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$

What is the *highest* principal quantum number that you see in aluminum's electron configuration?

It's n = 3, so all electrons with n = 3 are valence electrons, and all electrons with n < 3 are non-valence electrons. Both the electron in the 3p orbital *and* the electrons in the 3s orbital are valence electrons. ***Aluminum has 2 valence electrons in an s orbital, and 1 valence electron in a p orbital, for a total of 3 valence electrons.***

From Example 7 and Example 8, we have:

Boron	***has 2 valence electrons in an s orbital and 1 valence electron in a p orbital***
Aluminum	***has 2 valence electrons in an s orbital and 1 valence electron in a p orbital***

In fact, *all* elements in the **3A column** of the Periodic Table have ***2 valence electrons in an s orbital and 1 valence electron in a p orbital.*** That's a total of 3 valence electrons for atoms in the 3A column. Again, the chemical properties of 3A elements are similar, because they have the same number and type of valence electrons.

Group 4A-8A Continue to Add p Electrons to the Outermost Energy Level

By now, you may have noticed a pattern relating the number of valence electrons to the column number. Group **1**A elements have **1** valence electron. Group **2**A elements have **2** valence electrons. Group **3**A elements have **3** valence electrons. Group **4**A elements have… well, we haven't looked at them yet, but what would you guess? It's pretty obvious. Group **4**A elements have **4** valence electrons. Similarly, Group **5**A elements have **5** valence electrons. In fact, the pattern continues all the way up to Group **8**A elements, which have **8** valence electrons. Let's take a look at a few examples in order to figure out exactly what types of valence electrons are involved. First, we'll consider a Group 4A element.

Example 8:

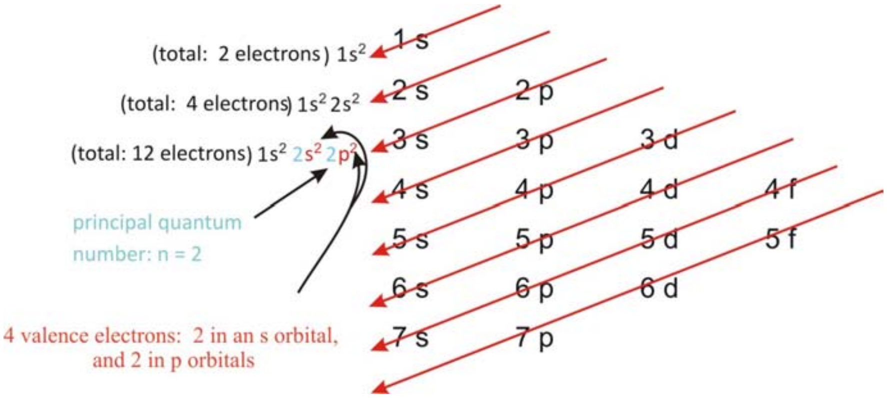
Write the electron configuration for carbon (C).

The Periodic Table tells you that the atomic number for carbon is Z = 6, thus neutral carbon has 6 protons and 6 electrons. You need to write the electron configuration for an atom with 6 electrons.

Therefore the electron configuration for C: $1s^2\ 2s^2\ 2p^2$.

What is the *highest* principal quantum number that you see in carbon's electron configuration?

It's n = 2, so all electrons with n = 2 are valence electrons, and all electrons with n < 2 are non-valence electrons. Both the electrons in the 2p orbitals *and* the electrons in the 2s orbital are valence electrons. ***Carbon has 2 valence electrons in an s orbital, and 2 valences electron in p orbitals, for a total of 4 valence electrons.***



non-valence electrons: $1s^2$

Figure 12: The diagonal rule applied to carbon (C).

Now let's consider a Group 5A element.

Example 9:

Write the electron configuration for nitrogen (N).

The Periodic Table tells you that the atomic number for nitrogen is Z = 7, neutral nitrogen has 7 protons and 7 electrons. You need to write the electron configuration for an atom with 7electrons.

Therefore the electron configuration for N: $1s^2\ 2s^2\ 2p^3$.

What is the highest principal quantum number that you see in phosphorus's electron configuration? It's n = 2, so all electrons with n = 2 are valence electrons, and all electrons with n < 2 are non-valence electrons. Both the electrons in the 2p orbitals *and* the electrons in the 2s orbital are valence electrons. ***Nitrogen has 2 valence electrons in an s orbital, and 3 valence electrons in p orbitals for a total of 5 valence electrons.***

As a final example, let's take a look at a Group 6A element (or Group 16).

Example 10:

Write the electron configuration for oxygen (O).

The Periodic Table tells you that the atomic number for oxygen is Z = 8; neutral oxygen has 8 protons and 8 electrons. You need to write the electron configuration for an atom with 8 electrons.

Therefore the electron configuration for O: $1s^2\ 2s^2 2p^4$.

What is the *highest* principal quantum number that you see in oxygen 's electron configuration?

It's n = 2, so all electrons with n = 2 are valence electrons, and all electrons with n < 2 are non-valence electrons. Both the electrons in the 2p orbitals *and* the electrons in the 2s orbital are valence electrons. ***Oxygen has 2 valence electrons in an s orbital, and 4 valence electrons in p orbitals, for a total of 6 valence electrons.***

So let's summarize what we know so far:

Group 1A elements have	1 valence electron in an s orbital
Group 2A elements have	2 valence electrons in an s orbital
Group 3A elements have	2 valence electrons in an s orbital and **1** valence electron in a p orbital
Group 4A elements have	2 valence electrons in an s orbital and **2** valence electrons in p orbitals
Group 5A elements have	2 valence electrons in an s orbital and **3** valence electrons in p orbitals
Group 6A elements have	2 valence electrons in an s orbital and **4** valence electrons in p orbitals

Can you guess how the valence electrons in columns 7A (Group 17) and 8A (Group 18) are arranged?

Group 7A elements have	2 valence electrons in an s orbital and **5** valence electrons in p orbitals
Group 8A elements have	2 valence electrons in an s orbital and **6** valence electrons in p orbitals

Notice that, after column 3A, each column one step further to the right has one additional valence p electron. Group 4A elements have one more valence p electron than Group 3A elements. Similarly, Group 5A elements have one more valence p electron than Group 4A elements. But what happens when you reach Group 8A elements? Why does the Periodic Table end at column 8A? Let's think about that carefully. Group 8A elements have 6 valence electrons in p orbitals. In the last chapter, you learned that the *maximum number* of p electrons at any energy level is 6. Therefore, there couldn't be a '9A' column, because a '9A' column would have 7 p electrons in the valence energy level, which is *impossible.*

The fact that Group 8A elements have *completely filled* valence s sublevel and p sublevel is important in terms of their chemical properties. Group 8A elements are called **Noble Gases.**

They are all gases, and they are not very reactive at all.

Lesson Summary

- All known elements are organized into the Periodic Table in such a way that elements in the same column have similar chemical properties. Only the highest energy electrons (valence electrons) are involved in chemical reactions. Therefore it is only these high-energy electrons that are important in determining an elements chemical properties. Two different elements are likely to have similar chemical properties when they have the same number of valence electrons. Elements with the same number of valence electrons are found in the same column of the Periodic Table.
- All elements in the first column of the Periodic Table have 1 valence electron in an s orbital. These elements are known as Group 1A metals, or alkali metals. All elements in the second column of the Periodic Table have 2 valence electrons in an s orbital. These elements are known as Group 2A metals, or alkaline earth metals. All elements in column 3A of the Periodic Table have 2 valence electrons in an s orbital and 1 valence electron in a p orbital. All elements in column 4A of the Periodic Table have 2 valence electrons in an s orbital and 2 valence electrons in p orbitals…etc. Column 8A has 2 valence electrons in an s orbital and 6 valence in p orbitals. Since any given energy level can have at most 6 p electrons, column 8A elements have a filled p sublevel. Therefore they are inert (non-reactive), because they are unlikely to either gain or lose electrons. Group 8A elements are called Noble Gases. Elements in Groups

3A – 8A can also be referred to as Groups 13 – 18.

Review Questions

1. Take a look at the Periodic Table. How would you describe it? Why do you think it has such a funny shape? **(Intermediate)**

2. Can you suggest how elements in the same column of the Periodic Table might be similar? **(Intermediate)**

3. Choose the correct statement. **(Beginning)**

a. Mg has only 1 valence electron in an s orbital

b. F has only 1 valence electron in an s orbital

c. O has only 1 valence electron in an s orbital

d. Kr has only 1 valence electron in an s orbital

e. Fr has only 1 valence electron in an s orbital

4. Circle the appropriate element for each blank. **(Beginning)**

a. _____________ (Mg/N) has 2 valence electrons in an s orbital, and 3 valence electrons in p orbitals.

b. _____________ (As/B) has 2 valence electrons in an s orbital, and 3 valence electrons in p orbitals

c. _____________ (Cl / P / Li) has 2 valence electrons in an s orbital, and 5 valence electrons in p orbitals

d. _____________ (Al / Li / Na) has 1 valence electron in a p orbital

5. Choose the correct statement. **(Beginning)**

a. Group 1A elements have a total of 3 valence electrons

b. Group 5A elements have a total of 2 valence electrons

c. Group 7A elements have a total of 4 valence electrons

d. Group 8A elements have a total of 8 valence electrons

e. Group 2A elements have a total of 5 valence electrons

f. Group 1A elements have a total of 3 valence electrons

6. Fill in the blanks. **(Intermediate)**

a. N has ___ valence electrons in an s orbital

b. N has ___ valence electrons in p orbitals

c. N has a total of ___ valence electrons

d. Ca has ___ valence electrons in s orbitals

e. Ca has ___ valence electrons in p orbitals

f. Ca has a total of ___ valence electrons

7. Decide whether each of the following statements is true or false. **(Intermediate)**

a. K has 1 valence electron in an s orbital

b. Ge has 2 valence electrons in an s orbital

c. Se has 4 valence electrons in p orbitals

d. B has 3 valence electrons in p orbitals

e. F has 2 valence electrons in an s orbital, and 7 valence electrons in p orbitals

f. Ca has a total of 4 valence electrons

8. Match the element to its valence electrons. **(Intermediate)**

a.	Sr	i.	a total of 8 valence electrons
b.	I	ii.	a total of 2 valence electrons
c.	Ne	iii.	a total of 5 valence electrons
d.	N	iv.	a total of 7 valence electrons

9. Fill in the blanks. **(Intermediate)**

a. Ba has __ valence electron(s) in an s orbital, and __ valence electron(s) in p orbitals

b. Sn has __ valence electron(s) in an s orbital, and __ valence electron(s) in p orbitals

c. S has __ valence electron(s) in an s orbital, and __ valence electron(s) in p orbitals

d. Po has __ valence electron(s) in an s orbital, and __ valence electron(s) in p orbitals

e. Na has __ valence electron(s) in an s orbital, and __ valence electron(s) in p orbitals

10. List all of the elements with exactly 2 valence electrons in p orbitals. **(Intermediate)**

11. An element has 2 valence electrons in an s orbital and 4 valence electrons in p orbitals. If the element is in the second row of the Periodic Table, which element is it? **(Beginning)**

12. An element has 2 valence electrons in an s orbital and 6 valence electrons in p orbitals. If the element is in the same row as In, which element is it? **(Beginning)**

Further Reading / Supplemental Links

http://www.wou.edu/las/physci/ch412/perhist.htm

http://www.aip.org/history/curie/periodic.htm

http://web.buddyproject.org/web017/web017/history.html

http://www.dayah.com/periodic

http://www.chemtutor.com/perich.htm

Vocabulary

periodic table	Scientists use the Periodic Table to summarize what they know about the existing elements. Elements of similar size are found in the same row, while elements with similar chemical properties are found in the same column.
chemical properties	The ways in which an element reacts with another element or compound.
valence electrons	The electrons in an atom with the highest value of n (the electrons in the highest energy level).
non-valence electrons	All electrons in atom which are not valence electrons. Non-valence electrons are not important in determining an element's chemical properties because they rarely get involved in chemical reactions.
alkali metals	Group 1A metals. These are elements found in the first column of the Periodic Table, excluding hydrogen.
alkaline earth metals	Group 2A metals. These are elements found in the second column of the Periodic Table.
noble gases	Group 8A elements. These are elements found in the eight column of the Periodic Table. They are inert, which means that they are very non-reactive.

Review Answers

1. (strange shape, reflects something about the chemical properties of the elements, related to the s, p, d and f sublevels, etc.)

2. (similar chemical properties)

3. e

4. (a) N (b) As (c) Cl (d) Al

5. d

6. (a) 2 (b) 3 (c) 5 (d) 2 (e) 0 (f) 2

7.

(a) true

(b) true

(c) true

(d) false

(e) false

(g) false

8. a. ii, b. iv, c. i, d. iii

9. (a) 2, 0 (b) 2, 2 (c) 2, 4 (d) 2, 4 (e) 1, 0

10. C, Si, Ge, Sn, Pb

11. O

12. Xe

Orbital Configurations

Lesson Objectives

- Draw orbital diagrams.
- Define Hund's Rule.
- Use Hund's Rule to decide how electrons fill sublevels with more than one orbital.

Introduction

In the last lesson, you learned a little bit about valence electrons. You saw how the number and type of valence electrons are important in determining the chemical properties of a particular element. Group 1A metals were highly reactive, because they have a strong tendency to lose their single valence s electrons. Group 2A metals are reactive as well, but less so, because they had 2 valence s electrons. Finally, Group 8A elements were *inert* (not reactive at all), because they had completely filled valences and p sublevels, meaning they could neither lose nor gain electrons very easily. Now you might be wondering why we didn't talk much about the chemical properties of the elements in columns 4A-7A. It turns out that understanding the behavior of these elements requires a bit more information. Specifically, we need to know *how* the electrons fill up the p orbitals. Carbon, for instance, is a Group 4A element, so it has 2 valence s electrons, and 2 valence p electrons. Obviously, the 2 valence s electrons are paired together in the s orbital, but what about the 2 valence p electrons? Are the valence p electrons paired in a single p orbital, or are they each in their own p orbital (remember, there are a total of three p orbitals that the valence p electrons could be found in). What about nitrogen? Nitrogen is a Group 5A element, so it has 2 valence s electrons, and 3 valence p electrons. Again, the 2 valence s electrons must be paired in the s orbital, but what about the 3 valence p electrons? Are two of them paired in a single p orbital, or do all three have their own p orbitals?

Orbital Representation

Before we discuss the order and manner in which the orbitals in a p sublevel are filled, we have to introduce a symbolic notation that scientists use to show orbital filling. Frequently, scientists will use boxes to represent orbitals. Figure 1 shows a set of boxes for orbitals up to the n = 2 energy level.

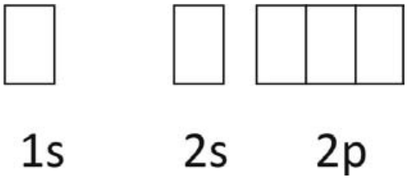


Figure 1: A set of boxes depicting electron orbitals for the n = 1 and n = 2 energy levels. Notice that for n = 1, there is a single s orbital, while for n = 2 there is one s orbital and three p orbitals.

When a 'spin-up' electron is present in an orbital, scientists draw an upward pointing arrow in that orbital's box. This leads to what is known as an *orbital diagram.* For example, hydrogen has a single electron in the 1s orbital. If that single electron were a spin-up, the orbital diagram for hydrogen would be:

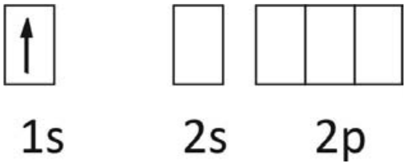


Figure 2: The orbital diagram for hydrogen, assuming that hydrogen's single electron is 'spin-up' (m_s = +1/2).

When a 'spin-down' electron is present in an orbital, scientists draw a downward pointing arrow in that orbital's box. Helium, for instance, has two electrons in the 1s orbital. We know that one of these electrons must be 'spin-up' and the other must be 'spin-down,' so the orbital diagram for helium would be:

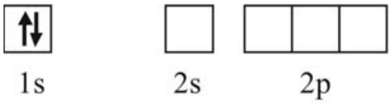
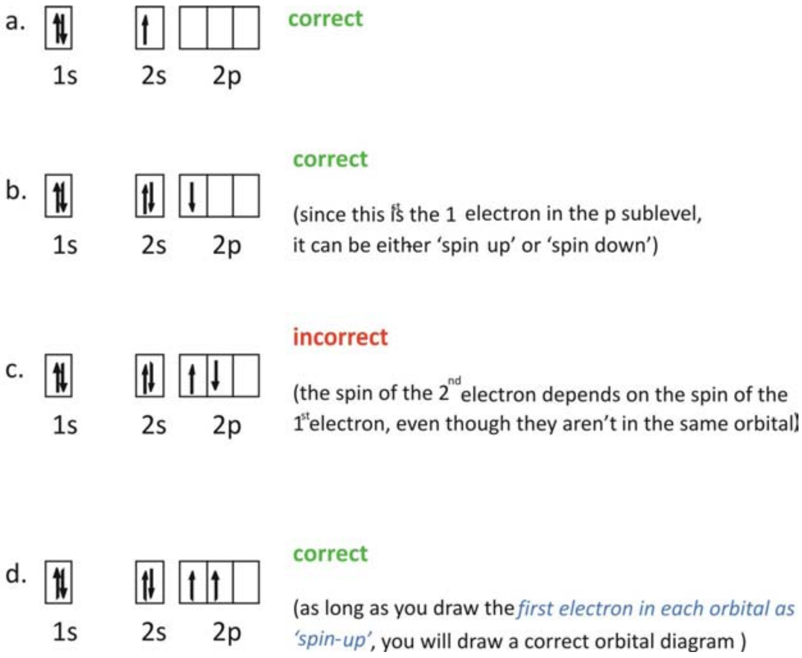


Figure 3: The orbital diagram for helium. Notice that when electrons are paired in an orbital, one of the electrons is 'spin-up,' while the other is 'spin-down.'

By comparing Figures 1 and 2, it should be fairly obvious to you, which electrons are paired and which are unpaired. That is one of the advantages of an orbital diagram. An orbital diagram is a clear way of showing *exactly* how many paired and unpaired electrons there are in a particular atom's electronic configuration.

Now you might be wondering about the unpaired electrons – how do you know whether to draw them as 'spin-up,' or 'spin-down.' Technically speaking, the *first* electron in a sublevel (1s, 2s, 2p, etc) could be either 'spin-up' *or* 'spin-down.' In other words, for hydrogen ($1s^1$), you could draw the arrow in the 1s orbital box pointing either up or down. Similarly, for boron ($1s^2 2s^2 2p^1$), you could draw the arrow in the 2p orbital box pointing either up or down. Once you've chosen the spin of the first electron *in a sublevel*, though, the spins of *all* of the other electrons in that sublevel depend on the spin you chose for the first. To avoid confusion, scientists ***always draw the first electron in an orbital as 'spin-up.'*** If you stick with this rule, you'll never get into trouble. If you insist on breaking this rule, you might draw an orbital diagram that is incorrect, as shown in Figure 4.



correct

correct

(since this is the 1st electron in the p sublevel, it can be either 'spin up' or 'spin down')

incorrect

(the spin of the 2nd electron depends on the spin of the 1st electron, even though they aren't in the same orbital)

correct

(as long as you draw the *first electron in each orbital as 'spin-up'*, you will draw a correct orbital diagram)

Figure 4: By convention, scientists usually draw all unpaired electrons as 'spin-up.' This prevents them from drawing incorrect orbital diagrams like the one in shown in (c). In the next section, you'll learn that the orbital diagram in (c) is incorrect because it does not obey Hund's Rule.

Notice that by drawing the first electron in each orbital as 'spin-up,' all of the unpaired electrons in the sublevel have the same spin, even if they are in different orbitals! This is due to a principle known as Hund's Rule.

We'll discuss Hund's Rule in more detail in the next section.

Orbitals in p Sublevel Fill Individually Before Pairing

Previously we learned that the energy of an electron in any given orbital depends on the energy level of the orbital (which is determined by the principal quantum number, **n**) and the sublevel of the orbital (s, p, d, etc. which is determined by the azimuthal quantum number: ℓ). We also learned that according to the *Aufbau principle,* electrons will fill the lowest energy orbitals first, and then move up to higher energy orbitals only after the lower energy orbitals are full. If you think carefully, though, you'll realize that there's still a problem. Certainly, 1s orbitals should be filled before 2s orbitals, because the 1s orbitals have a lower value of n, and thus a lower energy. Similarly, 2s orbitals should be filled before 2p orbitals, because 2s orbitals have a lower value of l (l = 0), and thus a lower energy. What about the three different 2p orbitals? In what order do electrons fill the 2p orbitals? To answer this question, we need to turn to a principle known as Hund's Rule. Hund's rule states that: (1) Every orbital in a sublevel is singly occupied before any orbital is doubly occupied. (2) All of the electrons in singly occupied orbitals have the same spin.

According to the first rule, electrons will always occupy an empty orbital before they pair up. This should make sense given what you know about electrons. Electrons are negatively charged and, as a result, they repel each other. Since electron-electron repulsion raises the energy of the electrons involved, electrons tend to minimize repulsion (and thus minimize their energies) by occupying their own orbital, rather than sharing an orbital with another electron. Take a look at Figure 5.

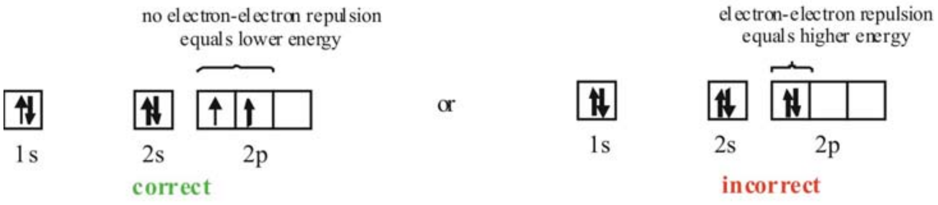


Figure 5: Possible orbital diagrams for carbon (C). The orbital diagram on the left is correct, because it obeys Hund's Rule. The orbital diagram on the right is incorrect, because it does not obey Hund's Rule.

Notice how the two 2p electrons in the orbital diagram on the left are in separate orbitals, while the two 2p electrons in the orbital diagram on the right are sharing a single orbital. The orbital diagram on the left is the correct orbital diagram, because it obeys Hund's Rule, meaning that there is less electron-electron repulsion and, as a result, the electrons have lower energies (remember, electrons *always* minimize their energies).

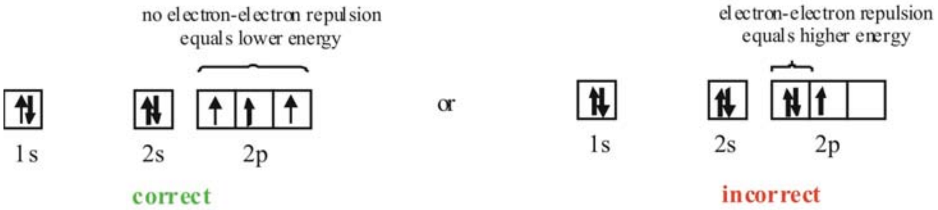


Figure 6: Possible orbital diagrams for nitrogen (N). The orbital diagram on the left is correct, because it obeys Hund's Rule. The orbital diagram on the right is incorrect, because it does not obey Hund's Rule.

Figure 6 is similar to Figure 5. Notice how all three 2p electrons in the orbital diagram on the left are in separate orbitals, while two of the three 2p electrons in the diagram on the right are sharing a single orbital. The orbital diagram on the left is the correct orbital diagram, because it obeys Hund's Rule. Again, this means that there is less electron-electron repulsion and, as a result, the electrons have lower energies.

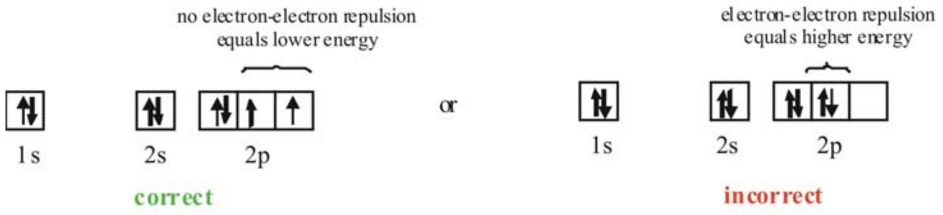


Figure 7: Possible orbital diagrams for oxygen (O). The orbital diagram on the left is correct, because it obeys Hund's Rule. The orbital diagram on the right is incorrect, because it does not obey Hund's Rule.

Figure 7 shows possible electron configurations for an atom with four 2p electrons. This time, two of the electrons have no choice – they must pair up. The other two electrons, however, could either pair up, as shown in the orbital diagram on the right, or occupy their own orbitals, as shown in the orbital diagram on the left. Which do you think is correct? Obviously, the orbital diagram on the left, because it minimizes electron-electron repulsion. The orbital diagram on the left is also the orbital diagram, which follows Hund's Rule, since all orbitals are singly occupied *before* any are doubly occupied. The orbital diagram on the right *does not* follow Hund's Rule, since the first two orbitals are doubly occupied before the third is singly occupied.

While it's easy to understand why electrons would occupy empty orbitals before pairing up, it's a lot harder to understand why unpaired electrons in different orbitals must all have the same spin. Electron spins in different orbitals align (all point in the same direction), because spins, which are aligned have lower energy than spins which are not aligned. Notice that as long as you ***always draw the first electron in an orbital as 'spin-up'*** you will always draw spins which are aligned. Take a look at Figure 4 again. Now that you know Hund's Rule, it should be obvious why the orbital diagram in 4.c is incorrect – the two electrons in the singly occupied 2p orbitals have *different* spins, and thus this orbital diagram does *not* obey Hund's Rule. Compare the orbital diagram in 4.c to the orbital diagram in 4.d. The orbital diagram in 4.d *does* obey Hund's Rule, because the two electrons in the singly occupied 2p orbitals have *the same* spin.

Nitrogen Has Three Unpaired Electrons

Now that we know about orbital diagrams and Hund's rule, we can begin to explain the chemistry of the elements in Groups 4A through 7A. Let's take a look at nitrogen as an example.

Example 1:

Draw the orbital diagram for nitrogen.

First, we need to write the electron configuration for nitrogen just as we did previously: which gives $1s^2$ $2s^2$ $2p^3$. To draw the orbital diagram we will write the following: the first two electrons will pair up in the 1s orbital; the next two electrons will pair up in the 2s orbital. That leaves 3 electrons, which must be placed in the 2p orbitals. According to Hund's Rule, all orbitals will be singly occupied before any is doubly occupied. Therefore, we know that each p orbital gets one electron. Hund's Rule also tells us that all of the unpaired electrons must have the same spin. Keeping with convention, we draw all of these electrons as 'spin-up', which gives.

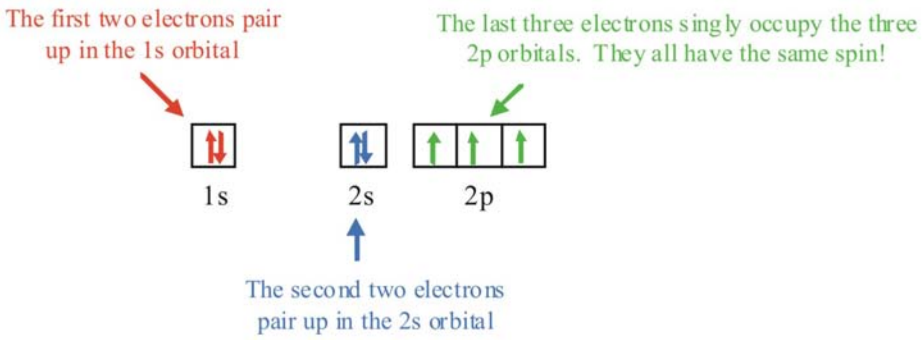


Figure 8: The orbital diagram for nitrogen (N).

Orbital diagrams can help you to make predictions about the ways in which certain elements will react, and the chemical 'compounds' or 'molecules' that different elements will form. We aren't ready to discuss compounds, or molecules yet. The principles that you're learning now will help you to understand the behavior of all chemicals, from the most basic elements like hydrogen and helium, to the most complex proteins (huge biological chemicals made of thousands of different atoms bound together) found in your body.

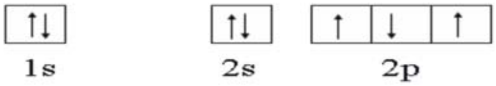
Lesson Summary

- Orbital diagrams are drawn by representing each orbital as a box, each 'spin-up' electron in an orbital as an upward pointing arrow in the box, and each 'spin-down' electron in an orbital as a downward pointing arrow in the box. You can only have two arrows in each box, and they must be pointing in opposite directions.
- Scientists use the convention that the first electron in any orbital is 'spin-up,' therefore, the first arrow in an orbital 'box' should point up. Hund's Rule states: (1) Every orbital in a sublevel is singly occupied before any orbital is doubly occupied. (2) All of the electrons in singly occupied orbitals have the same spin.
- Electrons will occupy separate orbitals rather than pairing up, since this minimizes electron-electron repulsions, thereby minimizing energy. Electron spins in different orbitals within the same sublevel align because aligned spins have lower energy.

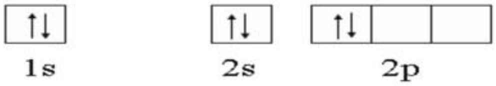
Review Questions

1. Which of the following is a valid orbital diagram? **(Beginning)**

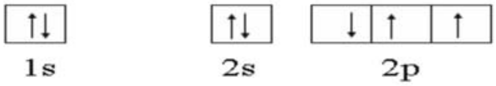
a.



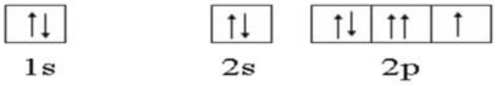
b.



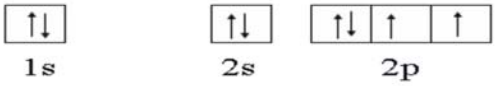
c.



d.



e.



2. Draw the orbital diagram for lithium (Li). **(Beginning)**

3. Draw the orbital diagram for carbon (C). **(Beginning)**

4. Draw the orbital diagram for fluorine (F). **(Beginning)**

5. Draw the orbital diagram for oxygen, O. Use it to answer the following questions: **(Beginning)**

a. an oxygen atom has ___ unpaired valence electrons

b. an oxygen atom has ___ paired valence electrons

c. an oxygen atom has ___ paired non-valence electrons

d. an oxygen atom has ___ unpaired non-valence electrons

6. Draw the orbital diagram for neon, Ne. Use it to answer the following questions: **(Beginning)**

a. a neon atom has ___ unpaired valence electrons

b. a neon atom has ___ paired valence electrons

c. a neon atom has ___ paired non-valence electrons

d. a neon atom has ___ unpaired non-valence electrons

7. Decide whether each of the following statements is true or false. **(Intermediate)**

a. Every orbital in a sublevel is doubly occupied before any orbital is singly occupied.

b. Every orbital in a sublevel is singly occupied before any orbital is doubly occupied.

c. All electrons in singly occupied orbitals have the same spin.

d. The two electrons in a single orbital have the same spin.

e. All electrons in singly occupied orbitals have different spins.

f. The two electrons in a single orbital have different spins.

8. Draw the orbital diagram for phosphorus P. **(Beginning)**

9. Draw an orbital diagram for silicon, Si. Use it to answer the following questions: **(Beginning)**

a. a silicon atom has ___ unpaired valence electrons

b. a silicon atom has ___ paired valence electrons

c. a silicon atom has ___ paired non-valence electrons

d. a silicon atom has ___ unpaired non-valence electrons

10. Draw an orbital diagram for Mn. Use it to determine the total number of unpaired electrons in an Mn atom. **(Intermediate)**

Further Reading / Supplemental Links

http://www.chempractice.com/drills/java_AO.php

http://library.thinkquest.org/3659/structures/electronconfig.html

http://www.chem.latech.edu/~deddy/Lectnote/Chap7B.html

http://www.mi.mun.ca/users/edurnfor/1100/atomic%20structure/sld036.htm

Vocabulary

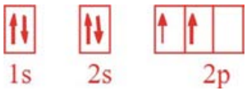
orbital diagram	Orbital diagrams are drawn by representing each orbital as a box, each ‘spin-up’ electron in an orbital as an upward pointing arrow in the box, and each ‘spin-down’ electron in an orbital as a downward pointing arrow in the box.
Hund’s rule	Every orbital in a sublevel is singly occupied before any orbital is doubly occupied. All of the electrons in singly occupied orbitals have the same spin.

Review Answers

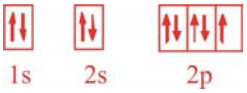
1. e

2.

3.



4.



5. (a) 2 (b) 4 (c) 2 (d) 0

6. (a) 0 (b) 8 (c) 2 (d) 0

7.

(a) false

(b) true

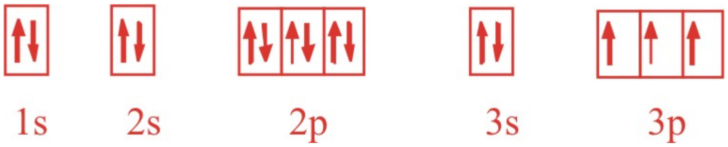
(c) true

(d) false

(e) false

(f) true

8.



9. (a) 2 (b) 2 (c) 10 (d) 0

10. 5

The Periodic Table and Electron Configurations

Lesson Objectives

- Relate an element's position in the PT to the energy level of its valence electrons (excluding transition metals, lanthanides and actinides).
- Relate an element's position in the PT to the sublevel of its highest energy valence electrons.
- Explain why there are only two elements in the first row of the PT.

Introduction

With what we have already discussed, you might realize that just as electron configurations can be used to explain the shape and organization of the Periodic Table, the shape and organization of the Periodic Table can, in turn, be used to predict electron configurations. In fact, if you can locate an element on the Periodic Table, you can use the element's position to figure out the energy level of the element's valence electrons. Furthermore, an element's position on the Periodic Table tells you the sublevel of the element's *highest* energy valence electrons. In this lesson, we'll take a close look at how the Periodic Table relates to the electron configurations.

Rows Across on the PT are Consistent With the Energy Level in An Atom

First, let's try to figure out what we can learn from an element's row or period in the Periodic Table. Figure 1 shows how the different rows in the Periodic Table are numbered.

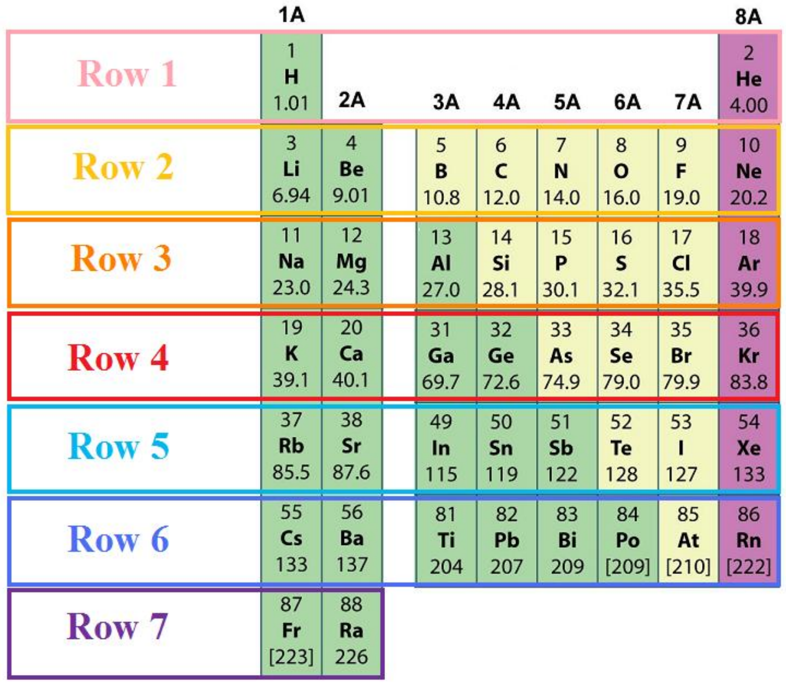


Figure 1: How the rows in the Periodic Table are numbered. The transition metals and the lanthanides and actinides have been omitted.

(*Source:* CK-12 Foundation, *License:* SA-BY-CC)

To understand what this means in terms of an element's electron configuration, let's consider the Group 1A metals. If we write the electron configuration for the Group 1A metal from each row of the Periodic Table, we have:

row **2** Li: $1s^2\ \mathbf{2s}^1$
row **3** Na: $1s^2 2s^2 2p^6\ \mathbf{3s}^1$
row **4** K: $1s^2 2s^2 2p^6 3s^2 3p^6\ \mathbf{4s}^1$
row **5** Rb: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6\ \mathbf{5s}^1$
row **6** Cs: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6\ \mathbf{6s}^1$
row **7** Fr: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6\ \mathbf{7s}^1$

Do you see any pattern? For Group 1A metals, it seems that element's row corresponds to the energy level of that element's valence electron. Lithium (Li), for instance, is found in row **2** of the Periodic Table, and its valence electron is found in the n = **2** energy level. Cesium (Cs) is found in row **6** of the Periodic Table, and its valence electron is found in the n = **6** energy level. Let's see if this same pattern holds for Group 2A metals:

row **2** Li: $1s^2\ \mathbf{2s}^2$
row **3** Na: $1s^2 2s^2 2p^6\ \mathbf{3s}^2$

row **4** K: $1s^22s^22p^63s^23p^6\ \mathbf{4}s^2$
row **5** Rb: $1s^22s^22p^63s^23p^64s^23d^{10}4p^6\ \mathbf{5}s^2$
row **6** Cs: $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^6\ \mathbf{6}s^2$
row **7** Fr: $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^66s^24f^{14}5d^{10}6p^6\ \mathbf{7}s^2$

For Group 2A metals, the same rule applies! Magnesium (Mg) is found in row **3** of the Periodic Table, and its valence electrons are found in the n = **3** energy level. Similarly, Radium (Ra) is found in row **7** of the Periodic Table, and its valence electrons are found in the n = **7** energy level.

So far so good – but does the same pattern apply to the Group 3A – 8A elements (also known as Groups 13 – 18). Let's find out by writing the electron configuration for the Group 3A element in each row.

row **2** B: $1s^2\ \mathbf{2}s^2\ \mathbf{2}p^1$
row **3** Al: $1s^22s^22p^6\ \mathbf{3}s^2\ \mathbf{3}p^1$
row **4** Ga: $1s^22s^22p^63s^23p^6\ \mathbf{4}s^23d^{10}\ \mathbf{4}p^1$
row **5** In: $1s^22s^22p^63s^23p^64s^23d^{10}4p^6\ \mathbf{5}s^24d^{10}\ \mathbf{5}p^1$
row **6** Tl: $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^6\ \mathbf{6}s^25d^{10}\ \mathbf{6}p^1$

Even though the valence electrons in Group 3A elements are found in both s and p orbitals, it turns out that an element's row *still* corresponds to the energy level of that element's valence electrons. For example, Gallium (Ga) is found in row **4** of the Periodic Table, and its valence electrons are found in the n = **4** energy level. Likewise, Thallium (Tl) is found in row **6** of the Periodic Table, and its valence electrons are found in the n = **6** energy level.

It really does seem as if we can predict the energy level of an element's valence electrons using the row number for that element in the Periodic Table. Let's try one last example, though, just to be sure. Let's write the electron configuration for the Group 7A element in each row.

row **2** B: $1s^2\ \mathbf{2}s^2\ \mathbf{2}p^5$
row **3** Al: $1s^22s^22p^6\ \mathbf{3}s^2\ \mathbf{3}p^5$
row **4** Ga: $1s^22s^22p^63s^23p^6\ \mathbf{4}s^23d^{10}\ \mathbf{4}p^5$
row **5** In: $1s^22s^22p^63s^23p^64s^23d^{10}4p^6\ \mathbf{5}s^24d^{10}\ \mathbf{5}p^5$
row **6** Tl: $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^6\ \mathbf{6}s^25d^{10}\ \mathbf{6}p^5$

Once again, it turns out that an element's row can be used to determine the energy level of that element's valence electrons. Chlorine (Cl), for instance, is found in row **3** of the Periodic Table, and its valence electrons are found in the n = **3** energy level. Similarly, Iodine (I) is found in row 5 of the Periodic Table, and its valence electrons are found in the n = **5** energy level.

You should make note of one final point when it comes to energy levels and how they relate to the Periodic Table. Our rule for determining the energy level of an element's valence electrons using the element's row in the Periodic Table works for Group 1A – 8A elements. This rule *doesn't* apply, however, to the Group 1B – 8B (also known as Groups 3 – 12) elements. The elements in that lower portion of the Periodic Table (the middle portion of the Periodic Table 'blacked out' in Figure 1) are known as transition metals. They behave differently, and you can't apply the same rules to them as far as valence electrons are concerned. The same goes for the isolated lower portion of the Periodic Table (also 'blacked out' in Figure 1). This block contains elements known as *lanthanides* and *actinides.* Like transition metals, lanthanides and actinides do not obey the same rules as the Group 1A-8A elements when it comes to valence electrons and valence electron energy levels.

Hydrogen and Helium Occupy the First Period

You probably noticed that, in the last section, we didn't mention the first row at all. Instead, we always started from row 2. The first row in the Periodic Table is a 'special row' for several reasons. To begin with, the first row of the Periodic Table contains only two elements – hydrogen and helium. Can you figure out *why* there are only two elements in the first row?

According to what we learned in the last section, an element's row number corresponds to the energy level of that element's valence electrons. Therefore, the first row must contain elements with valence electrons in the n = 1 energy level. By now you should know that there is *only one orbital* in the n = 1 energy level. That orbital, of course, is the 1s orbital. Hydrogen has one valence electron in the 1s orbital, (its electron configuration is $1s^1$), and helium has two valence electrons in the 1s orbital (its electron configuration is $1s^2$). Since it's impossible to fit *more* than two electrons into the 1s orbital, atoms with a total of *three or more* electrons *must* have valence electrons in an energy level with n = 2 or greater. Clearly, then, atoms with a total of *three or more* electrons do *not* belong in the first row of the Periodic Table.

The first row of the Periodic Table is also special because its elements have special properties. Hydrogen, for example, is not a metal like the rest of the Group 1A elements. Instead, hydrogen atoms react with each other and form what's known as *hydrogen gas,* H_2. As was mentioned in the last lesson, some scientists will put hydrogen in a category all by itself, rather than including it at the top of the 1A column. We won't do that here, but you should always keep in mind the fact that hydrogen is 'different,' and that you shouldn't compare the hydrogen's chemical properties with the chemical properties of the other Group 1A elements.

Helium is also a special atom. You might wonder why helium appears at the far right-hand side of the Periodic Table, rather than right next to hydrogen. Again, helium's placement in the Periodic Table reflects its special chemical properties. Earlier you learned that Group 8A elements were 'inert' and that includes helium. Even though helium only has two valence electrons, while the rest of the Group 8A elements have eight valence electrons, helium is placed on the top of the 8A column since helium's chemical behavior is similar to the chemical behavior of the other Noble Gases because it has a completed outer energy level.

The s Sublevel Block on PT

So far we know that, with the exception of transition metals, lanthanides and actinides, we can use the row in which an element is found to determine the energy level of that element's valence electrons. Can the organization of the Periodic Table, and the placement of an element within the Periodic Table, tell us anything else about the elements electron configuration? The answer is – 'yes.' Remember that the highest energy valence electrons in Group 1A and Group 2A elements are *always* in s orbitals. In fact, the *only* valence electrons in Group 1A and Group 2A elements are in s orbitals! Lithium, (Li) for instance, has the electron configuration $1s^22\mathbf{s}^{\mathbf{1}}$. Notice that lithium's single valence electron is in an s orbital. Similarly, magnesium (Mg) has the electron configuration $1s^22s^22p^63\mathbf{s}^{\mathbf{2}}$. Again, notice that magnesium's two valence electrons are in an s orbital. Since all of the valence electrons in Group 1A and Group 2A elements exist in s orbitals, the first two columns of the Periodic Table (**columns 1A and 2A**) are known as the ***'s sublevel block.'*** The s sublevel block is shown in Figure 2. From Figure 2, it is clear that the s sublevel block consists of all of the metals from Li down to Fr in column 1A, and all of the metals from Be down to Ra in column 2A. Hydrogen is not included in the s sublevel block, again, because of its special properties.

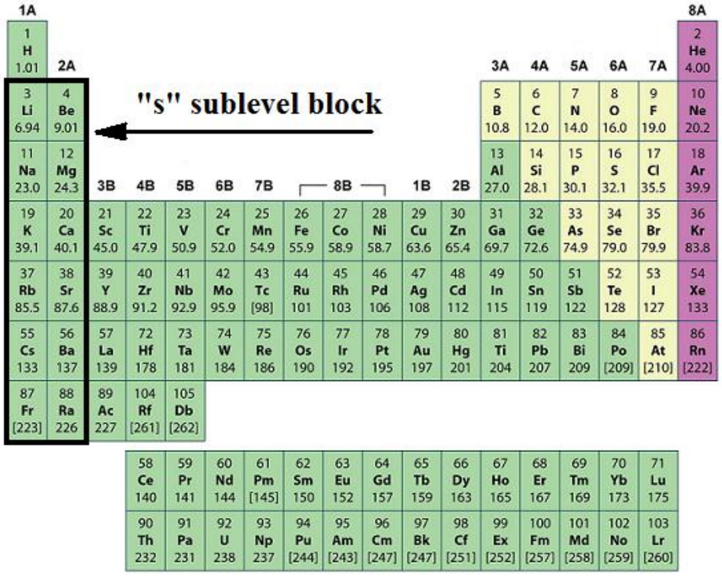


Figure 2: The s sublevel block of the Periodic Table includes the Group 1A metals and the Group 2A metals.

(*Source:* CK-12 Foundation, *License:* SA-BY-CC)

The p Sublevel Block on PT

What can we say about the valence electrons in Group 3A-Group 8A elements? In particular, what can we say about the *highest* energy valence electrons? If you look carefully, you'll notice that for Group 3A - Group 8A (or if you prefer, Groups 13 – 18) elements, the highest energy valence electrons are always in p orbitals. Boron, (B) for instance, has the electron configuration $1s^2 2\mathbf{s}^{\mathbf{2}}\ 2\mathbf{p}^{\mathbf{1}}$. While boron has both 2s and 2p valence electrons, the 2p valence electrons are higher in energy. Similarly, Krypton (Kr) has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4\mathbf{s}^{\mathbf{2}}\ 3d^{10} 4\mathbf{p}^{\mathbf{6}}$. Again, while krypton has both 4s and 4p valence electrons, the 4p valence electrons are higher in energy. Since the highest energy valence electrons in Group 3A - Group 8A elements exist in p orbitals, the final six columns of the Periodic Table (**columns 3A through 8A**) are known as the **'p sublevel block.'** The p sublevel block is shown in Figure 2. From Figure 2, it is clear that the p sublevel block consists of all of the elements from B down to Tl in column 3A, all of the elements from C down to Pb in column 4A, all of the elements from N down to Bi in column 5A, all of the elements from O down to Po in column 6A, all of the elements from F down to At in column 7A and, finally, all of the elements from Ne down to Rn in column 8A. Helium is not included in the p sublevel block, which should make sense, since helium has *no* p electrons!

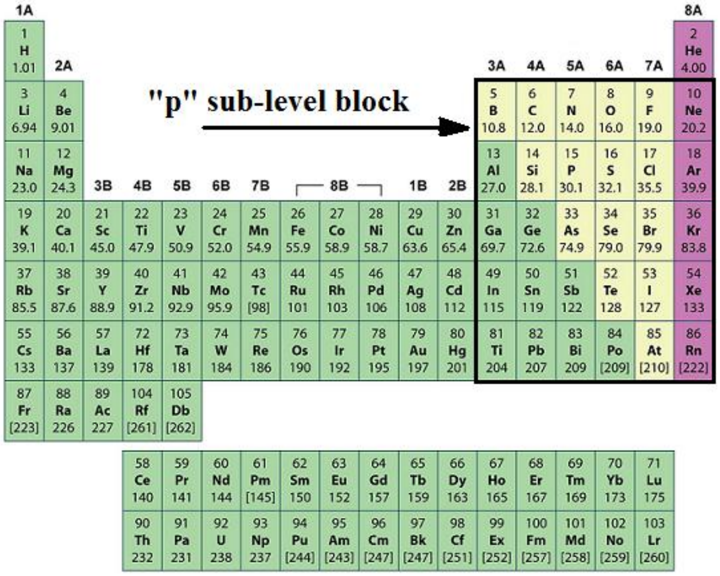


Figure 3: The p sublevel block of the Periodic Table includes the Group 3A – Group 8A elements.

(*Source:* CK-12 Foundation, *License:* SA-BY-CC)

Just as the Periodic Table has an s sublevel block and a p sublevel block, it also has a d sublevel block and an f sublevel block. Defining valence electrons in the d and f sublevel blocks can be more difficult but, in general, most of the high energy valence electrons in the d sublevel block are in d orbitals while most of the high energy valence electrons in the f sublevel block are in f orbitals. Figure 4 shows how the complete Periodic Table divides into the s, p, d and f sublevel blocks.

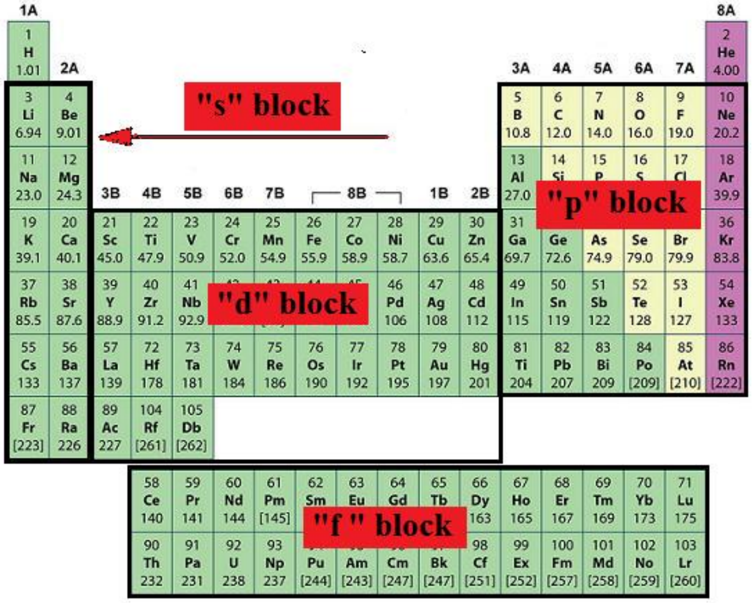


Figure 4: The Periodic Table divided into the s sublevel block, the p sublevel block, the d sublevel block, and the f sublevel block.

(*Source:* CK-12 Foundation, *License:* SA-BY-CC)

A complete summary of the Periodic Table, and the information it contains about an element's valence electrons is shown in Figure 5.

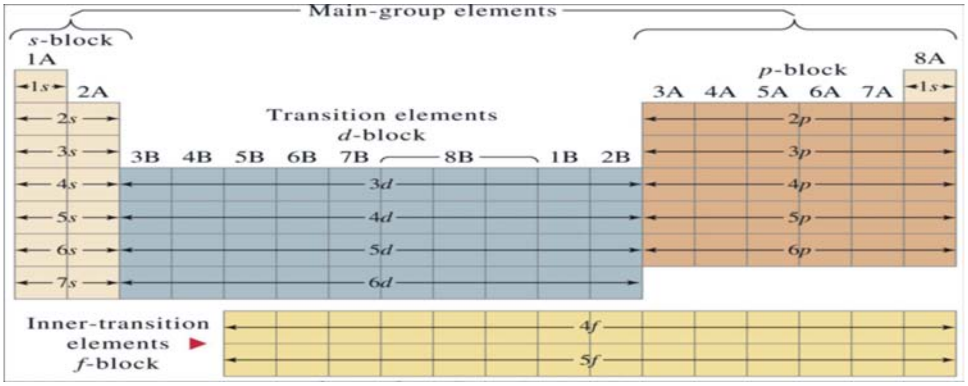


Figure 5: A complete summary of the information the Periodic Table contains about an elements valence electrons.

(*Source:* http://en.wikipedia.org/wiki/Image:800px-PTable.png, *License:* GNU-FDL)

Earlier you learned that the Periodic Table was a convenient way to summarize all of the information that scientists know about the different elements found in our world. The Periodic Table probably even looked funny to you, because you had no way of understanding what its shape and organization meant. Now that we've discussed electron orbitals and electron energy levels, though, the Periodic Table shouldn't seem so strange anymore. In fact, the shape of the Periodic Table actually reflects the way in which electrons are organized in atoms of the different elements.

Lesson Summary

- For Group 1A, 2A, 3A, 4A, 5A, 6A, 7A and 8A elements, the row in which an element is found corresponds to the energy level of that element's valence electrons. For example, lithium (Li) is in row 2, and its valence electrons are in the n = 2 energy level. You can predict the energy level of an element's valence electrons using the element's row number in the Periodic Table.
- Elements in the first row have special properties. Hydrogen is *not* an alkali metal, and is usually found as a gas. Helium is a Noble Gas, and exhibits chemical properties similar to the other Noble Gases found in Group 8A. The Periodic Table can be divided into s, d, p and f sublevel blocks. For elements in the s sublevel block, all valence electrons are found in s orbitals. For elements in the p sublevel block, the highest energy valence electrons are found in p orbitals.

Review Questions

1. Use the Periodic Table to determine the energy level of the valence electrons in each of the following elements. **(Beginning)**

a. B

b. Ga

c. Rb

d. At

e. He

2. Fill in the blanks: **(Beginning)**

a. B is in the __ level block of the Periodic Table

b. Sr is in the __ level block of the Periodic Table

c. Fe is in the __ level block of the Periodic Table

d. Cs is in the __ level block of the Periodic Table

e. O is in the __ level block of the Periodic Table

3. Use the Periodic Table to determine the energy level and sublevel of the highest energy electrons in each of the following elements: **(Intermediate)**

a. N

b. Ca

c. Rb

d. P

e. In

4. Decide whether each of the following statements is true or false. **(Beginning)**

a. Li has valence electrons in the n = 1 energy level.

b. Si has valence electrons in the n = 3 energy level.

c. Ga has valence electrons in the n = 3 energy level.

d. Xe has valence electrons in the n = 5 energy level.

e. P has valence electrons in the n = 2 energy level.

5. Match the element to the sublevel block it is found in: **(Beginning)**

a.	C	i.	s sublevel block
b.	Cs	ii.	p sublevel block
c.	Ce	iii.	d sublevel block
d.	Cr	iv.	f sublevel block

6. The first row of the Periodic Table has: **(Beginning)**

a. 1 element

b. 2 elements

c. 3 elements

d. 4 elements

e. 5 elements

7. Use the Periodic Table to determine which of the following elements has the highest energy valence electrons. **(Beginning)**

a. Sr

b. As

c. H

d. At

e. Na

8. Use the Periodic Table to determine which of the following elements has the lowest energy valence electrons. **(Beginning)**

a. Ga

b. B

c. Cs

d. Bi

e. Cl

9. Which energy level does the first row in the d sublevel block correspond to? **(Intermediate)**

Further Reading / Supplemental Links

http://learner.org/resources/series61.html'''

The ***learner.org*** website allows users to view streaming videos of the Annenberg series of chemistry videos. You are required to register before you can watch the videos but there is no charge. The website has one video that applies to this lesson called ***The Periodic Table*** .

http://dl.clackamas.cc.or.us/ch104-06/valence_electrons.htm

http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch8/index.php

http://www.cem.msu.edu/~reusch/VirtTxtJml/intro2.htm

http://en.wikipedia.org/wiki/Valence_electrons

Vocabulary

transition metals	Elements in the d sublevel block (columns 1-B through 8B) of the Periodic Table. The highest energy electrons in transition metals are found in d orbitals.
lanthanides and actinides	Elements in the f sublevel block of the Periodic Table. The highest energy electrons in lanthanides and actinides are found in f orbitals.
s sublevel block	The elements in the Periodic Table in columns 1A and 2A (excluding hydrogen). All valence electrons for elements in the s sublevel block are in s orbitals.
p sublevel block	The elements in the Periodic Table in columns 3A through 8A (excluding helium). The highest energy valence electrons for elements in the p sublevel block are in p orbitals.
d sublevel block	The elements in the Periodic Table in columns 1B through 8B (also known as transition metals).
f sublevel block	The elements in the lanthanide and actinide rows of the Periodic Table.
noble gases	Group 8A elements. These are elements found in the eight column of the Periodic Table. They are inert, which means that they are very non-reactive.

inert	Non-reactive.

Review Answers

1.

(a) n = 2

(b) n = 4

(c) n = 5

(d) n = 6

(e) n = 1

2.

(a) p

(b) s

(c) d

(d) s

(e) p

3.

(a) 2p

(b) 4s

(c) 5s

(d) 3p

(e) 5p

4.

(a) false

(b) true

(c) false

(d) true

(e) false

5. a. ii, b. i, c. iv, d. iii

6. b

7. d

8. b

9. n = 3

9. Relationships Between the Elements

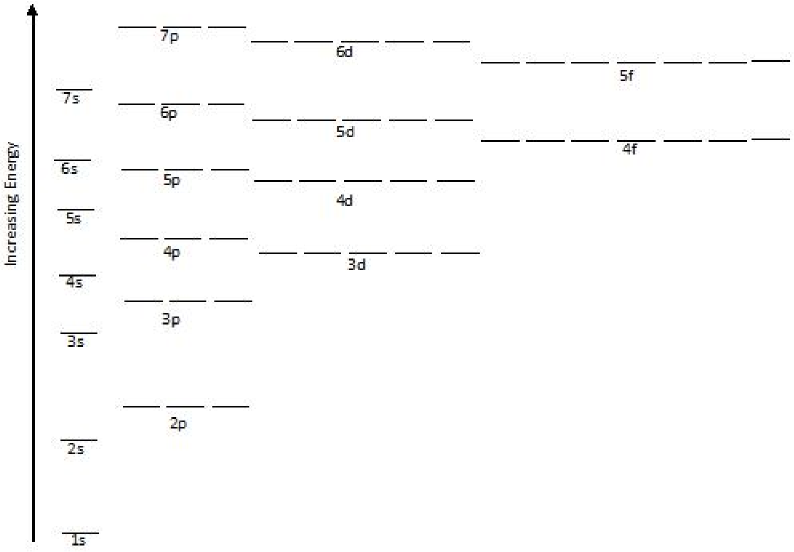
Families on Periodic Table

Lesson Objectives

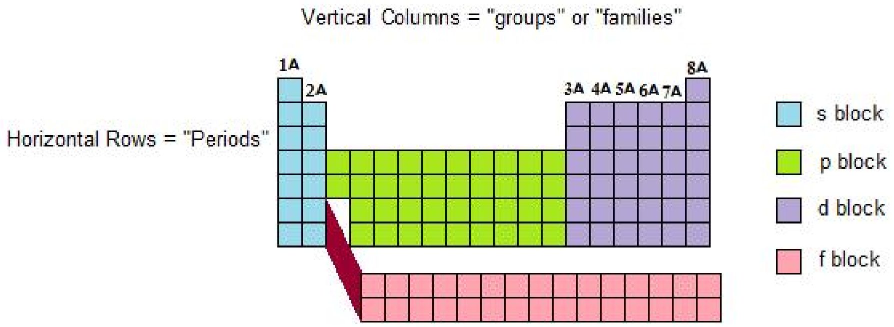
- Describe the patterns that exist in the electron configurations for the main group elements.
- Identify the columns in the periodic table that contain 1) the alkali metals, 2) the alkaline earth metals, 3) the halogens, and 4) the noble gases, and describe the differences between each family's electron configuration.
- Given the outermost energy level electron configuration for an element, determine its family on the periodic table.

Introduction

With the introduction of electron configurations, we began to get a deeper understanding of the periodic table. An understanding of these electron configurations will prove to be invaluable as we look at bonding and chemical reactions. The orbital representation method for representing electron configuration is shown below. The orbital representation was learned in an earlier chapter but like many of the skills you learn in chemistry, it will be used a great deal in this chapter and in several chapters later in the course.



In this lesson, we will focus on the connection between the electron configuration and the main group elements of the periodic table. We will need to remember the sub-level filling groups in the periodic table. Keep the following figure in mind. We will use it for the next two chapters.



Elements Ending with s^1 = Alkali

In the periodic table, the elements are arranged in order of increasing atomic number. In previous material we learned that the atomic number is the number of protons in the nucleus of an atom. For a neutral atom, the number of protons is equal to the number of electrons. Therefore, for neutral atoms, the periodic table is also arranged in order of increasing number of electrons. Take a look now at the first ***group*** or column in the periodic table. It is the one marked “1A” in Figure 1. The groups or families are the vertical rows of elements. The first group has seven elements representing the seven periods of the periodic table. Remember that a ***period*** in the periodic table is a horizontal row. Group 1A is the only group with seven elements in it.

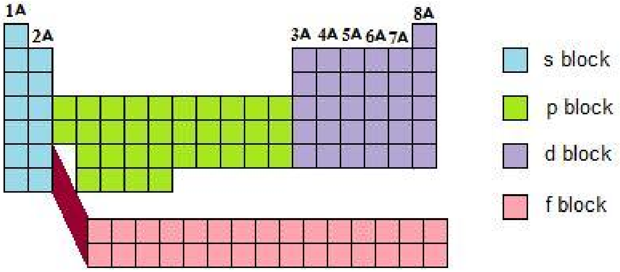


Figure 1: Group 1A of the Periodic Table (*Created by:* Richard Parsons, *License:* CC-BY-SA)

Table 1: Electron Configurations for Group 1 Metals

Element	**Atomic Number**	**Electron Configuration**
Lithium (Li)	3	$1s^2\ 2s^1$
Sodium (Na)	11	$1s^2\ 2s^2\ 2p^6\ 3s^1$
Potassium (K)	19	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$
Rubidium (Rb)	37	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^1$
Cesium (Cs)	55	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ 6s^1$
Francium (Fr)	87	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ 6s^2\ 4f^{14}\ 5d^{10}\ 6p^6\ 7s^1$

What do you notice about all of the elements in Group 1? They all have s^1 as the outermost energy level electron configuration. The whole number in front of the “s” tells you what period the element is in. For example sodium, Na, has the electron configuration $1s^22s^22p^63s^1$, so it is in period 3. It is the first element of this period.

This group of elements is called the alkali metals. They get their name from ancient Arabic (*al kali*) because “scientists” of the time found that the ashes of the vegetation they were burning contained a large amount of sodium and potassium. In Arabic, *al kali* means *ashes*. We know today that all alkali metals have electronic configurations ending in s^1. You might want to note that while hydrogen is often placed in group 1, it is not considered an alkali metal. The reason for this will be discussed later.

Elements Ending with s^2 = Alkaline Earth

Taking a look at Group 2A in the figure below, we can use the same analysis we used with group 1 to see if we can find a similar trend. It is the second vertical group in the periodic table and it contains only six elements.

Table 2: Electronic Configurations for Group 2A Metals

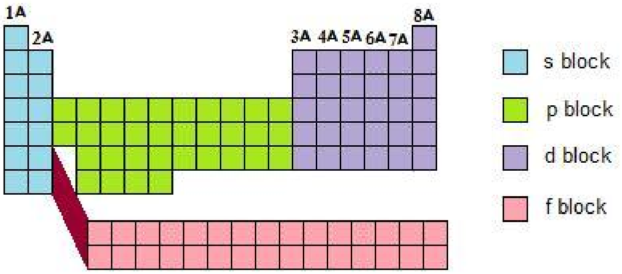
Element	Atomic Number	Electron Configuration
Beryllium (Be)	4	$1s^2\ 2s^2$
Magnesium (Mg)	12	$1s^2\ 2s^2\ 2p^6\ 3s^2$
Calcium (Ca)	20	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$
Strontium (Sr)	38	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2$
Barium (Ba)	56	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ 6s^2$
Radium (Ra)	88	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ 6s^2\ 4f^{14}\ 5d^{10}\ 6p^6\ 7s^2$

What do you notice about all of the elements in group 2A? They all have an outermost energy level electron configuration of s^2. The whole number in front of the “s” tells you what period the element is in. For example, magnesium, Mg, has the electron configuration $1s^2\ 2s^2\ 2p^6\ 3s^2$, so it is in period 3 and is the second element in that period. Remember that the s sublevel may hold two electrons, so in Group 2A, the s orbital has been filled.

Elements in this group are given the name **alkaline earth metals**. They get their name because early “scientists” found that all of the alkaline earths were found in the earth’s crust. Alkaline earth metals, although not as reactive as the alkali metals, are still highly reactive. All alkaline earth metals have electron configurations ending in s^2.

Elements Ending with s^2p^6 = Noble Gases

The first person to isolate a noble gas was Henry Cavendish, who isolated argon in the late 1700s. The noble gases were actually considered inert gases until the 1960’s when a compound was formed between xenon and fluorine which changed the way chemists viewed the “inert” gases. In the English language, inert means to be lifeless or motionless; in the chemical world, inert means *does not react*. Later, the name "noble gas" replaced "inert gas" for the name of Group 8A.



When we write the electron configurations for these elements, we see the same general trend that was observed with groups 1A and 2A; that is, similar electron configurations within the group.

Table 3: Electron Configurations for Group 8A Gases

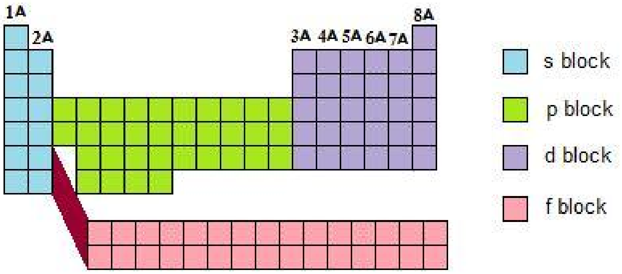
Element	Atomic Number	Electron Configuration

Helium (He)	2	$1s^2$
Neon (Ne)	10	$1s^2\ 2s^2\ 2p^6$
Argon (Ar)	28	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$
Krypton (Kr)	36	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6$
Xenon (Xe)	54	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6$
Radon (Rn)	86	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ 6s^2\ 4f^{14}\ 5d^{10}\ 6p^6$

Aside from helium, He, all of the noble gases have outer energy level electron configurations that are the same, ns^2np^6, where n is the period number. So Argon, Ar, is in period 3, is a noble gas, and would therefore have an outer energy level electron configuration of $3s^2\ 3p^6$. Notice that both the s and p sublevels are filled. Helium has an electron configuration that might fit into Group 2A. However, the chemical reactivity of helium, because it has a full first energy level, is similar to that of the noble gases.

Elements Ending with s^2p^5 = Halogens

The halogens are an interesting group. Halogens are members of Group 7A, which is also referred to as 17. It is the only group in the periodic table that contains all of the states of matter at room temperature. Fluorine, F_2, is a gas, as is chlorine, Cl_2. Bromine, Br_2, is a liquid and iodine, I_2, and astatine, At_2, are both solids. What else is neat about Group 7A is that it houses four (4) of the seven (7) diatomic compounds. Remember the diatomics are H_2, N_2, O_2, F_2, Cl_2, Br_2, and I_2. Notice that the latter four are Group 17 elements. The word halogen comes from the Greek meaning *salt forming*. French chemists discovered that the majority of halogen ions will form salts when combined with metals. We all know some of these already: LiF, NaCl, KBr, and NaI.



Taking a look at Group 7A in the figure, we can find the same pattern of similar electron configurations as found with group 1A, 2A, and 8A. It is the 17th group in the periodic table and it contains only five elements.

Table 4: Electron Configurations for Group 7A Elements

Element	Atomic number	Electronic configuration
Fluorine (F)	9	$1s^2\ 2s^2\ 2p^5$
Chlorine (Cl)	17	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$
Bromine (Br)	35	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^5$
Iodine (I)	53	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^5$
Astatine (At)	85	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ 6s^2\ 4f^{14}\ 5d^{10}\ 6p^5$

What is the general trend for the elements in Group 7A? They all have, as the outermost energy level electron configuration, ns^2np^5, where n is the period number. You should also note that these elements are one group away from the noble gases (the ones that generally don't react!) and the outermost electron configuration of the halogens is one away from being filled. For example, chlorine (Cl) has the electron configuration [Ne] $3s^2$ $3p^5$ so it is in period 3, the seventh element in the ***main group elements.*** The main group elements, as you recall, are equivalent to the s + p blocks of the periodic table (or the teal and purple groups in the diagram above).

Elements Ending with s^2p^4 = the Oxygen Family

Oxygen and the other elements in Group 6A have a similar trend in their electron configurations. Oxygen is the only gas in the group; all others are in the solid state at room temperature. Oxygen was first named by Antoine Lavoisier in the late 1700s but really the planet has had oxygen around since plants were first on the earth. Taking a look at Group 6A in the figure below, we find the same pattern in electron configurations that we found with the other groups. Oxygen and its family members are in the 16th group in the periodic table. In Group 16, there are, again, only five elements.

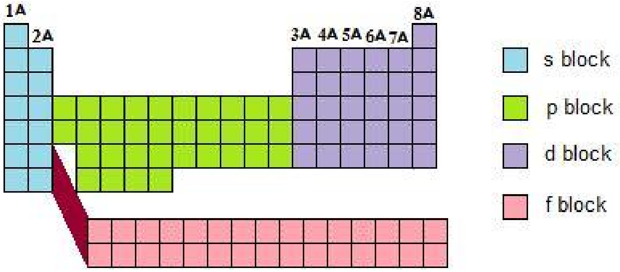


Table 4: Electron Configurations for Group 6A Elements

Element	**Atomic Number**	**Electron Configuration**
Oxygen (O)	8	$1s^2$ $2s^2$ $2p^4$
Sulfur (S)	16	$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^4$
Selenium (Se)	34	$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $4s^2$ $3d^{10}$ $4p^4$
Tellurium (Te)	52	$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $4s^2$ $3d^{10}$ $4p^6$ $5s^2$ $4d^{10}$ $5p^4$
Polonium (Po)	84	$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $4s^2$ $3d^{10}$ $4p^6$ $5s^2$ $4d^{10}$ $5p^6$ $6s^2$ $4f^{14}$ $5d^{10}$ $6p^4$

When we examine the electron configurations of the Group 6A elements, we see that all of these elements have the outer energy level electron configuration of ns^2np^4. We will see that this similar electron configuration gives all elements in the group similar properties for bonding.

These elements are two groups away from the noble gases and the outermost electron configuration is two away from being filled. Sulfur, for example, has the electron configuration $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^4$ so it is in period 3. Sulfur is the sixth element in the main group elements. We know it is the sixth element across the period of the main group elements because there are 6 electrons in the outermost energy level.

Elements Ending with s^2p^3 = the Nitrogen Family

Just as we saw with Group 16, Group 5A has a similar oddity in its group. Nitrogen is the only gas in the group with all other members in the solid state at room temperature. Nitrogen was first discovered by the Scottish chemist Rutherford in the late 1700's. The air is mostly made of nitrogen. Nitrogen has properties that are different in some ways from its group members. As we will learn in later lessons, the electron configuration for nitrogen provides the ability to form very strong triple bonds. Nitrogen and its family members belong in the 15th group in the periodic table. In Group 15, there are also only five elements.

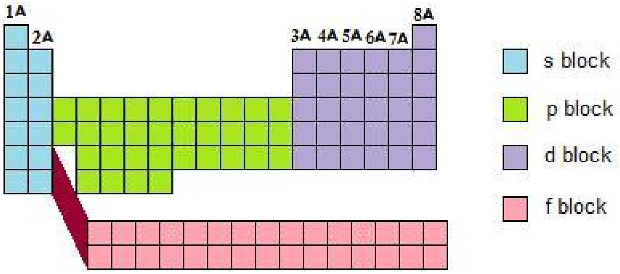


Table 6: Electronic Configurations for Group 5A Elements

Element	Atomic Number	Electron Configuration
Nitrogen (N)	7	$1s^2\ 2s^2\ 2p^3$
Phosphorus (P)	15	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$
Arsenic (As)	33	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^3$
Antimony (Sb)	51	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^3$
Bismuth (Bi)	83	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ 6s^2\ 4f^{14}\ 5d^{10}\ 6p^3$

What is the general trend for the elements in group 5A? They all have, as the electron configuration in the outermost energy level, $ns^2\ np^3$, where n is the period number. These elements are three groups away from the noble gases and the outermost energy level electron configuration is three away from having a completed outer energy level. In other words, the p sublevel in the Group 15 elements is half full. Arsenic, for example, has the electron configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^3$ so it is in period 4, the fifth element in the main group elements. We know it is the fifth element across the period of the main group elements because there are 5 electrons in the outermost energy level.

Lesson Summary

- Families in the periodic table are the vertical columns and are also referred to as groups.
- Group 1A elements are the alkali metals and all have one electron in the outermost energy level because their electron configuration ends in s^1.
- Group 2A elements are the alkaline earth metals and all have two electrons in the outermost energy level because their electron configuration ends in s^2.
- Group 5A elements all have five electrons in the outermost energy level because their electron configuration ends in $s^2\ p^3$.
- Group 6A elements all have six electrons in the outermost energy level because their electron configuration ends in $s^2\ p^4$.

- Group 7A elements are the halogens and all have seven electrons in the outermost energy level because their electron configuration ends in $s^2 p^5$.
- Group 8A elements are the noble gases and all have eight electrons in the outermost energy level because their electron configuration ends in $s^2 p^6$.
- Elements in group 8A have the most stable electron configuration in the outermost shell because the sublevels are completely filled with electrons.

Review Questions

1. If an element is said to have an outermost electronic configuration of $ns^2 np^3$, it is in what group in the periodic table? **(Beginning)**

(a) Group 3A

(b) Group 4A

(c) Group 5A

(d) Group 7A

2. What is the general electronic configuration for the Group 8A elements? **(Beginning)**

(Note: when we wish to indicate an electron configuration without specifying the exact energy level, we use the letter "n" to represent any energy level number. That is, ns^2np^3 represents any of the following; $2s^22p^3$, $3s^23p^3$, $4s^24p^3$, and so on.)

(a) $ns^2 np^6$

(b) $ns^2 np^5$

(c) $ns^2 np^1$

(d) ns^2

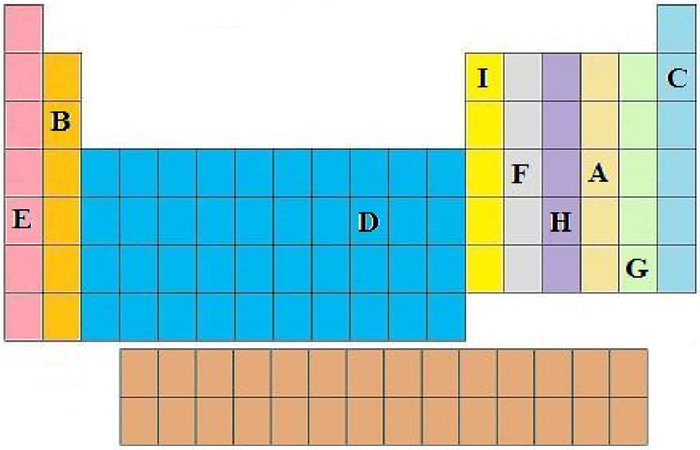
3. The group 2 elements are given what name? **(Beginning)**

(a) alkali metals

(b) alkaline earth metals

(c) halogens

(d) noble gases



4.

Using the diagram, identify: **(Beginning)**

(a) The alkali metal by giving the letter that indicates where the element would be located and write the outermost electronic configuration.

(b) The alkaline earth metal by giving the letter that indicates where the element would be located and write the outermost electronic configuration.

(c) The noble gas by giving the letter that indicates where the element would be located and write the outermost electronic configuration.

(d) The halogen by giving the letter that indicates where the element would be located and write the outermost electronic configuration.

(e) The element with an outermost electronic configuration of s^2 p^3 by giving the letter that indicates where the element would be located.

(f) The element with an outermost electronic configuration of s^2 p^1 by giving the letter that indicates where the element would be located.

5. In the periodic table, name the element whose outermost electronic configuration is found below. Where possible, give the name of the group. **(Intermediate)**

(a) $5s^2$

(b) $4s^2$ $3d^{10}$ $4p^1$

(c) $3s^2$ $3p^3$

(d) $5s^2$ $4d^{10}$ $5p^2$

(e) $3s^1$

(f) $1s^2$

(g) $6s^2$ $5d^{10}$ $6p^5$

(h) $4s^2$ $4p^4$

Further Reading / Supplemental Links

http://en.wikipedia.org

Vocabulary

group	Vertical columns of the periodic table.
period	Horizontal rows of the periodic table.

alkali metals	Group 1 in the periodic table (Li, Na, K, Rb, Cs, Fr).
alkaline earth metals	Group 2 in the periodic table (Be, Mg, Ca, Sr, Ba, Ra).
noble gases	Group 18 in the periodic table (He, Ne, Ar, Kr, Xe, Rn).
halogens	Group 17 in the periodic table (F, Cl, Br, I, At).
main group elements	Equivalent to the s + p blocks of the periodic table, also known as "representative elements."

Review Answers

1. (c) Group 5A

2. (a) $ns^2\ np^6$

3. (b) alkaline earth metals

4.

a. Element E: outermost electronic configuration = ns^1

b. Element B: outermost electronic configuration = ns^2

c. Element C: outermost electronic configuration = ns^2np^6

d. Element G: outermost electronic configuration = ns^2np^5

e. Element H

f. Element I

5.

(a) $5s^2$ Sr: Alkaline earth metals: Group 2A

(b) $4s^2\ 3d^{10}\ 4p^1$ Ga: Group 3A

(c) $3s^2\ 3p^3$ P: Group 5A

(d) $5s^2\ 4d^{10}\ 5p^2$ Sn: Group 4A

(e) $3s^1$ Na: Alkali metals: Group 1A

(f) $1s^2$ He: Noble Gases: Group 8A

(g) $6s^2\ 5d^{10}\ 6p^5$ At: Halogens: Group 7A

(h) $4s^2\ 4p^4$ Se: Group 6A

Electron Configurations

Lesson Objectives

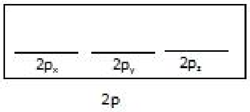
- Convert from orbital representation diagrams to electron configuration codes.
- Distinguish between outer energy level (valence) electrons and core electrons.
- Use the shortcut method for writing electron configuration codes for atoms and ions.

Introduction

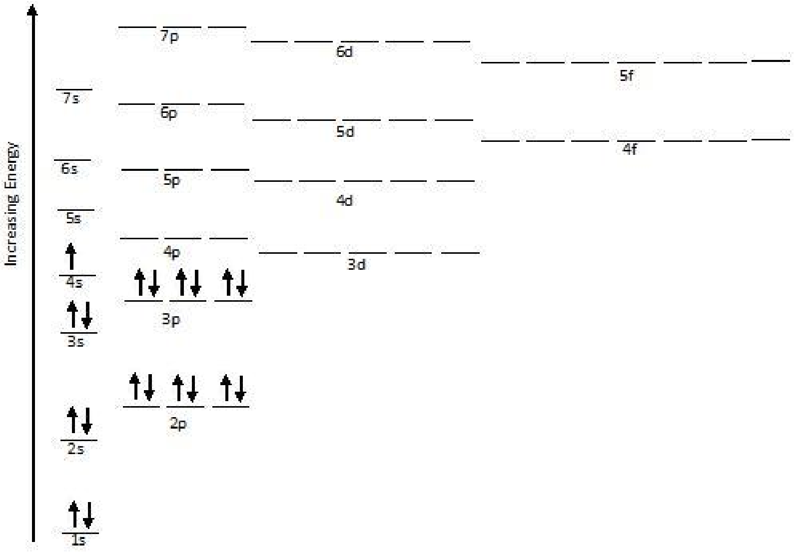
In the last section, we determined that the members of the chemical families (vertical columns on the periodic table) all have the same electron configuration in their outermost energy levels. In the next section, we will review the orbital representation for electron configuration and the electron configuration code. Then we will learn a shortcut for writing electron configuration codes.

Shortcut for Writing Electron Configurations

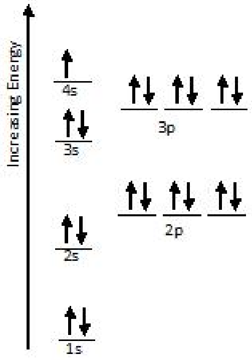
The diagram below represents the ***orbital representation diagram*** used in earlier chapters. The orbital representation diagram has a few different variations but all are used to draw electron configurations. Most show the orbitals in groups (or even in boxes or circles) with orbitals having their own line (or box) within each sublevel. The sublevel 2p has 3 orbitals ($2p_x$, $2p_y$, and $2p_z$) and each of these orbitals has its own line (or box).



Let's begin this section with the orbital box (or the orbital representation diagram) for a neutral atom. Draw the electronic configuration for potassium using the electron configuration diagram below. Remember that potassium is element number 19 so has 19 electrons. Every line in the energy diagram below holds 2 electrons of opposite spins.



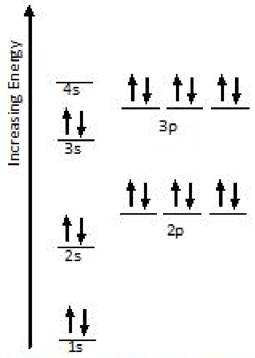
Now we can simplify this by excluding all of the levels and sublevels that are not in use or do not hold electrons.



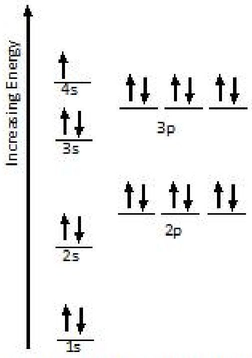
Writing the electron configuration code for potassium, we would get:

K: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$.

Remember, the noble gases are the elements that are nearly non-reactive, partially due to the fact that the outermost energy level electron configuration was full ($ns^2\ np^6$). Look at potassium on the periodic table and then find the preceding noble gas. Drag you finger counting backward from potassium to the nearest noble gas. What do you get? Argon (Ar) is correct. Now, let's draw the electron configuration for Argon and place the electron configuration for potassium beside it.



Electron configuration for Argon



Electron configuration for Potassium

What do you notice looking at the two diagrams? Potassium has the same electron configuration as argon + 1 electron. We can make this point when we write electronic configuration codes.

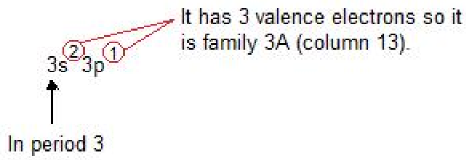
K: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$

Ar: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

Therefore

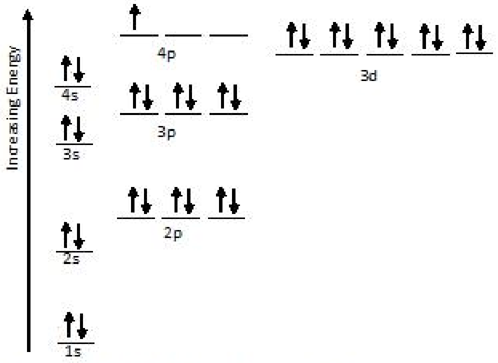
K: [Ar] $4s^1$. {This is known as the noble gas configuration code system or the "short-cut"}

Let's try another. Draw and write the electron configuration of gallium (Ga). Gallium is number 31 and therefore has 31 electrons. It is also in the 4th period, the third element in the period of main group elements. From this information, we know that the outermost electrons will be $4s^2\ 4p^1$.



Electron configuration of Gallium (Ga).

Writing the electron configuration code for gallium, we get: Ga: $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $4s^2$ $3d^{10}$ $4p^1$. In numerical order, the electronic configuration for gallium is: Ga: $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^{10}$ $4s^2$ $4p^1$.



Electron configuration for Gallium (Ga)

Now, go back to the previous noble gas. Again, we find the previous noble gas is argon. Remember argon has electronic configuration of $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$.

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

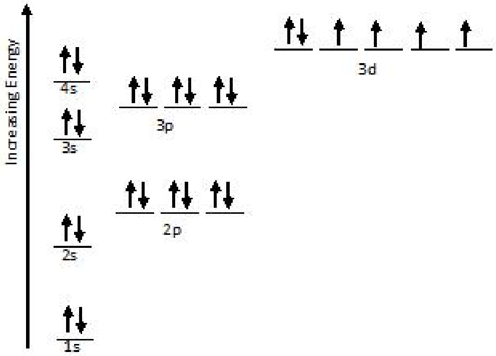
Ar: $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$

Therefore

Ga: [Ar] $4s^2$ $3d^{10}$ $4p^1$.

This seems to work well for neutral atoms, what about ions? Remember that a cation is formed when electrons are removed from a neutral atom and anions are formed when electrons are added to a neutral atom. But where do the electrons get added to or removed from? The electrons that are involved in chemical reactions are the ones that are in the outer shell. Therefore if electrons are to be removed or added, they get removed from or added to the shell with the highest value of n.

Let's now look at an example. Draw the electron configuration for Fe. Then, write the reaction for the formation of Fe^{2+}.



Electron configuration for Iron (Fe)

The reaction for the formation of the Fe^{2+} ion is: Fe ⟶ $Fe^{2+} + 2e^-$. Therefore we have to remove 2 electrons. From where do we remove the two electrons? The rule is to remove from the highest n value first which, in this case, means we remove from the electrons from the 4s sublevel first.

$$\begin{array}{lll} \text{Fe} & \longrightarrow & Fe^{2+} + 2e^- \\ 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6 & \longrightarrow & 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6 + 2e^- \end{array}$$

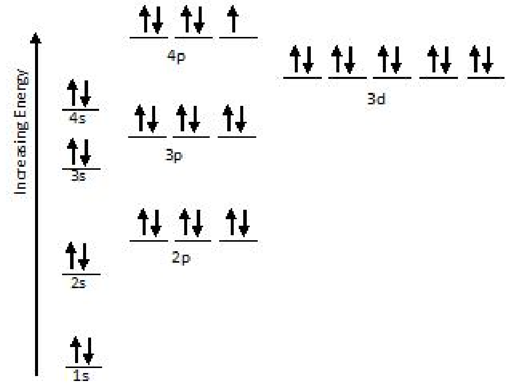
Remember that when we write electron configuration codes using noble gas configurations we use the previous noble gas. In writing the electron configuration code for Fe or Fe^{2+}, we would use the symbol [Ar] to substitute for $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$.

$$\begin{array}{lll} \text{Fe} & \longrightarrow & Fe^{2+} + 2e^- \\ [Ar]\ 3d^6\ 4s^2 & \longrightarrow & [Ar]\ 3d^6 + 2e^- \end{array}$$

In addition to forming Fe^{2+} ions, iron atoms are also capable of forming Fe^{3+} ions. Extra stability is gained by electron configurations that have exactly half-filled *d* orbitals. The third electron that is removed from an iron atom to form the Fe^{3+} ion is removed from the d orbital giving this iron ion a d orbital that is exactly half-filled. The extra stability of this configuration explains why iron can form two different ions.

$$\begin{array}{lll} \text{Fe} & \longrightarrow & Fe^{3+} + 3e^- \\ [Ar]\ 3ds^6\ 4s^2 & \longrightarrow & [Ar]\ 3ds^5 + 3e^- \end{array}$$

Now what about negative ions, the anions? Remember that negative ions are formed by the addition of electrons to the electron cloud. Look at bromine, Br. Neutral bromine has atomic number 35 and therefore, holds 35 electrons.



Electron configuration for Bromine (Br)

The reaction for the formation of the Br^- ion is: $Br + e^- \longrightarrow Br^-$. The bromide ion is formed by the addition of one electron. If you look at the electron configuration for bromine, you will notice that the 4p sublevel needs one more electron to fill the sublevel and if this sublevel is filled, the electron configuration for Br^- is the same as that of the noble gas krypton (Kr). When adding electrons to form negative ions, the electrons are added to the lowest unfilled n value.

$Br + e^- \longrightarrow Br^-$

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^5 + e^- \longrightarrow 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6$

Or

$Br + e^- \longrightarrow Br^-$

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^5 + e^- \longrightarrow [Kr]$

Notice how Br^- has the same electron configuration as Kr. When this happens, the two are said to be ***iso-electronic.***

Sample Question: Write the electron configuration codes for the following atoms or ions using the noble gas electron configuration shortcut.

(a) Se

(b) Sr

(c) O^{2-}

(d) Ca^{2+}

(e) Al^{3+}

Solution:

(a) Se : $[Ar]\ 4s^2\ 3d^{10}\ 4p^4$

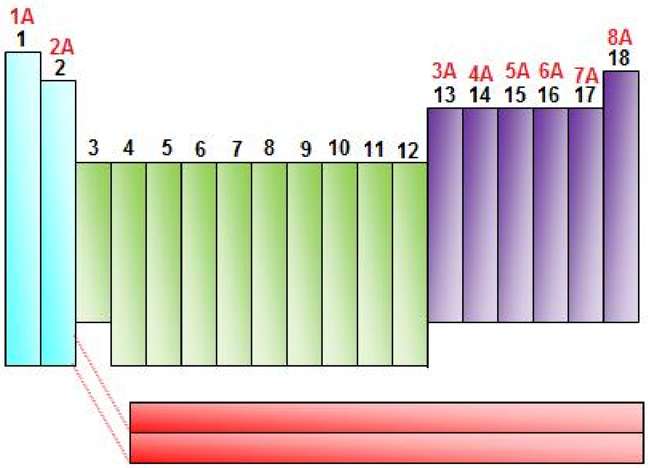
(b) Sr : $[Kr]\ 5s^2$

(c) O^{2-} : [Ne]

(d) Ca^{2+} : [Ar]

(e) Al^{3+} : [Ne]

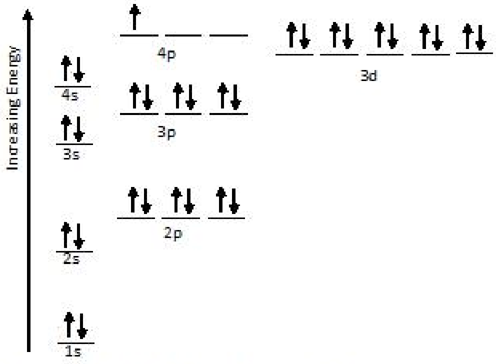
Core Electrons



When we look at the electron configuration for any element we can distinguish that there are two different types of electrons. There are electrons that work to do the reacting and there are those that don't. The outer shell electrons are the ***valence electrons*** and these are the electrons that are responsible for the reactions that the atoms undergo. The number of valence electrons increases as you move across the periodic table for the main group elements.

In older periodic tables, the groups were numbered using an A and B group numbering system. The representative groups (s and p blocks) were numbered with A and the transition elements were numbered with B. The table on the right has both numbering systems. The A numbering is shown for you in the diagram in red; this is all we will be concerned with for this lesson. The number of valence electrons in the A groups increases as the group number increases. In fact, the number of the A groups is the number of valence electrons. Therefore, if an element is in group 3A, it has 3 valence electrons, if it is in group 5A, it has 5 valence electrons.

All electrons other than valence electrons are called ***core electrons.*** These electrons are in inner energy levels. It would take a very large amount of energy to pull an electron away from these full shells, hence, they do not normally take part in any reactions. Look at the electron configuration for gallium (Ga). It has 3 valence electrons and 28 core electrons.



Electron configuration for Gallium (Ga)

Sample Question: How many core electrons and valence electrons are in each of the following?

(a) V

(b) As

(c) Po

(d) Xe

Solution:

(a) $_{23}$V : Core Electrons = 18, Valence electrons = 5

(b) $_{33}$ As : Core Electrons = 28, Valence electrons = 5

(c) $_{84}$ Po : Core Electrons = 78, Valence electrons = 6

(d) $_{54}$ Xe : Core Electrons = 46, Valence electrons = 8

Lesson Summary

- An orbital box diagram can be used to draw electron configurations for elements.
- The noble gas configuration system is the shorthand method for representing the electron configuration of an element.
- The noble gas symbol represents all of, or most of, the core electrons.
- For cations, the electrons are removed from the outermost sublevel having the greatest ***n*** value.
- For anions, the electrons are added to the unfilled energy level having the lowest ***n*** value.
- Isoelectronic species have the same electron configurations.
- Using an orbital box diagram, the core electrons and the valence electrons can easily be visualized.
- The valence electrons are those electrons that are in the outermost shell.

Review Questions

1. What is the difference between the standard electron configuration code and the electron configuration code using noble gas configurations? **(Beginning)**

2. The standard electron configuration is often called the ground state electron configuration.

Why do you think this is so? **(Beginning)**

3. How is it possible to have the same number of core electrons and valence electrons for two different ions? **(Challenging)**

4. Draw the orbital representation for the electron configuration of potassium, K. **(Intermediate)**

5. Write the electron configuration code for potassium, K. **(Intermediate)**

6. Write the noble gas electron configuration code for potassium, K. **(Intermediate)**

7. How many core electrons and valence electrons are in potassium, K? **(Intermediate)**

8. Write the electron configuration for potassium, K^+. **(Intermediate)**

9. Write the noble gas electron configuration code for potassium, K^+. **(Intermediate)**

10. With what species is K^+ isoelectronic? **(Intermediate)**

11. The electron configuration below is for which element? **(Intermediate)**

[Kr] $4d^{10}$ $5s^2$ $5p^2$

(a) Sb

(b) Sn

(c) Te

(d) Pb

12. The electron configuration below is for which element? **(Intermediate)**

[Xe] $5d^{10}$ $6s^2$ $6p^4$

(a) Pb

(b) Bi

(c) Po

(d) Tl

13. What is the noble gas electron configuration for the bromine element? **(Intermediate)**

(a) $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6 4s^2$ $4p^5$

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

(c) [Ar] $4s^2$ $4p^5$

(d) [Ar] $3d^{10}$ $4s^2$ $4p^5$

14. Write the noble gas electron configuration for each of the following. **(Intermediate)**

(a) Al

(b) N^{3-}

(c) Sr^{2+}

(d) Sn^{2+}

(e) I

15. How many core electrons and valence electrons are in each of the following? **(Intermediate)**

a. Mg

b. C

c. S

d. Kr

e. Fe

Vocabulary

orbital box diagram	A diagram for drawing the electron configurations where sub-levels are shown in groups (or even in boxes) and each orbital has its own line (or box) within each sub-level.
isoelectronic	Having the same electron configuration.
core electrons	Electrons that occupy energy levels below the outermost energy level.
valence electrons	Electrons that occupy the outer shell of the atom or ion.

Review Answers

1. The noble gas configuration includes all of the full orbitals up to the nearest shell to the element. For example for sodium, Na:

$_{11}$Na: $1s^2\ 2s^2\ 2p^6\ 3s^1$

The noble gas configuration would include everything up to and including the $2p^6$.

Therefore Na would become:

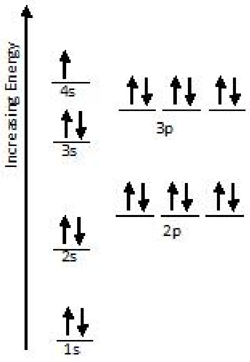
$_{11}$Na: [Ne] $3s^1$

2. The standard electronic configuration is probably called the ground state electronic configuration because it starts at the ground level (n = 1).

3. If you have an element and an ion or two ions, these can have the same number of core electrons and the same number of valence electrons. Look at Na^+ and Mg^{2+}

A sodium atom has 11 electrons, 10 core electrons and 1 valence electron. When the sodium atom becomes a +1 ion, it has 10 core electrons and zero valence electrons. A magnesium atom has 12 electrons, 10 core electrons and 2 valence electrons. When the magnesium atom becomes a 2+ ion, it has 10 core electrons and zero valence electrons. Both ions have the same electron configuration as a neon atom.

4.



5. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$

6. [Ar] $4s^1$

7. 18 core electrons and 1 valence electron

8. $1s^2 2s^2 2p^6 3s^2 3p^6$

9. [Ar]

10. argon

11. (b) Sn

12. (c) Po

13. (d) [Ar] $3d^{10}$ $4s^2$ $4p^5$

14. (a) Al: [Ne] $3s^2$ $3p^1$

(b) N^{3-}: [Ne]

(c) Sr^{2+}: [Kr]

(d) Sn^{2+}: [Kr] $4d^{10}$ $5s^2$

(e) I: [Xe] $4d^{10}$ $5s^2$ $5p^5$

15.

(a) $_{12}Mg$: Core Electrons = 10, Valence electrons = 2

(b) $_{6}C$: Core Electrons = 2, Valence electrons = 4

(c) $_{16}S$: Core Electrons = 10, Valence electrons = 6

(d) $_{36}Kr$: Core Electrons = 28, Valence electrons = 8

(e) $_{26}Fe$: Core Electrons = 18, Valence electrons = 8

Lewis Electron Dot Diagrams

Lesson Objectives

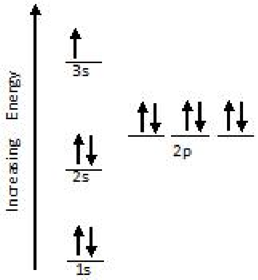
- Explain the meaning of an electron dot diagram.
- Draw electron dot diagrams for given elements.
- Describe the patterns of electron dot diagrams in the periodic table.

Introduction

This chapter will explore yet another shorthand method of representing the valence electrons. The method explored in this lesson will be a visual representation of the valence electrons. We will, as we observed in the previous lesson, finish the lesson with a look at how this visual representation flows in a pattern throughout the periodic table.

A Simplified Way to Show Valence Electrons

As defined earlier in this chapter, core electrons are all the electrons except the valence electrons and valence electrons are the electrons in the outermost energy level. Valence electrons are the electrons responsible for chemical reactions. Here is the electron configuration for sodium.



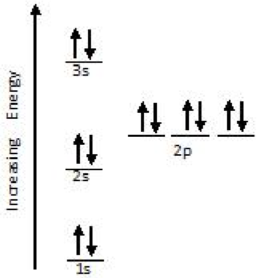
Electron configuration for Sodium (Na)

The electron configuration is Na: $1s^2\ 2s^2\ 2p^6\ 3s^1$. The core electrons are $1s^2\ 2s^2\ 2p^6$. The valence electron is $3s^1$. One way to represent this valence electron, visually, was developed by Gilbert N. Lewis. These visual representations were given the name ***Lewis electron dot diagrams.*** Lewis suggested that since the valence electrons are responsible for chemical reactions and the core electrons are not involved, we should use a diagram that shows just the valence electrons for an atom.

To draw a Lewis electron dot diagram for sodium you can picture the symbol for sodium in a box with the box having four sides. Each side of the box represents either the s or one of the three p orbitals in the outermost energy level of the atom. The first and second valence electrons are placed on the side representing the s orbital and the next electrons are placed in the p orbitals. Just as the electrons are placed singly before being doubled up in the orbital representation, so they are placed one at a time in the p orbitals of an electron dot formula. A single dot represents one valence electron. Thus, the Lewis dot formula for sodium is:

Na •

Look at the electron configuration for magnesium. Magnesium is element #12.

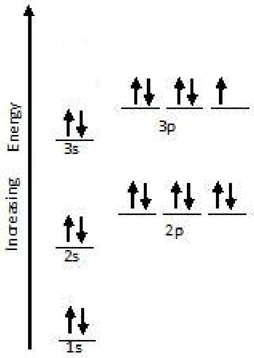


Electron configuration for Magnesium (Mg)

To draw the Lewis electron dot diagram we picture in our minds the symbol for Mg in a box with all of its core electrons (i.e., $1s^2\ 2s^2\ 2p^6$). Then we place the valence electrons around the sides of the box with each side representing an orbital in the outermost energy level. How many valence electrons does magnesium have? Correct, there are 2 valence electrons, $3s^2$.

Therefore the Lewis electron dot formula for magnesium is:

Look at the electron configuration for chlorine.



Electron configuration for Chlorine (Cl)

The electron configuration for chlorine could be written as: Cl: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$. The core electrons would be $1s^2\ 2s^2\ 2p^6$ while the valence electrons would be in the third shell (or where n = 3). Therefore, chlorine has 7 valence electrons. The Lewis electron dot diagram would look like the following:

Notice that the electrons are in groups of two. Think of the chlorine in a box and the box has 4 sides. Each side can have 2 electrons on it. Therefore there can be a maximum of 2 x 4 = 8 electrons normally on any Lewis electron dot diagram.

Sample question: Write the Lewis electron dot formula for:

(a) Oxygen

(b) Sulfur

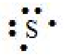
(c) Potassium

(d) Carbon

Solution:

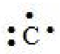
(a) Oxygen has the electron configuration: $1s^2\ 2s^2\ 2p^4$, therefore there are 2 core electrons and 6 valence electrons. The Lewis electron dot formula is:

(b) Sulfur has the electron configuration: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$, therefore there are 10 core electrons and 6 valence electrons. The Lewis electron dot formula is:



(c) Potassium has the electron configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$, therefore there are 18 core electrons and 1 valence electron. The Lewis electron dot formula is:

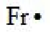
(d) Carbon has the electron configuration: $1s^2 2s^2 2p^2$, therefore there are 2 core electrons and 4 valence electrons. The Lewis electron dot formula is:



All the Elements in a Column Have the Same Electron Dot Diagram

In the previous lesson, it was shown that using the earlier version for numbering the periodic table, we could see a pattern for finding the number of valence electrons in each of the groups in the main group elements. Since the Lewis electron dot diagrams are based on the number of valence electrons, it would hold true that the elements in the same group would have the same electron dot diagram. In other words, if every element in Group 1A has 1 valence electron, then every Lewis electron dot diagram would have one single dot in their Lewis electron dot diagram. Take a look at the table below.

Table 1: Lewis Electron Dot Diagrams for Group 1A Elements

Element	1. Valence e^-	Lewis electron dot diagram
Hydrogen (H)	1	
Lithium (Li)	1	
Sodium (Na)	1	
Potassium (K)	1	
Rubidium (Rb)	1	
Cesium (Cs)	1	
Francium (Fr)	1	

The same pattern holds for all elements in the main group. Look at Table 2 for the Lewis dot diagrams for Group 2A elements.

Table 2: Lewis Electron Dot Diagrams for Group 2A Elements

Element	1. Valence e^-	Lewis electron dot diagram
Beryllium (Be)	2	$\text{Be}\,:$
Magnesium (Mg)	2	$\text{Mg}\,:$
Calcium (Ca)	2	$\text{Ca}\,:$
Strontium (Sr)	2	$\text{Sr}\,:$
Barium (Ba)	2	$\text{Ba}\,:$
Radium (Ra)	2	$\text{Ra}\,:$

A similar pattern exists for the Lewis electron dot diagrams for Group 3A.

Element	1. Valence e^-	Lewis electron dot diagram
Boron (B)	3	$\overset{\bullet\bullet}{\text{B}}\bullet$
Aluminum (Al)	3	$\overset{\bullet\bullet}{\text{Al}}\bullet$
Gallium (Ga)	3	$\overset{\bullet\bullet}{\text{Ga}}\bullet$
Indium (In)	3	$\overset{\bullet\bullet}{\text{In}}\bullet$
Thallium (Tl)	3	$\overset{\bullet\bullet}{\text{Tl}}\bullet$

Lesson Summary

- A Lewis Electron Dot Diagram is used to visually represent only the valence electrons.
- The core electrons are symbolized using the symbol of the element with the valence electron dots surrounding the element symbol.
- The maximum number of valence electron dots in the Lewis electron dot diagram is 8. Two electrons can go one each side (top, bottom, left, and right).
- Electrons are added to the electron dot formula by placing the first two valence electrons in the s orbital, then one in each p orbital until each p orbital has one electron, and then doubling up the electrons in the p orbitals.

- Each element in a group has the same number of valence electrons and therefore has the same Lewis electron dot diagram. (Same number of dots, different symbol.)

Review Questions

1. What is the advantage of the Lewis electron dot diagram? **(Intermediate)**

2. What is the maximum number of dots in a Lewis's Electron dot diagram? **(Beginning)**

3. Draw the Lewis electron dot diagram for lithium. **(Intermediate)**

4. Draw the Lewis electron dot diagram for calcium. **(Intermediate)**

5. Draw the Lewis electron dot diagram for bromine. **(Intermediate)**

6. Draw the Lewis electron dot diagram for selenium. **(Intermediate)**

7. Write the Lewis electron dot diagrams for each of the following. What observations can you make based of these diagrams? **(Intermediate)**

(a) Oxygen 2- ion

(b) Sulfur 2- ion

(c) Antimony

(d) Aluminum

8. Write the trend for the Lewis electron dot diagrams for Group 6A (or Group 16) by filling in the table below. **(Intermediate)**

Element	1. Valence e^-	Lewis Electron Dot Diagram
Oxygen (O)		
Sulfur (S)		
Selenium (Se)		
Tellurium (Te)		

Polonium (Po)		

Further Reading / Supplemental Links

http://en.wikipedia.org

Vocabulary

Lewis Electron Dot Diagram	A shorthand visual representation of the valence electrons for an element. (Lewis electron dot diagram for sodium with one valence electron: Na•

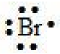
Review Answers

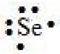
1. Answers will vary but students might comment on the fact that the Lewis dot diagram visualizes the valence electrons only and the core electrons are “hidden” with the symbol of the element.

2. The noble gas electronic configuration has a completed outer energy level (ns2 np6), which is 8 electrons.

3. Li•

4. Ca:

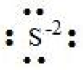
5. 

6. 

7.

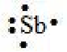
(a) Oxygen has the electronic configuration: $1s^2\ 2s^2\ 2p^4$, therefore the ion will be O^{2-} and have the electronic configuration of $1s^2\ 2s^2\ 2p^6$. The Lewis electron dot diagram is:

(b) Sulfur has the electronic configuration: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$, therefore the ion will be S^{2-} and have the electronic configuration of $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$. The Lewis electron dot diagram is:



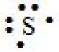
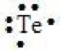
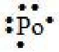
Notice this is the same Lewis electron dot diagram as the oxygen ion.

(c) Antimony has the electronic configuration: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^3$. The Lewis electron dot diagram is:



(d) Aluminum has the electronic configuration: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$. The Lewis electron dot diagram is:

8.

Element	1. Valence e^-	Lewis Electron Dot Diagram
Oxygen (O)	6	
Sulfur (S)	6	
Selenium (Se)	6	
Tellurium (Te)	6	
Polonium (Po)	6	

Chemical Family Members Have Similar Properties

Lesson Objectives

- Explain the role of the core electrons.
- Explain the role of valence electrons in determining chemical properties.
- Explain how the chemical reactivity trend in a chemical family is related to atomic size.

Introduction

Combining what we have learned from the previous lessons, we can now determine how the core electrons and the valence electrons relate to the properties of families in the periodic table. We have looked at the trend of the number of valence electrons within each group and now we will expand this to include a look at the trends that exist between the sublevel of valence electrons and the relative ability of an element to react in a chemical reaction. We will explore the possibility of predicting chemical reactivity based on the number of valence electrons and the sublevel to which they belong. Let's begin our lesson with a review of the core electrons and discuss their application in chemical reactions. Following this, we will have a similar discussion about valence electrons.

Core Electrons Can be Ignored in Determining an Element's Chemistry

As learned in an earlier lesson, the core electrons are the inner electrons found in the electron configuration for the element. These electrons fill up the inner sublevels and are thus not responsible for bonding and are not involved in chemical reactions. The core electrons also are not directly responsible for determining the properties of the elements. Remember that the core electrons represent all of the electrons except for the valence electrons.

Look at the electron configuration for beryllium (Be).

Be: $1s^2\ 2s^2$

There are two core electrons ($1s^2$) and two valence electrons ($2s^2$).

When we look at the electron configuration for Selenium (Se), we see the following.

Se: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^4$

There are 28 core electrons ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$) and six valence electrons ($4s^2\ 4p^4$). Again, none of the core electrons from either of these elements, or any element for that matter, will participate in chemical reactions.

Sample question: What are the core electrons in each of the following?

(a) O: $1s^2\ 2s^2\ 2p^4$

(b) In: [Kr] $5s^2\ 4d^{10}\ 5p^1$

Solution:

(a) O: core electrons = $1s^2$, therefore there are two of them.

(b) In: indium has three valence electrons and all the rest are core electrons. The core electrons include all the electrons in the energy levels below $n = 5$. ($4d^{10}$ are core electrons since they are held in a lower energy level.)

Valence Electrons Determine Chemical Properties

The valence electrons, unlike the core electrons, are responsible for all of the chemical reactions that take place between elements. They determine the properties of the elements. We have already learned that all metallic elements in the main group elements are able to lose their valence electrons since the energy requirements to do so are relatively low. The non-metallic elements (other than noble gases) are able to gain electrons readily because of high electron affinities. For elements in Group 3, the atoms will have to lose three electrons to have electron configurations similar to the previous noble gas. For elements in group 6, they will have to gain two electrons to have similar electron configurations as their nearest noble gas. Earlier we determined that all elements in the same group have the same Lewis Electron Dot diagram. What this means is that all elements in the same group have the same number of valence electrons and will react the same way to gain or lose electrons when participating in reactions. The number of valence electrons determines what types of chemical properties the elements will have.

When you look at the table below, you can see that the Group 1A metals all have the same number of valence electrons and also have the same appearance. These metals also react the same way under similar conditions.

Table 1: Electron Configuration and General Appearance for Group 1A Elements

Element	Electron Configuration	Appearance

Li	$1s^2\ 2s^1$	Silvery-white metal
Na	$1s^2\ 2s^2\ 2p^6\ 3s^1$	Soft, silvery-white metal
K	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$	Soft, silvery-white metal
Rb	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^1$	Soft, silvery-white metal
Cs	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ 6s^1$	Soft, silvery-white metal with gold sheen
Fr	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ 6s^2\ 4f^{14}\ 5d^{10}\ 6s^1$	? too short lived

We can see that all of the elements in the Group 1A metals all have one valence electron in their outer energy levels. This means that they can lose this one electron and become isoelectronic with a noble gas configuration. Thus, elements in Group 1A will readily lose this electron because it takes very low energy to remove this one outer electron.

As the atomic number increases for the elements in the alkali metal family group, the valence electron is further away from the nucleus. The attraction between the valence electron and the nucleus decreases as the atomic size increases. The further the electrons are away from the nucleus, the less hold the nucleus has on the electrons. Therefore the more readily the electrons can be removed and the faster the reactions can take place. So, the valence electrons will determine what reactions will occur and how fast they will occur based on the number of electrons that are in the valence energy level. All group 1A elements will lose one electron and form a 1+ cation.

Looking at the table for the electron configuration of the Group 2A metals, we see that the outer energy level holds two electrons for each of the metals in group 2.

Table 2: Electron Configuration for Group 2A Elements

Element	Electronic Configuration
Beryllium (Be)	$1s^2\ 2s^2$
Magnesium (Mg)	$1s^2\ 2s^2\ 2p^6\ 3s^2$
Calcium (Ca)	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$
Strontium (Sr)	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2$
Barium (Ba)	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ 6s^2$
Radium (Ra)	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ 6s^2\ 4f^{14}5d^{10}\ 6p^6\ 7s^2$

As with the Group 1A metals, the group 2A metals will form cations by losing the s electrons, but this time they will lose two electrons. And, as with the Group 1A elements, the elements are more reactive as the atomic number increases because the s electrons are held further away from the nucleus.

Consider the electron configurations for the elements in family 7A (the halogens).

Table 3: Electron Configuration for Group 7A Elements

Element	Electronic Configuration
Fluorine (F)	$1s^2\ 2s^2\ 2p^5$
Chlorine (Cl)	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$

Bromine (Br)	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^5$
Iodine (I)	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^5$

The elements in group 7A were placed in the same chemical family by Mendeleev because they all have similar chemistry, that is, they react with other substances in similar ways and their compounds with the same metals have similar properties. Now we know why they have similar chemical properties . . . because chemical properties are controlled by the valence electrons and these elements all have the same configuration of valence electrons.

The trend for chemical reactivity (speed of reaction) for the non-metal families is the reverse of the situation in the metal families. The metallic families lose electrons and the largest atoms lose their electrons most easily so the larger the atom, the faster it reacts. In the case of the non-metals, such as the halogens, the atoms react by taking on electrons. In these families, the smaller atoms have the largest electron affinity and therefore take on electrons more readily. Hence, in the non-metals, the smaller atoms will be more reactive.

Lesson Summary

- Core electrons are the inner electrons that are in filled orbitals and sublevels. Core electrons are not responsible for chemical reactivity and do not participate in chemical reactions. Valence electrons are the outermost electrons, are responsible for determining the properties, and are the electrons that participate in chemical reactions.
- Because the members of each group in the main group elements has the same number of valence electrons, there are similar properties and similar trends in chemical reactions found in the group. For metals, chemical reactivity tends to increase with increases in atomic size because the outermost electrons (or the valence electrons) are further away from the nucleus and therefore have less attraction for the nucleus.

Review Questions

1. What is the difference between valence electrons and core electrons? **(Beginning)**

2. Why would the valence electrons be responsible for the chemical reactivity? **(Intermediate)**

3. Which of the following pairs of elements would have the greatest similarities in terms of chemical properties? **(Intermediate)**

(a) Ca and Ca^{2+}

(b) Ca and Mg

(c) Ca and K

(d) Ca and Ar

4. What is the correct number of core electrons in the phosphorous atom? **(Beginning)**

(a) 3

(b) 5

(c) 10

(d) 15

5. What is the correct number of valence electrons in the iodine atom? **(Beginning)**

(a) 4

(b) 5

(c) 6

(d) 7

6. For the valence electrons in Group 6A, what conclusions can you draw about the trend in chemical reactivity? **(Intermediate)**

7. For the valence electrons in Group 7A, what conclusions can you draw about the trend in chemical activity? **(Intermediate)**

Further Reading / Supplemental Links

Website with lessons, worksheets, and quizzes on various high school chemistry topics.

- Lesson 3-8 is on Lewis Dot Structures.
- Lesson 1-8 is on Elemental Names and Symbols.

http://www.fordhamprep.org/gcurran/sho/sho/lessons/lesson31.htm

Vocabulary

noble gas core	When working with noble gas electronic configurations the core electrons are those housed in the noble gas symbolic notation.

Review Answers

1. Valence electrons are the electrons on the outer energy level of the atom. Core electrons are on those located on the inner energy levels.

2. Because the valence electrons are located in the outermost energy levels, most of these atoms have sublevels that are unfilled. It is in these unfilled sublevels where electrons are either lost or new electrons are gained. In other words, reactions take place with the valence electrons.

3. (b)

4. (c)

5. (d)

6.

Element	Electronic Configuration
Oxygen (O)	$1s^2\ 2s^2\ 2p^4$
Sulfur (S)	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$
Selenium (Se)	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^4$

Oxygen, sulphur and selenium each have six electrons in their outermost energy level and therefore can gain two electrons. Unlike the metallic counterparts, the chemical reactivity decreases going down this group.

7.

The elements in group 17 have seven electrons in their outermost energy level and therefore need one electron. Unlike the metallic counterparts, the chemical reactivity decreases going down this group.

Element	Electronic Configuration
Fluorine (F)	$1s^2\ 2s^2\ 2p^5$
Chlorine (Cl)	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$
Bromine (Br)	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^5$
Iodine (I)	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^5$

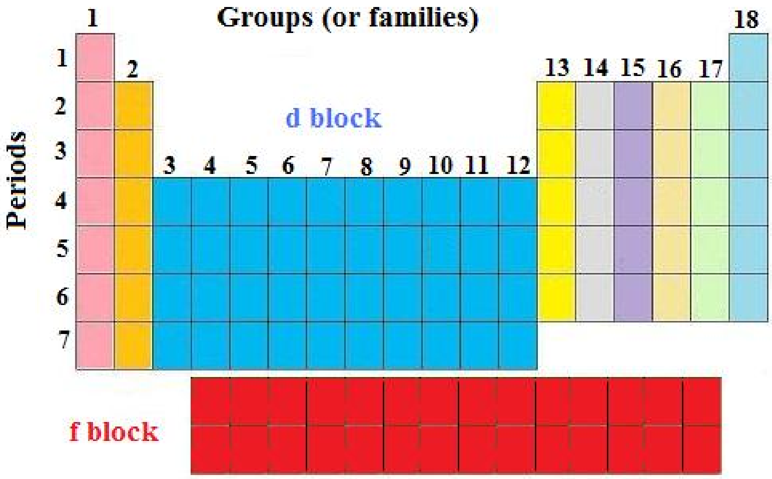
Transition Elements

Lesson Objectives

- Define transition metals.
- Explain the relationship between transition metals and the d sublevels.
- State the periods that contain transition metals.
- Write electron configurations for some transition metals.

Introduction

The main group elements are actually in two groups: the s block and the p block. These two, let's call them sub groups, are separated in the periodic table by a special group of highly colorful compounds known as the transition metals. The transition metals represent groups 3 through 12 of the diagram below and are formed as electrons are filling in the d orbitals. This is why they are referred to as the d block. We will look at all of this in the lesson that follows. Let's begin!!



Elements Whose Atoms are Filling d Sublevels

The elements in groups 3 through 12 are called the transition metals. Sometimes this block of elements are referred to as the d block. They are called d block elements because the electrons being added in this block of elements are being added to the d orbitals. Look at the electron configurations for Scandium (Sc), Titanium (Ti), and Vanadium (V), the first three transition metals of the first row in the d block.

$_{21}Sc: 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^1$

$_{22}Ti: 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^2$

$_{23}V: 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^3$

Notice that as the atomic number increases, the number of electrons in the d sublevels increases as well. This is why the phrase d block was started for the transition metals. The transition metals were given their name because they had a place between the 2A group (now Group 2) and the 3A (now Group 13) in the main group elements. Therefore, in order to get from calcium to gallium in the periodic table, you had to transition your way through the first row of the d block (Sc ⟶ Zn). To get from strontium to indium, you had to transition your way through the second row of the d block (Y ⟶ Cd).

One interesting point about the transition metals that is worth mentioning is that many of the compounds of these metals are highly colored and used in dyes and paint pigments. Also, metallic ions of transition elements are responsible for the lovely colors of many gems such as jade, turquoise and amethyst.

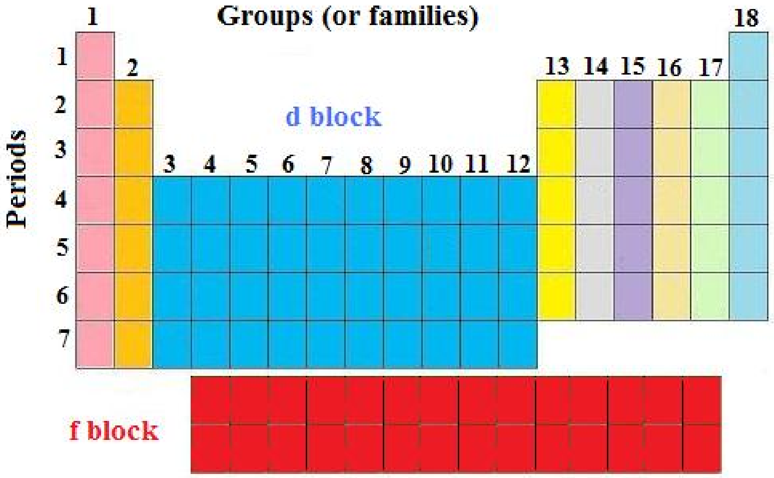
Sample question: Write the electron configuration code for Fe.

Solution:

$_{26}Fe: 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$

Transition Metals Occur in Periods 4 – 7

As stated before, transition metals are also called the d block because they fill up the d sublevels. Therefore, the first three periods do not have transition elements because those energy levels do not have d sub-shells. The transition metals have atomic numbers greater than 20 because the first d electron appears in element #21 after the 1s, 2s, 2p, 3s, 3p, and 4s orbitals are filled.



Lesson Summary

- Transition metals are those from the d block or those from Groups 3 through 12.
- Compounds of transition metals typically are those that are highly colored.
- Transition metals are found in Periods 4 through 7.

Further Reading / Supplemental Links

http://learner.org/resources/series61.html'''

The ***learner.org*** website allows users to view streaming videos of the Annenberg series of chemistry videos. You are required to register before you can watch the videos but there is no charge. The website has one video that apply to this lesson. It is called ***The Atom*** and deals with the internal structure of the atom.

Review Questions

1. Write the electron configuration for zirconium, Zr. **(Intermediate)**

2. How many valence electrons does zirconium, Zr, have? **(Intermediate)**

3. Write the noble gas electronic configuration for platinum, Pt. **(Intermediate)**

4. How many valence electrons does platinum, Pt, have? **(Intermediate)**

5. Why do the d block elements only start in the fourth period? **(Intermediate)**

6. What do copper, silver, and gold have in common as far as their electron configuration? **(Intermediate)**

7. Which of these is the electron configuration for nickel? **(Intermediate)**

(a) [Kr] $3d^8$ $4s^2$

(b) [Kr] $3d^{10}$

(c) [Ar] $3d^8$ $4s^2$

(d) [Ar] $3d^{10}$

8. How many d electrons are there in the electronic configuration for ruthenium? **(Intermediate)**

(a) 0

(b) 6

(c) 7

(d) 17

9. Write the electron configuration for Iridium, Ir. **(Intermediate)**

10. What are the valence electrons for Iridium, Ir? **(Intermediate)**

11. Write the noble gas electron configuration for mercury, Hg. **(Intermediate)**

12. How many valence electrons does mercury, Hg, have? **(Intermediate)**

Vocabulary

transition metal Groups 3 through 12 or the d block of the periodic table.

Review Answers

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

2. 2

3. [Xe] $6s^2$ $4f^{14}$ $5d^8$

4. 2

5. Period 4 is the first period in which a d sub-level is being filled.

6. Cu: [Ar] $3d^{10}$ $4s^1$

Ag: [Kr] $4d^{10}$ $5s^1$

Au: [Xe] $4f^{14}$ $5d^{10}$ $6s^1$

Notice that for each of these metals, they have all “borrowed” an electron from the s sublevel to fill up the d sublevel. This is done to gain stability.

7. c [Ar] $3d^8$ $4s^2$

8. b

9. Ir: $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6 3d^{10}$ $4s^2$ $4p^6$ $4d^{10}$ $4f^{14}$ $5s^2$ $5p^6$ $5d^7$ $6s^2$

10. Ir: [Xe] $4f^{14}$ $5d^7$ $6s^2$

Valence electrons = $6s^2$

11. Hg: [Xe] $4f^{14}$ $5d^{10}$ $6s^2$

12. Valence electrons = $6s^2$

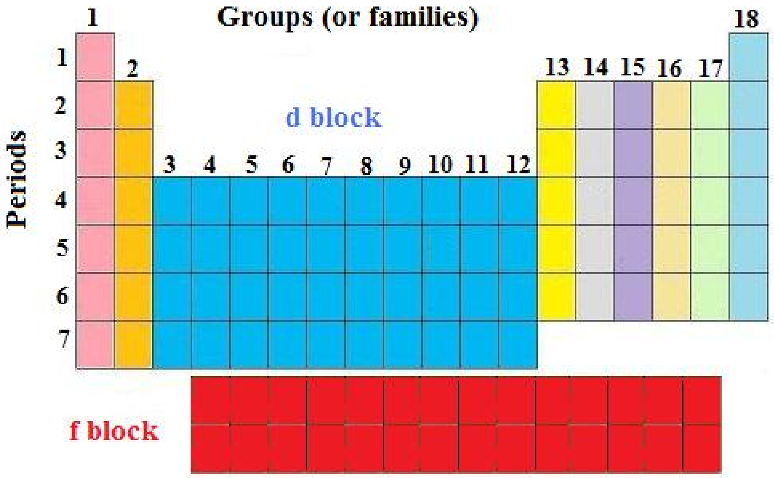
Lanthanides and Actinides

Lesson Objectives

- Define the lanthanides and actinides.
- Place the lanthanides and actinides in the periodic table.
- Explain the importance of both the lanthanides and actinides.
- Write electron configurations for lanthanides and actinides.

Introduction

To complete our look at the periodic table there is one more group we have to consider. This group holds its own unique position in any pictorial representation of the periodic table. The two rows that are generally placed underneath the main periodic table are called the lanthanide series and the actinide series. These two rows are produced when electrons are being added to f orbitals. Therefore, this block of elements are referred to as the "f block". The lanthanides are also occasionally referred to the ***rare earth elements*** . The f block, as shown in the figure below, are the two rows in red.

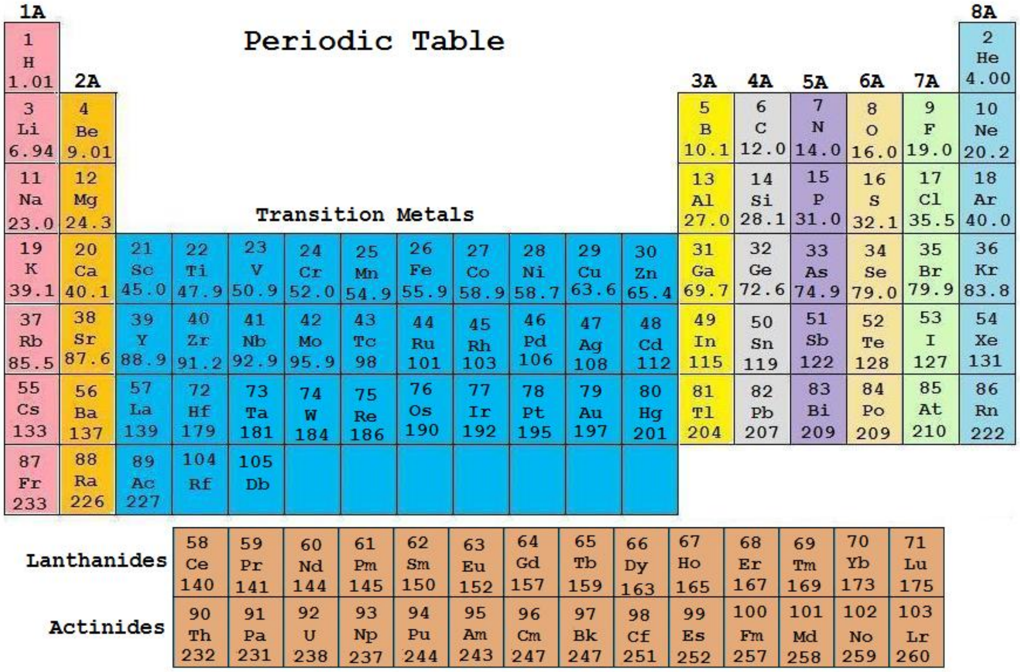


Lanthanides and Actinides are Elements Filling the f Sublevels

There is one group that we have neglected to mention throughout this chapter. This group belongs to a special group found almost disjointed, if you like, from the periodic table. They are given the names the Lanthanide Series and the Actinide Series or the ***lanthanides*** and the ***actinides.*** The lanthanides are an important group of elements. Most of them are formed when uranium and plutonium undergo nuclear reactions. The elements of the lanthanide series are also known as the ***rare earth*** elements. Both the lanthanides and the actinides make up what are known as the inner transition series. The f block is given this name because if the f block were placed in its proper numerical position in the periodic table, it would be in the transition metals between groups 2 and 3.

The lanthanide series includes elements from number 58 to 71, which is 14 elements. The f sub-level contains seven orbitals and each orbital will hold two electrons. Therefore, it is possible to place 14 electrons in the 4f sub-level.

The lanthanide series fills the 4f sublevel as you move from cerium (Ce) to lutetium (Lu). The same holds for the actinide series that runs from atomic number 90 through to number 103, again 14 elements. Thus, as you move from thorium (Th) at element number 90, you begin to fill up the 5f sublevel and continue to fill up the 5f sublevel until you finish the actinide series at lawrencium (Lr).



Periodic Table

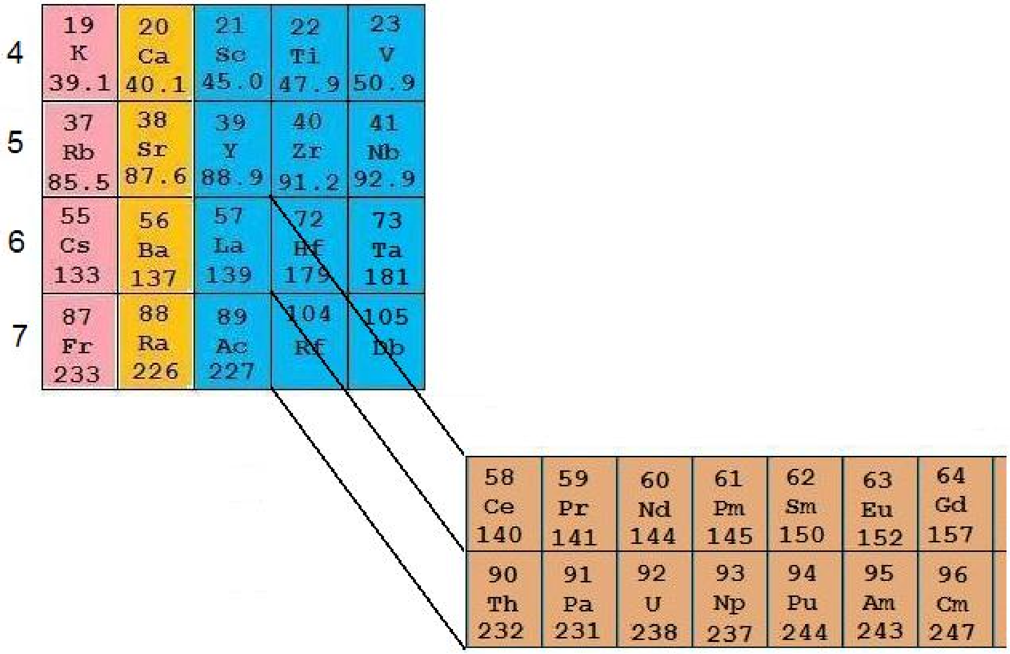
Transition Metals

1A	2A											3A	4A	5A	6A	7A	8A
1 H 1.01																	2 He 4.00
3 Li 6.94	4 Be 9.01											5 B 10.1	6 C 12.0	7 N 14.0	8 O 16.0	9 F 19.0	10 Ne 20.2
11 Na 23.0	12 Mg 24.3											13 Al 27.0	14 Si 28.1	15 P 31.0	16 S 32.1	17 Cl 35.5	18 Ar 40.0
19 K 39.1	20 Ca 40.1	21 Sc 45.0	22 Ti 47.9	23 V 50.9	24 Cr 52.0	25 Mn 54.9	26 Fe 55.9	27 Co 58.9	28 Ni 58.7	29 Cu 63.6	30 Zn 65.4	31 Ga 69.7	32 Ge 72.6	33 As 74.9	34 Se 79.0	35 Br 79.9	36 Kr 83.8
37 Rb 85.5	38 Sr 87.6	39 Y 88.9	40 Zr 91.2	41 Nb 92.9	42 Mo 95.9	43 Tc 98	44 Ru 101	45 Rh 103	46 Pd 106	47 Ag 108	48 Cd 112	49 In 115	50 Sn 119	51 Sb 122	52 Te 128	53 I 127	54 Xe 131
55 Cs 133	56 Ba 137	57 La 139	72 Hf 179	73 Ta 181	74 W 184	75 Re 186	76 Os 190	77 Ir 192	78 Pt 195	79 Au 197	80 Hg 201	81 Tl 204	82 Pb 207	83 Bi 209	84 Po 209	85 At 210	86 Rn 222
87 Fr 233	88 Ra 226	89 Ac 227	104 Rf	105 Db													

Lanthanides	58 Ce 140	59 Pr 141	60 Nd 144	61 Pm 145	62 Sm 150	63 Eu 152	64 Gd 157	65 Tb 159	66 Dy 163	67 Ho 165	68 Er 167	69 Tm 169	70 Yb 173	71 Lu 175
Actinides	90 Th 232	91 Pa 231	92 U 238	93 Np 237	94 Pu 244	95 Am 243	96 Cm 247	97 Bk 247	98 Cf 251	99 Es 252	100 Fm 257	101 Md 258	102 No 259	103 Lr 260

Lanthanides and Actinides Vary in Electron Filling Order

The lanthanides and the actinides make up the f block of the periodic table. The lanthanides are the elements produced as the 4f sublevel is filled with electrons and the actinides are formed while filling the 5f sublevel. Generally speaking, the lanthanides have electron configurations that follow the Aufbau rule. There are some variations, however, in a few of the lanthanide elements. We will expand a tiny portion of the periodic table below to show what happens to some of the electron configurations in the lanthanide and actinide series.



Look, for example, at the electron configuration for cerium, the first element of the lanthanide series. Cerium, Ce, is element number 58.

$_{58}$Ce: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ 6s^2\ 5d^1\ 4f^1$

or

$_{58}$Ce: $[Xe]\ 6s^2\ 5d^1\ 4f^1$

Now look at the electronic configuration for praseodymium, an element used in the making of aircraft engines but also in lighting for making movies. Praseodymium, Pr, is element number 59 and has the following electron configuration.

$_{59}$Pr: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ 6s^2\ 4f^3$

or

$_{59}$Pr: $[Xe]\ 6s^2\ 4f^3$

Notice the ***d*** electron is no longer a part of the electron configuration. There are three lanthanide metals that have properties similar to the d block. These are cerium, Ce, lutetium, Lu, and gadolinium, Gd. All of these metals contain a d electron in their electron configuration. The rest, like praseodymium, simply fill the 4f sublevel as the atomic number increases.

Unlike the lanthanide family members, most of the actinide series are radioactive. Most of the elements in the actinide series have the same properties as the d block. Members of the actinide series can lose multiple numbers of electrons to form a variety of different ions. The table below shows the noble gas electron configuration for the elements of the actinide series.

Table 1: Noble Gas Electron Configuration for the Actinide Series

Element	**Electron Configuration**
Thorium (Th)	$[Rn]\ 7s^2\ 6d^2$

Protactinium (Pa)	[Rn] $7s^2$ $5f^2$ $6d^1$
Uranium (U)	[Rn] $7s^2$ $5f^3$ $6d^1$
Neptunium (Np)	[Rn] $7s^2$ $5f^4$ $6d^1$
Plutonium (Pu)	[Rn] $7s^2$ $5f^6$
Americium (Am)	[Rn] $7s^2$ $5f^7$
Curium (Cm)	[Rn] $7s^2$ $5f^7$ $6d^1$
Berkelium (Bk)	[Rn] $7s^2$ $5f^9$
Californium (Cf)	[Rn] $7s^2$ $5f^{10}$
Einsteinium (Es)	[Rn] $7s^2$ $5f^{11}$
Fermium (Fm)	[Rn] $7s^2$ $5f^{12}$
Mendelevium (Md)	[Rn] $7s^2$ $5f^{13}$
Nobelium (No)	[Rn] $7s^2$ $5f^{14}$
Lawrencium (Lr)	[Rn] $7s^2$ $5f^{14}$ $6d^1$

Lesson Summary

- The lanthanide and actinide series make up the inner transition metals.
- The lanthanide series fill up the 4f sublevel and the actinide series fill up the 5f sublevel.
- The first, middle, and last member of the lanthanide series have properties of the f block and the d block.
- Many of the actinide series have properties of both the d block and the f block elements.

Review Questions

1. Why are the f block elements referred to by some as inner transition elements? **(Intermediate)**

2. What do europium and americium have in common as far as their electron configuration?

3. What is the electron configuration for Berkelium? **(Intermediate)**

(a) [Xe] $7s^2$ $5f^9$

(b) [Xe] $7s^2$ $5f^9$ $6d^1$

(c) [Rn] $7s^2$ $5f^9$

(d) [Rn] $7s^2$ $5f^9$ $6d^1$

4. How many f electrons are there in the electron configuration for einsteinium? **(Intermediate)**

(a) 0

(b) 11

(c) 14

(d) 25

5. Write the electron configuration for Ytterbium, Yb. **(Intermediate)**

6. What are the valence electrons for Ytterbium, Yb? What periods and sublevels are they in? **(Intermediate)**

7. Write the noble gas electronic configuration for uranium, U. **(Intermediate)**

8. What are the valence electrons for uranium, U? What periods and sublevels are they in? **(Intermediate)**

9. Write the electron configurations for neptunium and then for plutonium. Now write an explanation for what seems to be happening. **(Challenging)**

Further Reading / Supplemental Links

http://en.wikipedia.org/wiki/Group_number_of_lanthanides_and_actinides

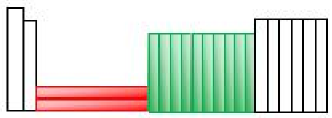
http://en.wikipedia.org/wiki/Lanthanide

Vocabulary

lanthanide	The rare earth elements found in the first period of the f block. These elements fill up the 4f sublevel.
actinide	The elements found in the second period of the f block. These elements fill up the 5f sublevel.

Review Answers

1. The 4f period can be squeezed into the periodic table between Lanthanum (#57) and Hafnium (#72) and then the 5f period just below it. Therefore the periodic table would look something like the following:



When the f block is put into the periodic table, then it does indeed, look like the inner transition elements.

2. $_{63}$Eu: [Xe] $6s^2$ $4f^7$

$_{95}$Am: [Rn] $7s^2$ $5f^7$

Notice that for each of the elements in this series, they have all "borrowed" an electron from the d sublevel to half fill up the f sublevel. This must be to gain some stability.

3. (c) [Rn] $7s^2$ $5f^9$

4. b

5. Yb: $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $4s^2$ $3d^{10}$ $4p^6$ $5s^2$ $4d^{10}$ $4f^{14}$ $5p^6$ $6s^2$

6. Yb: [Xe] $6s^2$ $4f^{14}$

Valence electrons = $6s^2$ and are therefore in period 6, sublevel s

7. U: [Rn] $7s^2\ 5f^2\ 6d^1$

8. Valence electrons = $7s^2$ and are therefore in period 7, sublevel s

9. Np: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ 6s^2\ 4f^{14}\ 5d^{10}\ 6p^6\ 7s^2\ 5f^4\ 6d^1$

Pu: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ 6s^2\ 4f^{14}\ 5d^{10}\ 6p^6\ 7s^2\ 5f^6$

The only reason, as learned from this chapter, that electrons make a shift away from the normal routine is for stability. For the electronic configuration of plutonium, there seems to be a discontinuity from the previous electronic configurations. All of the other electronic configurations in the 5f group, up until plutonium has one electron in the 6d sublevel. Then at plutonium it is dropped to get added to the 5f sublevel. This is an interesting and obviously more stable alternative for plutonium.

10. Trends on the Periodic Table

Atomic Size

Lesson Objectives

- Define atomic radius.
- State the boundary issue with atomic size.
- Describe measurement methods for atomic size.
- Define the shielding effect.
- Describe the factors that determine the trend of atomic size.
- Describe the general trend in atomic size for groups and for periods.
- Describe the trend of atomic radii in the rows in the periodic table.
- Describe how the trend of atomic radii works for transition metals.
- Use the general trends to predict the relative sizes of atoms.

Introduction

In the periodic table, there are a number of physical properties that are not really "similar" as it was previously defined, but are more trend-like. This means is that as you move down a group or across a period, you will see a trend-like variation in the properties. There are three specific periodic trends that we will discuss. The first three lessons of this chapter are devoted to the trend in atomic size in the periodic table. Following this we will discuss ionization energy and electron affinity. Each of these trends can be understood in terms of the electron configuration of the atoms.

The actual trends that are observed with atomic size have to do with three factors. These factors are:

(1) The number of protons in the nucleus (called the ***nuclear charge***).

(2) The number of energy levels holding electrons (and the number of electrons in the outer energy level).

(3) The number of electrons held between the nucleus and its outermost electrons (called the ***shielding effect***).

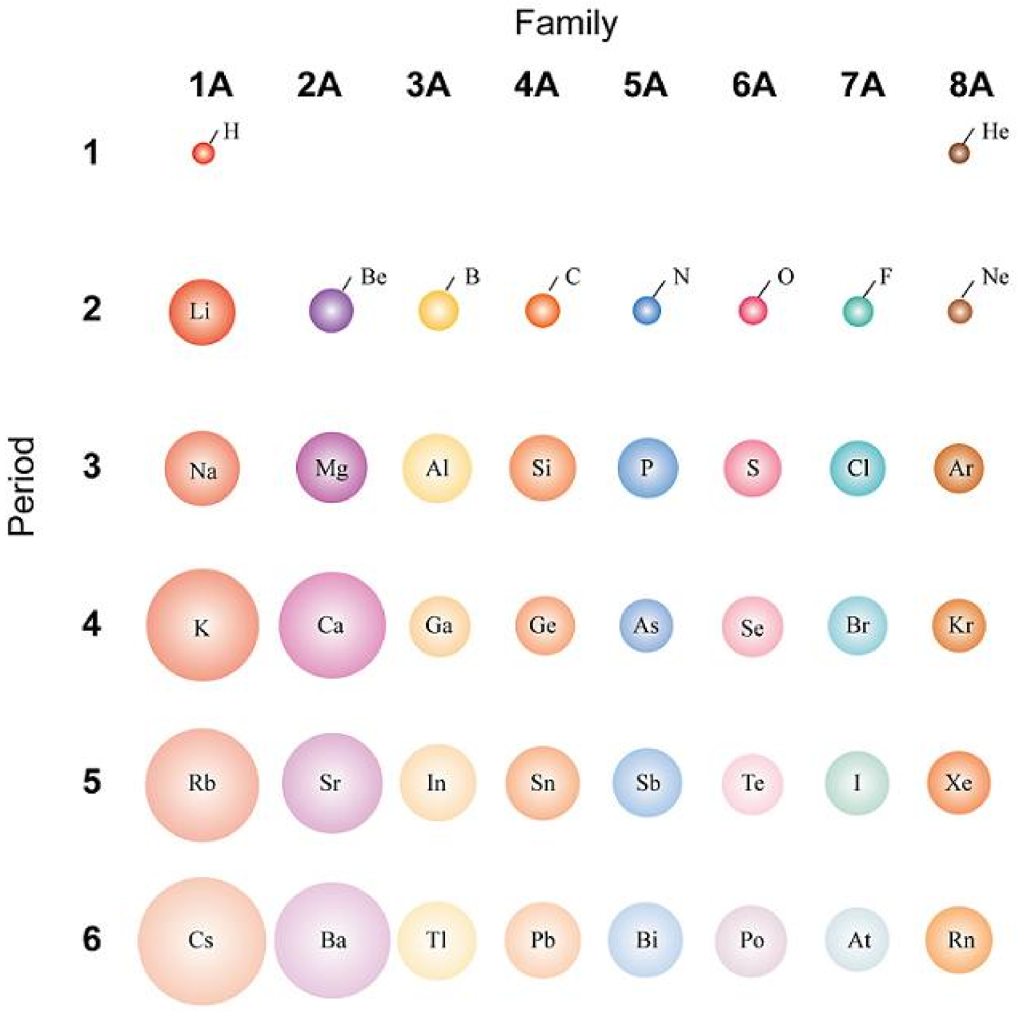


Figure 1: Comparative Atomic Sizes

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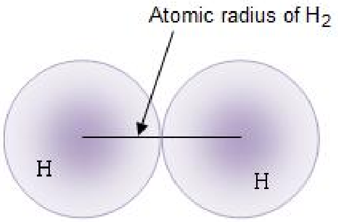
Atoms Have No Definite Boundary

The region in space occupied by the electron cloud of an atom is often thought of as a probability distribution of the electrons and therefore, there is no well-defined "outer edge" of the electron cloud. Atomic size is defined in several different ways and these different definitions often produce some variations in the measurement of atomic sizes.



Because it is so difficult to measure atomic size from the nucleus to the outermost edge of the electron cloud, chemists use other approaches to get consistent measurements of atomic sizes. One way that chemists define atomic size is by using the ***atomic radius*** . The atomic radius is one-half the distance between the centers of a homonuclear diatomic molecule (a diatomic molecule means a molecule made of exactly two atoms and homonuclear means both atoms are the same element). The figure below represents a visualization of the atomic size definition.

The image on the right is a visual representation of the atomic radius of a hydrogen atom. The measurement would be taken as one-half the distance between the nuclei of the hydrogen atoms in a diatomic hydrogen molecule.

How do we measure the size of the atom? Ernest Rutherford is famous for his experiments bombarding gold foil with alpha particles. The *gold foil experiment* by Rutherford, first done in 1911, is of particular interest to us in this unit because it was this experiment that first gave science an approximate measurement for the size of the atom. He was able, using technology available in the early part of the 1900s, to determine quantitatively that the nucleus had an approximate size of 4×10^{-12} cm. The size of the atom is slightly larger, approximately 2×10^{-8} cm in diameter.

Atomic Size in a Column Increases from Top to Bottom

Let’s now look at the atomic radii or the size of the atom from the top of a family or group to the bottom. Take, for example, the Group 1 metals. Each atom in this family (and all other main group families) has the same number of electrons in the outer energy level as all the other atoms of that family. Each row (period) in the periodic table represents another added energy level. When we first learned about principal energy levels, we learned that each new energy level was larger than the one before. Energy level 2 is larger than energy level 1, energy level 3 is larger than energy level 2, and so on. Therefore, as we move down the periodic table from period to period, each successive period represents the addition of a larger energy level. It becomes apparent that as we move downward through a family of elements, that each new atom has added another energy level and will, therefore, be larger.

Element	# of protons	Electron Configuration	# of energy levels
Li	3	$[He]2s^1$	2
Na	11	$[Ne]\ 3s^1$	3
K	19	$[Ar]\ 4s^1$	4
Rb	37	$[Kr]\ 5s^1$	5
Cs	55	$[Xe]\ 6s^1$	6

One other contributing factor to atomic size is something called the ***shielding effect*** . The protons in the nucleus attract the valence electrons in the outer energy level because of opposite electrostatic charges. The strength of this attraction depends on the size of the charges, the distance between the charges, AND the number of electrons in-between the nucleus and the valence electrons. The core electrons **shield** the valence electrons from the nucleus. The presence of the core electrons weakens the attraction between the nucleus and the valence electrons. This weakening of the attraction is called the shielding effect. The amount of *shielding* depends on the number of electrons between the nucleus and the valence electrons. The strength with which the nucleus pulls on the valence electrons can pull the valence shell in tighter when the attraction is strong and not so tight when the attraction is weakened. The more shielding that occurs, the further the valence shell can spread out.

For example, if you are looking at the element sodium, it has the electron configuration:

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

The outer energy level is n = 3 and there is one valence electron but the attraction between this lone valence electron and the nucleus that has those 11 protons is shielded by the other 10 inner (or core) electrons.

When we compare an atom of sodium to one of cesium, we notice that the number of protons increases as well as the number of energy levels occupied by electrons. There are also many more electrons between the outer electron and the nucleus, thereby shielding the attraction of the nucleus.

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

The outermost electron, $6s^1$, therefore, is held very loosely. In other words, because of shielding, the nucleus has less control over this $6s^1$ electron than it does over a $3s^1$ electron. The result of all of this is that the atom's size will be larger. Table 2 gives the values for the atomic radii for the group 1 metals plus a visual representation to appreciate the size change in a group in the periodic table.

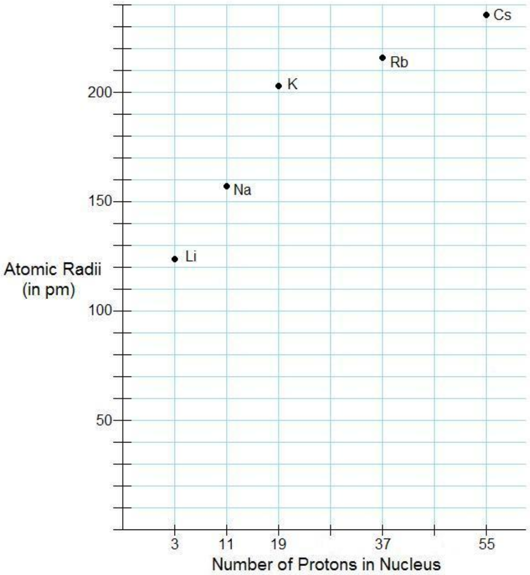


Table 2: Atomic Radii Values for Group 1 Metal

(measurement units for atomic radii are picometers (pm) or 1×10^{-12} meters)

Element	Atomic radii	Visual
Li	123 pm	
Na	157 pm	
K	203 pm	
Rb	216 pm	
Cs	235 pm	

What is true for the Group I metals is true for all of the groups, or families, across the periodic table. As you move downward in the periodic table through a family group, the size of the atoms increases. For instance, the atoms that are the largest in the halogen family are bromine and iodine (since astatine is radioactive and only exists for short periods of time, we won't include it in the discussion).

Sample question: Which of the following is larger? Explain.

(a) As or Sb

(b) Ca or Be

(c) Polonium or Sulfur

Solution:

(a) Sb because it is below As in Group 15.

(b) Ca because it is below Be in Group 2.

(c) Po because it is below S in Group 16.

As noted earlier for the main group metals, the outermost energy level in the electron configuration is indicated by the period number. So the element magnesium (Z = 12), is in period 3, group 2. According to this, we can say that there are 3 energy levels with 2 electrons in the outermost energy level. Let's look at the electron configuration for magnesium.

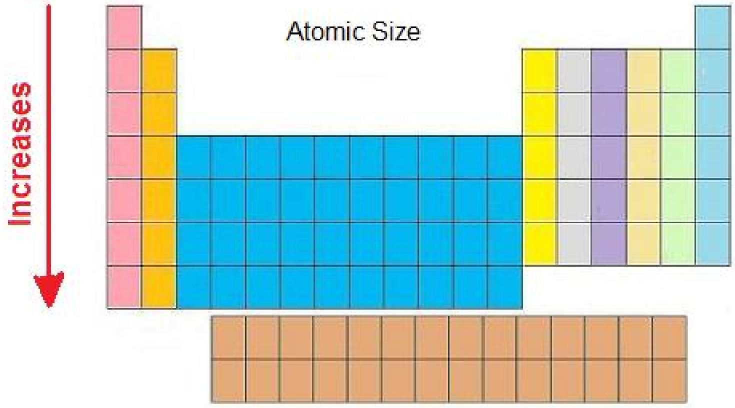
Mg: $1s^2\ 2s^2\ 2p^6\ 3s^2$

Moving from magnesium to strontium, strontium is in the 5th period of group 2. This means that there are two electrons in the valence energy level. Strontium also has electrons occupying five energy levels.

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

You can imagine that with the increase in the number of energy levels, the size of the atom must increase. The increase in the number of energy levels in the electron cloud takes up more space.

Therefore the trend within a group or family on the periodic table is that the atomic size increases with increased number of energy levels. The periodic table below shows the trend of atomic size for groups. The arrow indicates the direction of the increase.



Atomic Size in a Period Decreases from Left to Right

In order to determine the trend for the periods, we need to look at the number of protons (nuclear charge), the number of energy levels, and the shielding effect. For a row in the periodic table, the atomic number still increases (as it did for the groups) and thus the number of protons would increase. When we examine the energy levels for period 2, we find that the outermost energy level does not change as we increase the number of electrons. In period 2, each additional electron goes into the second energy level. So the number of energy levels **does not go up**. As we move from left to right across a period, the number of electrons in the outer energy level increases **but it is the same outer energy level**. Table 1 shows the electron configuration for the elements in period 2.

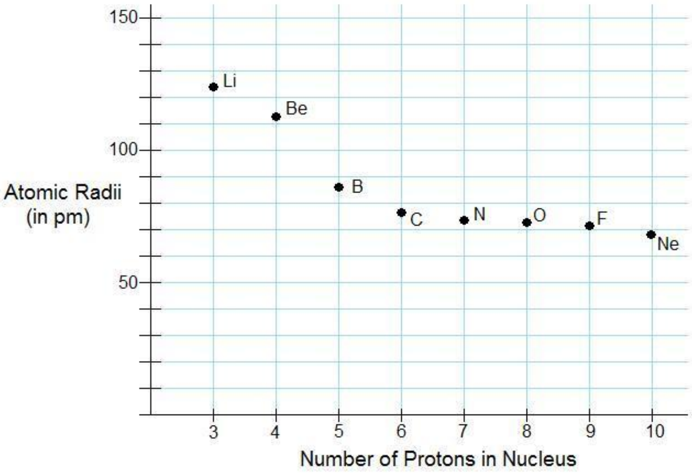
Table 1: Electronic Configuration for Elements in Row 2

Element	1. of protons	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	$1s^2\ 2s^2\ 2p^5$

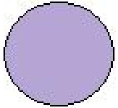
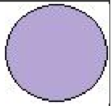
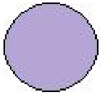
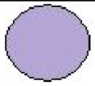
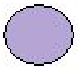
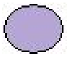
Looking at the elements in period 2, the number of protons increases from lithium with three protons, to fluorine with nine protons. Therefore, the nuclear charge increases across a period. Meanwhile, the number of energy levels occupied by electrons **remains the same**. The numbers of electrons in the outermost energy level increases from left to right along a period but how will this affect the radius? We know that every one of the elements in row #2 has two electrons in their inner energy level (2 core electrons). The core electrons shield the outer electrons from the charge of the nucleus. With lithium, there are two core electrons and one valence electron so those two core electrons will shield the one outer electron. In beryllium, there are four protons being shielded by the $1s^2$ electrons. With the increasing number of protons attracting the outer electrons and the same shielding from the core electrons, **the valence electrons are pulled closer to the nucleus, making the atom smaller**.

In group 7A, the first element in the group is fluorine. With fluorine, there are 9 protons and 9 electrons. The electronic configuration is $1s^2\ 2s^2\ 2p^5$. However, there are still the same core electrons as with lithium and beryllium, that is, the $1s^2$ electrons. Since there are more protons, there is an increase in the nuclear charge. With an increase in nuclear charge, there is an increase in the pull between the protons and the outer level, pulling the outer electrons toward the nucleus. The amount of shielding from the nucleus does not increase because the number of core electrons remains the same ($1s^2$ for this period). The net result is that the atomic size ***decreases*** going across the row. In the table below, the values are shown for the atomic radii for the row starting at lithium and ending with fluorine plus a visual representation to appreciate the size change in a group in the periodic table.

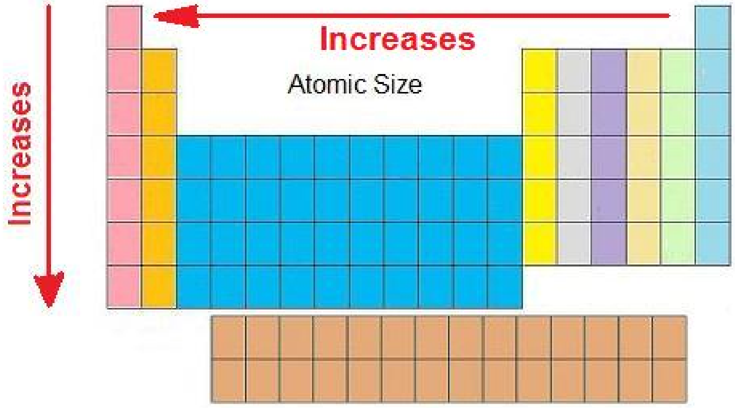
Table 2: Atomic Radii Values for Period 2



Element	Atomic radii	Visual

Li	123 pm	
Be	111 pm	
B	86 pm	
C	77 pm	
N	74 pm	
O	73 pm	
F	72 pm	

Let's add this new trend to the periodic table. Look at the diagram below of our new "periodic trend table". In the diagram you will notice that the trend arrow for the period shows the atomic radii increase going from right to left, which is the same as decreasing from left to right.

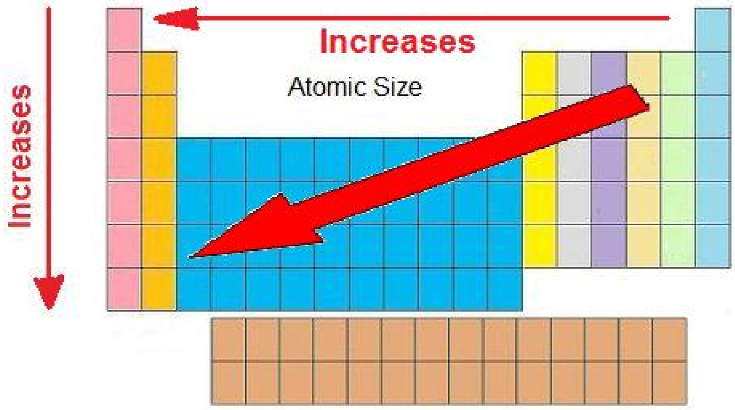


Considering all the information about atomic size, you will recognize that the largest atom on the periodic table is all the way to the left and all the way to the bottom, francium, #87, and the smallest atom is all the way to the right and all the way to the top, helium, #2.

The fact that the atoms get larger as you move downward in a family is probably exactly what you expected before you even read this section, but the fact that the atoms get smaller as you move to the right across a period is most likely a big surprise. Make sure you understand this trend and the reasons for it.

For the Transition Elements, the Trend is Less Systematic

A general trend for atomic radii in the periodic would look similar to that found in the diagram below. The elements with the smallest atomic radii are to the upper right; those with the largest atomic radii are to the lower left.



Until now, we have worked solely with the main group metals. Let's look at our three factors and see how these factors fit the transition metal series. Looking at the first row of the transition metals, the ***3d*** row, Table 3 shows the number of protons in each of the 10 elements in this row. The number of protons is increasing so the nuclear charge is increasing.

Table 3: Summary of Data for *3d* Metals

Element	# of protons	Electron Configuration
Scandium (Sc)	21	[Ar] $3d^1\ 4s^2$
Titanium (Ti)	22	[Ar] $3d^2\ 4s^2$
Vanadium (V)	23	[Ar] $3d^3\ 4s^2$
Chromium (Cr)	24	[Ar] $3d^5\ 4s^1$
Manganese (Mn)	25	[Ar] $3d^5\ 4s^2$
Iron (Fe)	26	[Ar] $3d^6\ 4s^2$
Cobalt (Co)	27	[Ar] $3d^7\ 4s^2$
Nickel (Ni)	28	[Ar] $3d^8\ 4s^2$
Copper (Cu)	29	[Ar] $3d^{10}\ 4s^1$
Zinc (Zn)	30	[Ar] $3d^{10}\ 4s^2$

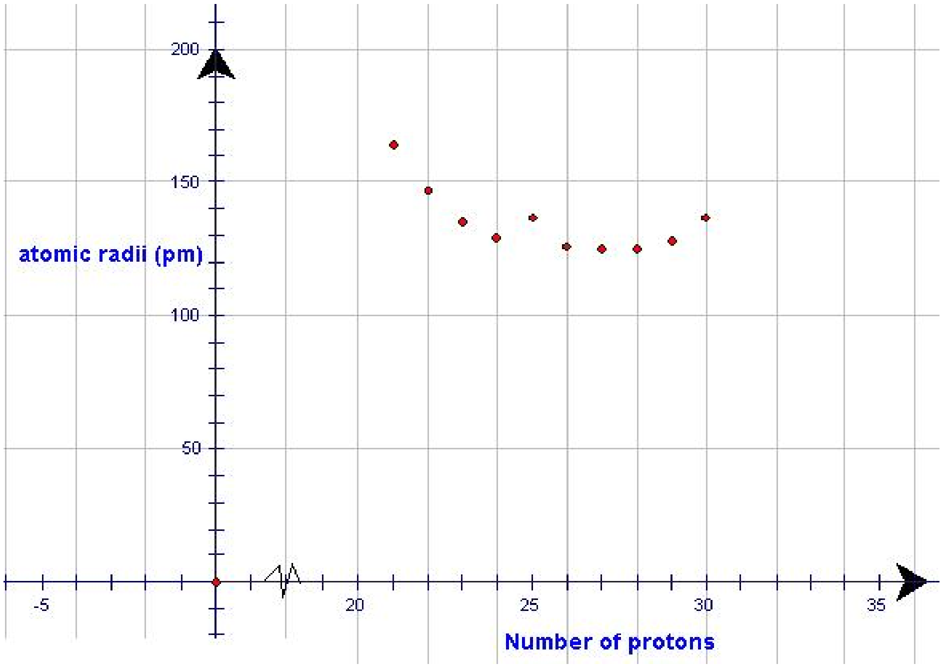
The number of electrons are increasing, but in a particular way. We know that as the number of electrons increases going across a period, there is more pull of these electrons toward the nucleus. However, with the d-electrons, there is some added electron-electron repulsion. Take a look at Table 3 and note the unusual electron configuration of chromium.

In chromium, there is a promotion of one of the 4s electrons to half fill the 3d sublevel, the electron-electron repulsions are less and the atomic size is smaller. The opposite holds true for the latter part of the row. Table 4 shows the first row of the transition metals along with their size.

Table 4: Atomic Radii for *3d* Metals

Element	Atomic radii (pm)
Scandium (Sc)	164
Titanium (Ti)	147
Vanadium (V)	135
Chromium (Cr)	129
Manganese (Mn)	137
Iron (Fe)	126
Cobalt (Co)	125
Nickel (Ni)	125
Copper (Cu)	128
Zinc (Zn)	137

The graph of the number of protons versus the atomic radii is shown below.



Graphing the atomic number (or the number of protons) versus the atomic radii, we can see the trend in the 3d transition metals isn't quite as systematic as with the main group elements.

Lesson Summary

- Atomic size is the distance from the nucleus to the valence shell where the valence electrons are located. The electrons surrounding the nucleus exist in an electron cloud. You can predict the probability of where the electron is but not its exact location. Atomic size is difficult to measure because it has no definite boundary. Atomic radius is a more definite and measureable way of defining atomic size. It is the distance from the center of one atom to the center of another atom in a homonuclear diatomic molecule. Rutherford led the way to determining the size of the atom with his gold foil experiment. Mass spectrometers and other machines are available to measure masses and determine structure directly. Atomic size is determined indirectly.

- There are three factors that help in the prediction of the trends in the periodic table: number of protons in the nucleus, number of shells, and shielding effect. The atomic size increases from the top to the bottom in any group as a result of increases in all of the three factors. The number of energy levels increases and therefore the size must increase.
- Going across a period (from left to right), the number of protons increases and therefore the nuclear charge increases. Going across a period, the number of electron energy levels remains the same but the number of electrons increases within these energy levels. Therefore the electrons are pulled in closer to the nucleus. Shielding is relatively constant since the core electrons remain the same. The trend in the periodic table is that as you move across the periodic table from left to right, the atomic radii decrease. This trend is not as systematic for the transition metals because other factors come into play.

Review Questions

1. Why is the atomic size considered to have “no definite boundary”? **(Intermediate)**

2. How is atomic size measured? **(Intermediate)**

(a) using a spectrophotomer

(b) using a tiny ruler (called a nano ruler)

(c) indirectly

(d) directly

3. Draw a visual representation of the atomic radii of an iodine molecule. **(Beginning)**

4. Which of the following would be smaller? **(Intermediate)**

a. In or Ga

b. K or Cs

c. Te or Po

5. Explain in your own words why Iodine is larger than Bromine. **(Intermediate)**

6. What three factors determine the trend of atomic size going down a group? **(Intermediate)**

7. What groups tend to show this trend? **(Intermediate)**

8. Which of the following would have the largest atomic radii? **(Intermediate)**

(a) Si

(b) C

(c) Sn

(d) Pb

9. Which of the following would have the smallest atomic radius? **(Intermediate)**

(a) $2s^2$

(b) $4s^2\ 4p^3$

(c) $2s^2\ 2p^4$

(d) $4s^2$

10. Arrange the following in order of increasing atomic radii: Tl, B, Ga, Al, In. **(Intermediate)**

11. Arrange the following in order of increasing atomic radii: Ge, Sn, C, **(Intermediate)**

12. Which of the following would be larger? **(Intermediate)**

a. Rb or Sn

b. Ca or As

13. Place the following in order of increasing atomic radii: Mg, Cl, S, Na. **(Intermediate)**

14. Describe the atomic size trend for the rows in the periodic table. **(Beginning)**

15. Draw a visual representation of the periodic table describing the trend of atomic size. **(Beginning)**

16. Which of the following would have the largest atomic radii? **(Intermediate)**

(a) Sr

(b) Sn

(c) Rb

(d) In

17. Which of the following would have the smallest atomic radii? **(Intermediate)**

(a) K

(b) Kr

(c) Ga

(d) Ge

18. Place the following elements in order of increasing atomic radii: In, Ca, Mg, Sb, Xe. **(Intermediate)**

19. Place the following elements in order of decreasing atomic radii: Al, Ge, Sr, Bi, Cs. **(Intermediate)**

20. Knowing the trend for the rows, what would you predict to be the effect on the atomic radius if an atom were to gain an electron? Use an example in your explanation. **(Challenging)**

21. Knowing the trend for the rows, what would you predict to be the effect on the atomic radius if the atom were to lose an electron? Use an example in your explanation. **(Challenging)**

Vocabulary

atomic size	Atomic size is the distance from the nucleus to the valence shell where the valence electrons are located.
atomic radius	One-half the distance between the centers of the two atoms of a homonuclear molecule.
nuclear charge	The number of protons in the nucleus.

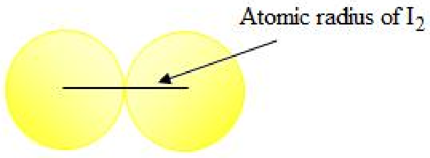
shielding effect	The core electrons in an atom interfere with the attraction of the nucleus for the outermost electrons.
electron-electron repulsion	The separation that occurs because electrons have the same charge.

Review Answers

1. Atomic size is the distance from the nucleus to the outer edge of the electron cloud and there is no definite line marking the outer edge of the electron cloud.

2. (c) indirectly

3. Iodine is diatomic therefore has the formula I_2. The visual representation is:



4. (a) Ga (b) K (c) Te

5. Iodine has one more electron energy level than bromine. Each new energy level is larger.

6. The three factors are:

(1) the number of protons in the nucleus (called the nuclear charge),

(2) the number of energy levels holding electrons (and the number of electrons in the outer shell)

(3) the effect of the core electrons shielding the outer electrons (the shielding effect)

7. The trend only holds true for the main group elements and even then, does not necessarily hold true for group 8 or the last row of each group.

8. (d) Pb

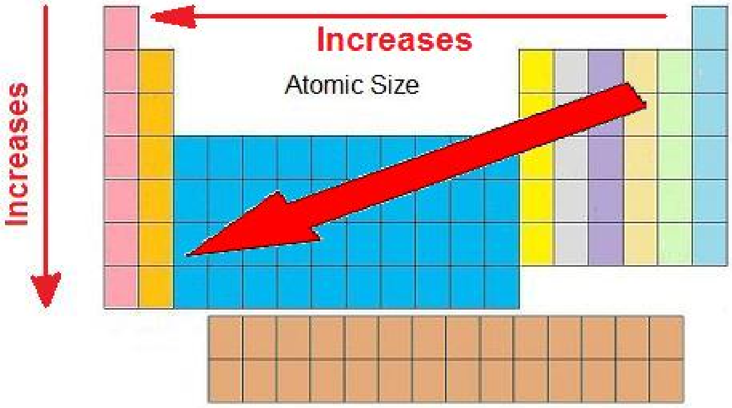
9. (c) $2s^2\ 2p^4$

10. B < Al < Ga < In < Tl

11. C < Ge < Sn

12. (a) Rb (b) Ca

13. Cl < Mg < Na 14. As you move across each row, for the main group elements, the atomic radii decreases. 15.



16. (c) Rb 17. (b) Kr 18. Xe < Sb < Mg < In < Ca 19. Cs < Sr < Bi < Al < Ge 20. To gain an electron means to make a negative ion or to have the same electronic configuration as the element after it. If chlorine were to gain one electron, it would then have the same electron configuration as argon but it would not have the same nuclear charge as argon. Gaining an electron to become a negative ion increases the number of electrons by one but it does not increase the number of protons. Therefore, you would have no increase in nuclear charge but you would have an increase in the electron-electron repulsion. The valence electrons would be held less tightly by the protons and so the size increases. 21. To lose an electron means to make a positive ion or to have the same electronic configuration as the element before it. Take for example the third row we had used in the above example. If sodium had lost one electron, it would then have the same electronic configuration as neon. Neon is above Argon in the periodic table, atomic size goes up as you go down a group, and therefore Na^+ would be smaller than Na. A better explanation is that when an electron is lost, there are less electrons so there is greater attraction for each electron by the protons in the nucleus and the remaining valence electrons are pulled in closer.

Ionization Energy

Lesson Objectives

- Define ionization energy.
- Describe the trend that exists in the periodic table for ionization energy.
- Describe the ionic size trend that exists when elements lose one electron.

Introduction

When we study the trends in the periodic table, we cannot stop at just atomic size. In this section of the chapter, we will begin an understanding of an important concept, namely ionization energy and recognize its trend on the periodic table.

Ionization Energy is the Energy Required to Remove an Electron

Lithium has an electron configuration of $1s^2\ 2s^1$. Lithium has one electron in its outermost energy level. In order to remove this electron, energy must be added to the system. Look at the equation below:

$$\text{energy} + Li_{(g)} \rightarrow Li^+_{\ (g)} + e^-$$

$1s^2\ 2s^1$ $\quad$ $1s^2$

With the addition of energy, a lithium ion can be formed from the lithium atom by losing one electron. This energy is known as the ionization energy. The ***ionization energy*** is the energy required to remove the most loosely held electron from a gaseous atom or ion. "In the gaseous phase" is specified because in liquid or solid, other energies get involved. The general equation for the ionization energy is as follows.

$$\text{energy} + A_{(g)} \longrightarrow A^{+}{}_{(g)} + e^{-}$$

The higher the value of the ionization energy, the harder it is to remove that electron. We can see a trend when we look at the ionization energies for the elements in period 2. Table 1 summarizes the electron configuration and the ionization energies for the elements in the second period.

Table 1: First Ionization Energies (IE_1) for Period 2 Main Group Elements

Element	**Electron configuration**	**First Ionization Energy, IE_1**
Lithium (Li)	[He] $2s^1$	520 kJ/mol
Beryllium (Be)	[He] $2s^2$	899 kJ/mol
Boron (B)	[He] $2s^2$ $2p^1$	801 kJ/mol
Carbon (C)	[He] $2s^2$ $2p^2$	1086 kJ/mol
Nitrogen (N)	[He] $2s^2$ $2p^3$	1400 kJ/mol
Oxygen (O)	[He] $2s^2$ $2p^4$	1314 kJ/mol
Fluorine (F)	[He] $2s^2$ $2p^5$	1680 kJ/mol

When we look closely at the data presented in table 1, we can see that as we move across the period from left to right, in general, the ionization energy increases. At the beginning of the period, with the alkali metals and the alkaline earth metals, losing one or two electrons allows these atoms to become ions.

$$\text{energy} + \text{Li(g)} \longrightarrow \text{Li}^{+}\text{(g)} + e^{-}$$

$$\text{energy} + \text{Mg(g)} \longrightarrow \text{Mg}^{2+} + 2\ e^{-}$$

$$[\text{He}]\ 2s^1 \longrightarrow [\text{He}] + e^{-}$$

$$[\text{Ne}]\ 3s^2 \longrightarrow [\text{Ne}] + 2\ e^{-}$$

As we move across the period, the atoms become smaller which causes the nucleus to have greater attraction for the valence electrons. Therefore, the electrons are more difficult to remove.

A similar trend can be seen for the elements within a family. Table 2 shows the electron configuration and the first ionization energies (IE_1) for some of the elements in the first group, the alkali metals.

Table 2: Ionization Energies for Some Group 1 Elements

Element	**Electron configuration**	**First Ionization Energy, IE_1**
Lithium (Li)	[He] $2s^1$	520 kJ/mol
Sodium (Na)	[He] $3s^1$	495.5 kJ/mol

Potassium (K)	[He] $4s^1$	418.7 kJ/mol

Comparing the electron configurations of lithium to potassium, we know that the electron to be removed is further away from the nucleus. We know this because the ***n*** value is larger meaning the energy level where the valence electron is held is larger. Therefore it is easier to remove the most loosely held electron because the atom is larger with a greater shielding effect which means that the nucleus has less control over potassium's outer electron, $4s^1$.

Therefore IE_1 for potassium (418.7 kJ/mol) is less than IE_1 for lithium (520 kJ/mol).

If a second electron is to be removed from an atom, the general equations are the following:

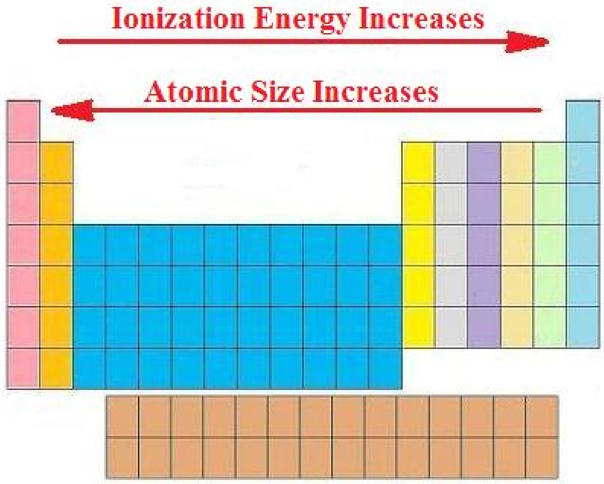
$$J_{(g)} + \text{energy} \longrightarrow J^{1+} + e^- \quad IE_1$$

$$J^+_{(g)} + \text{energy} \longrightarrow J^{2+}_{(g)} + e^- \quad IE_2$$

Since there is an imbalance of positive and negative charges when a second electron is being removed, the energy required for the second ionization (IE_2) will be greater than the energy required for the first ionization (IE_1). Simply put, $IE_1 < IE_2 < IE_3 < IE_4$.

The Charge on the Nucleus Increases and Size Decreases

So if we look at the ionization energy trend in the periodic table and add it to the trend that exists with atomic size we can show the following on our periodic table chart.

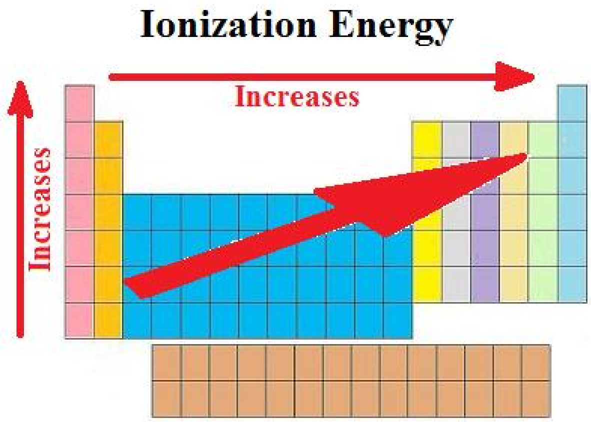


But why does the ionization energy increase going across a period and decrease going down a group? It has to do with two factors. One factor is that the atomic size decreases. The second factor is that the effective nuclear charge increases. The ***effective nuclear charge*** is the charge experienced by a specific electron within an atom. Remember, the nuclear charge was used to describe why the atomic size decreased going across a period. When we look at the data in Table 1 again, we can see how the effective nuclear charge increases going across a period. Table 3 shows the effective nuclear charge along with the ionization energy for the elements in period 2.

Table 3: Effective Nuclear Charge for Period 2 Main Group Elements

Element	Electron configuration	# of protons	# of core electrons	Effective nuclear charge	Ionization Energy
Lithium (Li)	[He] $2s^1$	3	2	1	520 kJ/mol
Beryllium (Be)	[He] $2s^2$	4	2	2	899 kJ/mol
Boron (B)	[He] $2s^2$ $2p^1$	5	2	3	801 kJ/mol
Carbon (C)	[He] $2s^2$ $2p^2$	6	2	4	1086 kJ/mol
Nitrogen (N)	[He] $2s^2$ $2p^3$	7	2	5	1400 kJ/mol
Oxygen (O)	[He] $2s^2$ $2p^4$	8	2	6	1314 kJ/mol
Fluorine (F)	[He] $2s^2$ $2p^5$	9	2	7	1680 kJ/mol

The electrons that are shielding the nuclear charge are the core electrons, or in the case of period 2, the $1s^2$ electrons. The effective nuclear charge is the difference between the total charge in the nucleus (the number of protons) and the number of shielded electrons. Notice how as the effective nuclear charge increases, so does the ionization energy. Overall the general trend for ionization energy is shown below.



Sample question: What would be the effective nuclear charge for Cl? Would you predict the ionization energy to be higher or lower than fluorine?

Solution:

Chlorine has the electronic configuration of:

Cl [Ne] $3s^2$ $3p^5$

The effective nuclear charge is 7, the same as fluorine. Predicting the ionization energy would be difficult with this alone. The atomic size, however, is larger for chlorine than for fluorine because now there are three energy levels (chlorine is in period 3). Now we can say that the ionization energy should be lower than that of fluorine because the electron would be easier to pull off the level further away from the nucleus. (Indeed, the value for chlorine is 1251 kJ/mol).

Some Anomalies With the Trend in Ionization Energy

There are a few anomalies that exist with respect to the ionization energy trends. Going across a period there are two ways in which the ionization energy may be affected by the electron configuration. When we look at period 3, we can see that there is an anomaly observed as we move from the 3s sublevels to the 3p sublevel. Look at Table 4. The table shows the electron configurations for the main group elements in period 3 along with the first ionization energy for these elements.

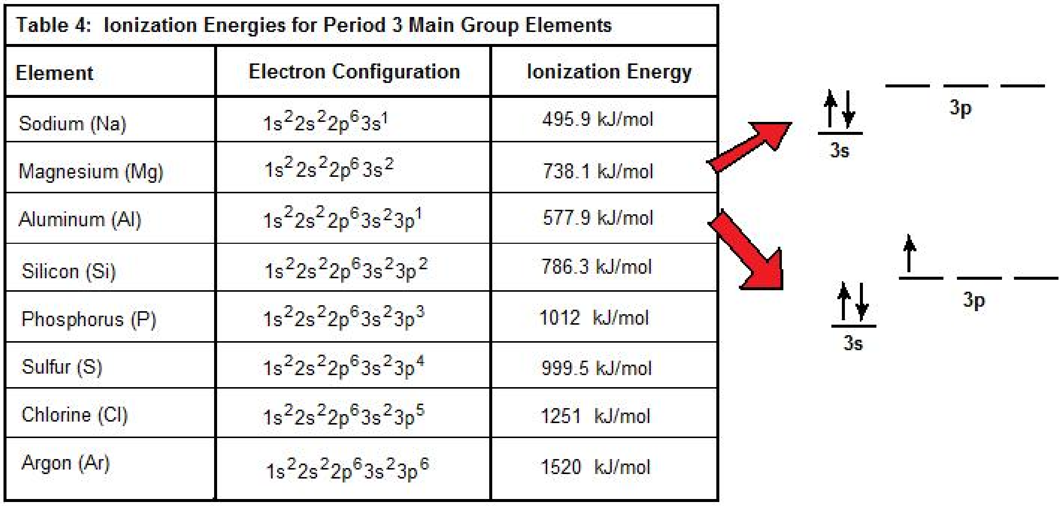


Table 4: Ionization Energies for Period 3 Main Group Elements

Element	Electron Configuration	Ionization Energy
Sodium (Na)	$1s^22s^22p^63s^1$	495.9 kJ/mol
Magnesium (Mg)	$1s^22s^22p^63s^2$	738.1 kJ/mol
Aluminum (Al)	$1s^22s^22p^63s^23p^1$	577.9 kJ/mol
Silicon (Si)	$1s^22s^22p^63s^23p^2$	786.3 kJ/mol
Phosphorus (P)	$1s^22s^22p^63s^23p^3$	1012 kJ/mol
Sulfur (S)	$1s^22s^22p^63s^23p^4$	999.5 kJ/mol
Chlorine (Cl)	$1s^22s^22p^63s^23p^5$	1251 kJ/mol
Argon (Ar)	$1s^22s^22p^63s^23p^6$	1520 kJ/mol

In the table we see that when we compare magnesium to aluminum the first IE decreases instead of increasing as we would have expected. So why would this be so? Magnesium has its outermost electrons in the s sublevel. The aluminum atom has its outermost electron in the 3p sublevel. Since p electrons have just slightly more energy than s electrons, it takes a little less energy to remove that electron from aluminum. One other slight factor is that the electrons in $3s^2$ shield the electron in $3p^1$. These two factors allow the IE_1 for Al to be less than IE_1 for Mg.

When we look again at Table 1, we can see that the ionization energy for nitrogen seems out of place.

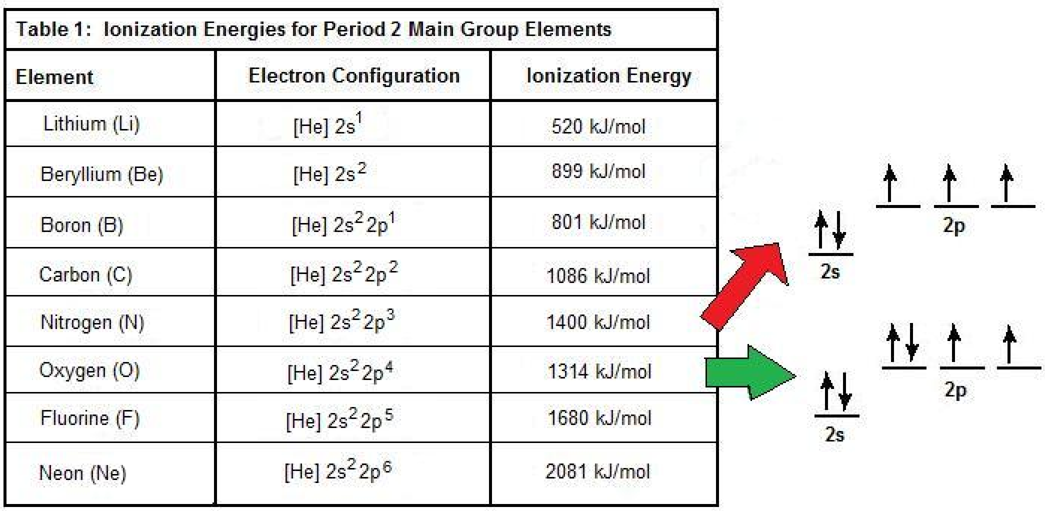


Table 1: Ionization Energies for Period 2 Main Group Elements

Element	Electron Configuration	Ionization Energy
Lithium (Li)	[He] $2s^1$	520 kJ/mol
Beryllium (Be)	[He] $2s^2$	899 kJ/mol
Boron (B)	[He] $2s^2 2p^1$	801 kJ/mol
Carbon (C)	[He] $2s^2 2p^2$	1086 kJ/mol
Nitrogen (N)	[He] $2s^2 2p^3$	1400 kJ/mol
Oxygen (O)	[He] $2s^2 2p^4$	1314 kJ/mol
Fluorine (F)	[He] $2s^2 2p^5$	1680 kJ/mol
Neon (Ne)	[He] $2s^2 2p^6$	2081 kJ/mol

While nitrogen has one electron occupying each of the three p orbitals in the 2nd sublevel, oxygen has two orbitals occupied by only one electron but one orbital containing a pair of electrons. The greater electron-electron repulsion experienced by these 2 p electrons allows for less energy to be needed to remove one of these. Therefore, IE_1 for oxygen is less than nitrogen.

Lesson Summary

- Ionization energy is the energy required to remove the most loosely held electron from a gaseous atom or ion. Ionization energy generally increases across a period and decreases down a group. The effective nuclear charge is the charge of the nucleus felt by the valence electron.
- The effective nuclear charge and the atomic size help explain the trend of ionization energy. Going down a group the atomic size gets larger and the electrons can be more readily removed, therefore, ionization energy decreases. Going across a period the effective nuclear charge increase so the electrons are harder to remove and the ionization energy increases. Once one electron has been removed, a second electron can be removed but $IE_1 < IE_2$. If a third electron is removed, $IE_1 < IE_2 < IE_3$ and so on.

Review Questions

1. Define ionization energy and show an example ionization equation. **(Intermediate)**

2. Draw a visual representation of the periodic table describing the trend of ionization energy. **(Intermediate)**

3. Which of the following would have the largest ionization energy? **(Intermediate)**

(a) Na

(b) Al

(c) H

(d) He

4. Which of the following would have the smallest ionization energy? **(Intermediate)**

(a) K

(b) P

(c) S

(d) Ca

5. Place the following elements in order of increasing ionization energy: Na, O, Ca, Ne, K. **(Intermediate)**

6. Place the following elements in order of decreasing ionization energy: N, Si, S, Mg, He. **(Intermediate)**

7. Using experimental data, the first ionization energy for an element was found to be 600 kJ/mol. The second ionization energy for the ion formed was found to be 1800 kJ/mol. The third ionization energy for the ion formed was found to be 2700 kJ/mol. The fourth ionization energy for the ion formed was found to be 11600 kJ/mol. And finally the fifth ionization energy was found to be 15000 kJ/mol. Write the reactions for the data represented in this question. Which group does this element belong? Explain. **(Challenging)**

8. Using electron configurations and your understanding of ionization energy, which would you predict would have higher second ionization energy: Na or Mg? **(Challenging)**

Further Reading / Supplemental Links

http://en.wikipedia.org

Vocabulary

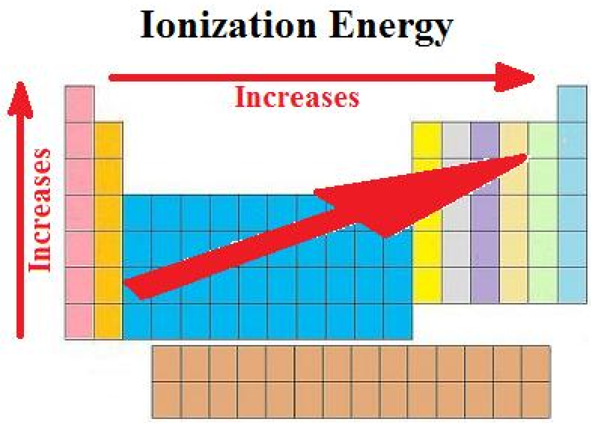
ionization energy	The energy required to remove an electron from a gaseous atom or ion: energy + J(g) $\longrightarrow$ $J^+(g) + e^-$ (first ionization energy).
effective nuclear charge	The charge on the atom or ion felt by the outermost electrons (valence electrons).

Review Answers

1. Ionization energy is the energy required to remove an electron from a gaseous atom or ion. For example:

$$Na(g) + 495.5\ kJ/mol \longrightarrow Na^+(g) + e^-$$

2.



3. d He

4. a K

5. K < Na < Ca < O < Ne

6. He > N > S > Si > Mg

7.

$D(g) \longrightarrow D^+(g) + e^-$ IE_1 = 600 kJ/mol

$D^+(g) \longrightarrow D^{2+}(g) + e^-$ IE_2 = 1800 kJ/mol

$D^{2+}(g) \longrightarrow D^{3+}(g) + e^-$ IE_3 = 2700 kJ/mol

$D^{3+}(g) \longrightarrow D^{4+}(g) + e^-$ IE_4 = 11600 kJ/mol

$D^{4+}(g) \longrightarrow D^{5+}(g) + e^-$ IE_5 = 15000 kJ/mol

The element is most likely a member of Group 13 since the big jump in energy took place after the element lost 3 electrons. This means the electronic configuration was very stable and therefore did not want to give up any more electrons.

8. Ionization energy is the energy required to remove an electron from a gaseous atom or ion. For Na and Mg, the first and second ionization energy reactions are shown below including the electronic configurations for each.

$_{11}Na(g) \longrightarrow {}_{11}Na^+ (g) + e^-$	IE_1	$_{12}Mg(g) \longrightarrow {}_{12}Mg^+ (g) + e^-$	IE_1
$1s^2\ 2s^2\ 2p^6\ 3s^1 \longrightarrow 1s^2\ 2s^2\ 2p^6 + e^-$		$1s^2\ 2s^2\ 2p^6\ 3s^2 \longrightarrow 1s^2\ 2s^2\ 2p^6\ 3s^1 + e^-$	
$_{11}Na^+(g) \longrightarrow {}_{11}Na^{2+} (g) + e^-$	IE_2	$_{12}Mg^+(g) \longrightarrow {}_{12}\}Mg^{2+} (g) + e^-$	IE_2
$1s^2\ 2s^2\ 2p^6 \longrightarrow 1s^2\ 2s^2\ 2p^5 + e^-$		$1s^2\ 2s^2\ 2p^6\ 3s^1 \longrightarrow 1s^2\ 2s^2\ 2p^2 + e^-$	

Remembering that the elements want to have noble gas electronic configurations, if Mg forms a 2+ ion, it will indeed achieve this. Sodium, on the other hand is already at a noble gas configuration at IE_1. At IE_2, we are removing an electron away from the very stable noble gas configuration. Since sodium is not likely to do this, the value will be quite high, higher than IE_2 for magnesium.

Electron Affinity

Lesson Objectives

- Define electron affinity.
- Describe the trend for electron affinity on the periodic table.

Introduction

The final periodic trend for our discussion is electron affinity. We have talked about atomic structure, electronic configurations, size of the atoms and ionization energy. And now, the final periodic trend we will study is how an atom can gain an electron and the trends that exist in the periodic table.

The Energy Process When an Electron is Added to an Atom

Atoms can gain or lose electrons. When an atom gains an electron, energy is given off and is known as the electron affinity. ***Electron affinity*** is defined as the energy released when an electron is added to a gaseous atom or ion.

$T(g) + e^- \rightarrow T^-_{(g)}$

When most reactions occur that involve the addition of an electron to a gaseous atom, potential energy is released.

$Br_{(g)} + e^- \rightarrow Br^{1-}_{(g)}$ EA = -325 kJ/mol

$[Ar]\ 4s^2\ 4p^5$ $[Ar]\ 4s^2\ 4p^6$

Let's look at the electron configurations of a few of the elements and the trend that develops within groups and periods. Take a look at Table 10.5.1, the electron affinity for the Halogen family.

Table 1: Electron Affinities for Group 7A

Element	Electron configuration	Electron affinity, kJ/mol
Fluorine (F)	$[He]\ 2s^2\ 2p^5$	-328
Chlorine (Cl)	$[Ne]\ 3s^2\ 3p^5$	-349
Bromine (Br)	$[Ar]\ 4s^2\ 4p^5$	-325
Iodine (I)	$[Kr]\ 5s^2\ 5p^5$	-295

As you can see, the electron affinity generally decreases (becomes less negative) going down a group because of the increase in size of the atoms. Remember that the atoms located within a family but lower on the periodic table are larger since there are more electrons filling more energy levels. For example, an atom of chlorine is smaller than iodine; or, an atom of oxygen is smaller than sulfur. When an electron is added to a large atom, less energy is released because the electron cannot move as close to the nucleus as it can in a smaller atom. Therefore, as the atoms in a family get larger, the electron affinity gets smaller.

There is an exception to this when it involves certain small atoms. Electron affinity for fluorine is less than chlorine most likely due to the electron-electron repulsions that occur between the electrons where n = 2. This phenomenon is observed in other families as well. For instance, the electron affinity for oxygen is less than the electron affinity for sulfur. Electron affinity of all of the elements in the second period is less than the ones below them due to the fact that the elements in the second period have such small electron clouds that electron repulsion is greater than that of the rest of the family.

Nonmetals Tend to Have the Highest Electron Affinity

Overall, the periodic table shows the general trend similar to the one below.

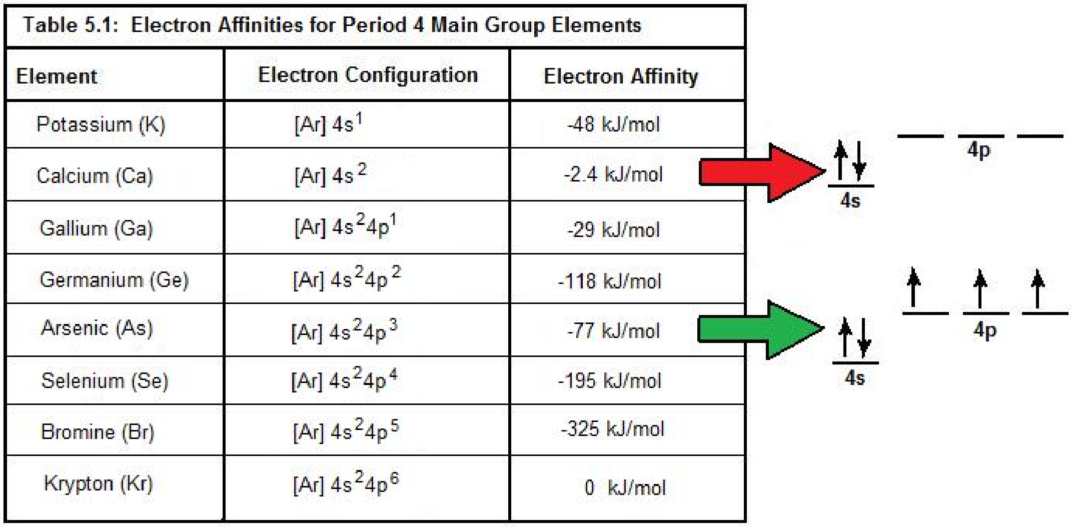


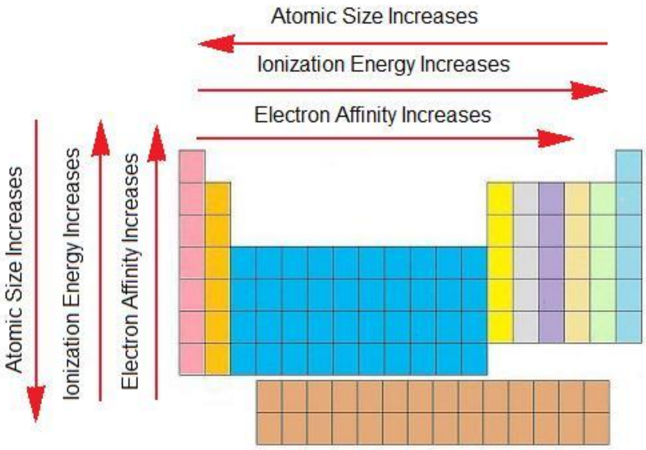
Table 5.1: Electron Affinities for Period 4 Main Group Elements

Element	Electron Configuration	Electron Affinity
Potassium (K)	[Ar] $4s^1$	-48 kJ/mol
Calcium (Ca)	[Ar] $4s^2$	-2.4 kJ/mol
Gallium (Ga)	[Ar] $4s^2 4p^1$	-29 kJ/mol
Germanium (Ge)	[Ar] $4s^2 4p^2$	-118 kJ/mol
Arsenic (As)	[Ar] $4s^2 4p^3$	-77 kJ/mol
Selenium (Se)	[Ar] $4s^2 4p^4$	-195 kJ/mol
Bromine (Br)	[Ar] $4s^2 4p^5$	-325 kJ/mol
Krypton (Kr)	[Ar] $4s^2 4p^6$	0 kJ/mol

The general trend in the electron affinity for atoms is almost the same as the trend for ionization energy. This is because both electron affinity and ionization energy are highly related to atomic size. Large atoms have low ionization energy and low electron affinity. Therefore, they tend to lose electrons and do not tend to gain electrons. Small atoms, in general, are the opposite. Since they are small, they have high ionization energies and high electron affinities. Therefore, the small atoms tend to gain electrons and tend not to lose electrons. The major exception to this rule are the noble gases. They are small atoms and **do** follow the general trend for ionization energies. The noble gases, however, **do not** follow the general trend for electron affinities. Even though the noble gases are small atoms, their outer energy levels are completely filled with electrons and therefore, an added electron cannot enter their outer most energy level. Any electrons added to a noble gas would have to be the first electron in a new (larger) energy level. This causes the noble gases to have essentially zero electron affinity. This concept is discussed more thoroughly in the next chapter.

When atoms become ions, the process involves either the energy released through electron affinity or energy being absorbed with ionization energy. Therefore, the atoms that require a large amount of energy to release an electron will most likely be the atoms that give off the most energy while accepting an electron. In other words, non-metals will most easily gain electrons since they have large electron affinities and large ionization energies; and, metals will lose electrons since they have the low ionization energies and low electron affinities.

Now let's add this last periodic trend to our periodic table representation and our periodic trends are complete.



Note: Both the trend in atomic size and the trend in ionization energy extend all the way left to right and top to bottom in the periodic table, but the trend in electron affinity only extends through family 7A, the halogens. The noble gases, family 8A, essentially have zero electron affinity.

Lesson Summary

- Electron affinity is the energy required (or released) when an electron is added to a gaseous atom or ion. Electron affinity generally increases going up a group and increases left to right across a period.
- Non-metals tend to have the highest electron affinities.

Review Questions

1. Define electron affinity and show an example equation. **(Intermediate)**

2. Choose the element in each pair that has the lower electron affinity: **(Intermediate)**

a. Li or N

b. Na or Cl

c. Ca or K

d. Mg or F

3. Why is the electron affinity for calcium much higher than that of potassium? **(Intermediate)**

4. Draw a visual representation of the periodic table describing the trend of electron affinity. **(Intermediate)**

5. Which of the following would have the largest electron affinity? **(Intermediate)**

(a) Se

(b) F

(c) Ne

(d) Br

6. Which of the following would have the smallest electron affinity? **(Intermediate)**

(a) Na

(b) Ne

(c) Al

(d) Rb

7. Place the following elements in order of increasing electron affinity: Te, Br, S, K, Ar. **(Intermediate)**

8. Place the following elements in order of decreasing electron affinity: S, Sn, Pb, F, Cs. **(Intermediate)**

9. Describe the trend that would occur for electron affinities for elements in period 3. Are there any anomalies? Explain. **(Challenging)**

Vocabulary

electron affinity The energy required to add an electron to a gaseous atom or ion. $T(g) + e^{-} \longrightarrow T^{-}(g)$

Review Answers

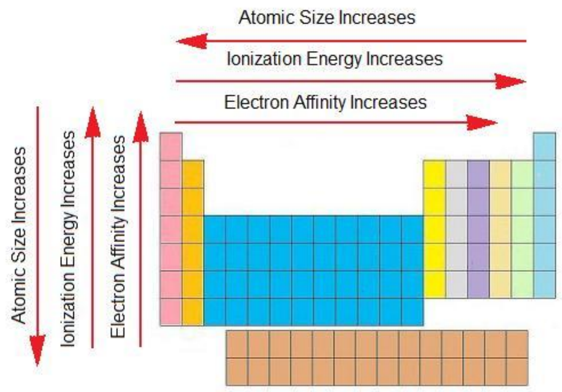
1. Electron affinity is the energy required to add an electron to a gaseous atom or ion. For example:

$Cl(g) + e^{-} \longrightarrow Cl^{-}(g) + 349\ kJ/mol$

2. (a) Li (b) Na (c) K (d) Mg

3. The extra electron is going to be added to the s orbital in potassium but for the calcium the added electron will be added to the higher energy p sublevel.

4.



Note: Both the trend in atomic size and the trend in ionization energy extend all the way left to right and top to bottom in the periodic table, but the trend in electron affinity only extends through family 7A, the halogens. The noble gases, family 8A, essentially have zero electron affinity.

5. (b) F

6. (d) Rb

7. K < Te < S < Br < Ar

8. Cs < Pb < Sn < S < F

9. The general trend is that the electron affinity increases (becomes more negative) as you move from left to right across a period. Anomalies exist with magnesium (Group 2) where the ***3s*** sublevel is full and magnesium does not want to add an electron to the higher ***p*** sublevel. Another anomaly exists at phosphorous (group 15) where the 3p sublevel is half full and therefore there is some half-filled shell stability.

11. Ions and the Compounds They Form

The Formation of Ions

Lesson Objectives

- The student will define an ion.
- The student will identify the atoms most likely to form positive ions and the atoms most likely to form negative ions.
- The student will explain why atoms form ions.
- The student will predict the charge on ions from the electron affinity, ionization energies, and electron configuration of the atom.

Introduction

Before students begin the study of chemistry, they usually think that the most stable form for an element is that of a neutral atom. As it happens, that particular idea is not true. If we were to consider the amount of sodium in the earth, we would find a rather large amount, approximately 190,000,000,000,000,000 kilotons. How much of this sodium would we find in the elemental form of sodium atoms? The answer is almost none. The only sodium metal that exists in the earth in the elemental form is that which has been man-made and is kept in chemistry labs and storerooms. Because sodium reacts readily with oxygen in the air and reacts explosively with water, it must be stored in chemistry storerooms under kerosene or mineral oil to keep it away from air and water. If those 1.9×10^{17} kilotons of sodium are not in the form of atoms, in what form are they? Virtually all the sodium in the earth is in the form of sodium ions, Na^+. The oceans of the earth contain a large amount of sodium ions in the form of dissolved salt, many minerals have sodium ions as one component, and animal life forms require a certain amount of sodium ions in their systems to regulate blood and bodily fluids, facilitate nerve function, and aid in metabolism.

If all those tons of sodium ion can be found in nature and no sodium atoms can be found, it seems reasonable to suggest that, at least in the case of sodium, the ions are chemically more stable that the atoms. By *chemically stable*, we mean less likely to undergo chemical change. This is true not only for sodium but for many other elements as well.

One of the major tendencies that cause change to occur in chemistry (and other sciences as well) is the tendency of matter to alter its condition to achieve lower potential energy. Some scientists, chemists in particular, frequently use the term **enthalpy** as a synonym for potential energy. In chemistry, this natural drive to achieve the lowest potential energy is called the ***tendency toward minimum enthalpy.*** You can place objects in positions of higher potential energy such as stretching a rubber band, putting a rock on a hillside, pushing the south poles of two magnets together but if you want them to remain like that, you must hold them there. If you release the objects, they will move toward lower potential energy. In the macroscopic world (where we deal with things larger than molecules and atoms), you can build a house of playing cards or a pyramid of champagne glasses and they will remain balanced providing no one wiggles the table.

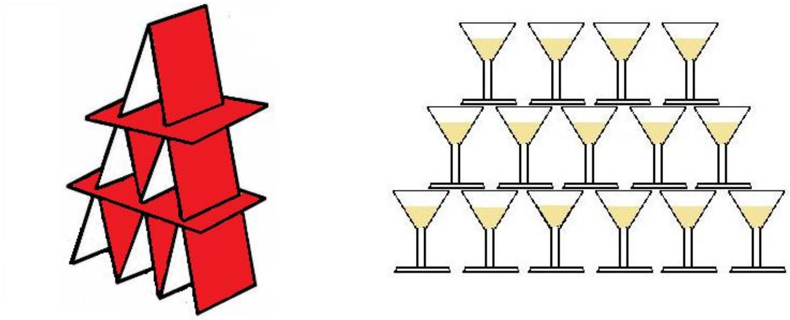


Figure 1: Delicate structures of playing cards and champagne glasses.

(*Created by:* Richard Parsons, *License:* CC-BY-SA)

If someone wiggles the table, however, the structures will fall to lower potential energy. In the case of atoms and molecules, the particles themselves have constant random motion. For atoms and molecules, this molecular motion is like constantly shaking the table.

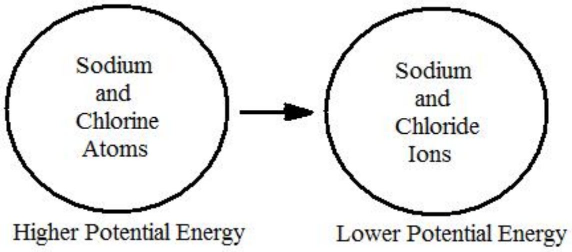


Figure 2: Sodium and chlorine atoms versus sodium and chloride ions.

(*Created by:* Richard Parsons, *License:* CC-BY-SA)

Comparing a system that contains sodium atoms and chlorine atoms to a system that contains sodium ions and chloride ions, we find that the system containing the ions has lower potential energy. The random motion of the atoms and molecules causes collisions between the particles and these collisions are adequate to initiate the change to lower potential energy.

Why Positive or Negative Ions are Formed

An atom becomes an ion when it gains or loses electrons. The ions that are formed when an atom loses electrons are positively charged because they have more protons in the nucleus than electrons in the electron cloud. Positively charged ions are called **cations** (pronounced CAT-ions). The ions that are formed when an atom gains electrons are negatively charged because they have more electrons in the electron cloud than protons in the nucleus. Negatively charged ions are called **anions** (pronounced AN-ions).

Which atoms gain electrons, which atoms lose electrons, and how many electrons an atom gains or loses, is controlled by the ionization energies and the electron affinities of the atoms. At this point, you should already know the general trends of ionization energy and electron affinity in the periodic table. As we move across a period from left to right in the periodic table, the atoms become smaller and therefore, the ionization energy increases. This is because the outermost electrons in the atom are closer to the nucleus and are, therefore, held with greater electrostatic attraction. As we move from bottom to top in a group or family in the periodic table, the atoms become smaller and the ionization energy, again, increases. The atom with the greatest ionization energy will be all the way to the right and all the way to the top of the table. That atom is helium. The atom with the least ionization energy will be all the way to the left and all the way to the bottom of the table, and that atom is francium.

The trend for electron affinity is very similar to that for ionization energy but there is one major exception. In general, large atoms have low electron affinity and small atoms have high electron affinity but the noble gases do not follow the trend. Even though the noble gases are the smallest atoms in their periods, they have very low electron affinity. The reason that the noble gases differ so significantly in electron affinity from other small atoms is that their outermost energy level is full. An atom's attraction for adding electrons is related to how close the new electron can approach the nucleus of the atom.

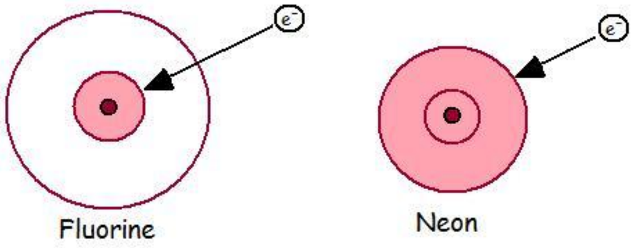


Figure 3: The first two energy levels for fluorine and neon.

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In the case of fluorine, the electron configuration is $1s^22s^22p^5$. The first energy level is full but the second one is not full. This allows an approaching electron to penetrate the second energy level and approach the nucleus as close as the first energy level. In the case of neon, both the first energy level and the second energy levels are full. This means that an approaching electron cannot penetrate either energy level and its closest approach is outside the atom. You can see these situations sketched in Figure 3 and it should be apparent to you that the approaching electron can get much closer to the nucleus with fluorine than it can with neon. Therefore, fluorine will attract this extra electron more strongly than neon and fluorine will have much greater electron affinity. Neon, in fact, has zero electron affinity. For comparison, the electron affinity of fluorine is -328 kJ/mole. This means that when one mole of fluorine atoms take on one mole of electrons, 328 kJ of energy is released. When fluorine takes on an extra electron, it moves toward lower potential energy. If neon took on an extra electron, there would be no decrease in potential energy. The changes that occur in these structures are caused by the movement toward lower potential energy. When a fluorine atom takes on an electron and becomes an ion, its potential energy becomes lower and therefore this activity occurs. If a neon atom were to take on an electron, the potential energy would not decrease and therefore, this activity does not occur.

The electron affinity of sodium is +52.8 kJ/mole. This tells us that we must put in energy to force a sodium atom to accept an extra electron. Forcing sodium to take on an extra electron requires an increase in potential energy and therefore, that activity also will not occur. The spontaneous changes that occur are accompanied by a decrease in potential energy. Without the decrease in potential energy, there is no reason for the activity to occur.

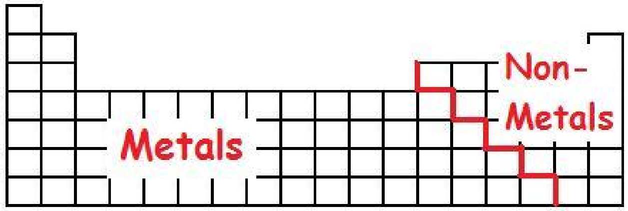

Figure 4: The division of the periodic table into metals and non-metals.

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The atoms designated as metals on the periodic table, the ones on the left side of the table, are large atoms and have low ionization energies and low electron affinities. Therefore, they will lose electrons fairly readily, but they will not gain electrons. The atoms designated as non-metals, the ones on the right side of the table, are small atoms and have high ionization energies and high electron affinities. Thus, they will not lose electrons, but they will gain electrons. The noble gases have high ionization energies and low electron affinities so they will neither gain nor lose electrons. This is the reason they almost never react with other atoms. The noble gases were called inert gases (because they wouldn't react with anything) until 1962 when Neil Bartlett forced xenon with very high temperature and pressure to combine with fluorine. With a few exceptions, the conclusion is that metals tend to lose electrons and become cations and non-metals tend to gain electrons and become anions. Noble gases tend to do neither.

In many cases, all that is necessary to effect the complete transfer of one or more electrons from a metallic atom to a non-metallic atom is that the atoms bump into each other during their normal random motion. This collision at room temperature is sufficient to remove an electron from an atom with low ionization energy and that electron will immediately be absorbed by an atom with high electron affinity. Adding the electron to the non-metal causes a release of energy to the surroundings. The energy release that occurs by adding this electron to an atom with high electron affinity is greater than the energy release that would occur if this electron returned to the atom from which it came. Hence, this electron transfer is accompanied by a lowering of potential energy – a move toward minimum enthalpy. This complete transfer of electrons produces positive and negative ions which then stick together due to electrostatic attraction.

How Many Electrons Will Atoms Gain or Lose?

So far, we have been considering the ionization energy of atoms when one electron is removed. It is possible, using high voltage equipment, to continue removing electrons from atoms after the first one is gone. Of course, after removing the first electron from a neutral atom, the next electron will be removed from a positively charged ion. When a second electron is removed, the energy required is called the second ionization energy. The energy required to remove a third electron is called the third ionization energy and so on.

Table 1: The first four ionization energies for the atoms sodium, magnesium, and aluminum. The electron configurations for these atoms are:

Na: $1s^22s^22p^63s^1$

Mg: $1s^22s^22p^63s^2$

Al: $1s^22s^22p^63s^23p^1$

Table 1: The first four ionization energies of selected atoms

Atom	**Ionizations Energies in kJ/mol**

Symbol	1st	2nd	3rd	4th
Na	496	4562	6912	9643
Mg	738	1450	7732	10,540
Al	578	1816	2745	11,577

There are a number of variations in the table and most of them are what we would expect. When you remove successive electrons from an atom, the second electron is being removed from an ion with a +1 charge and therefore, we would expect the second ionization energy to be larger than the first. The next electron would be removed from an ion with a +2 charge and so we again would expect the ionization energy to be higher. For each of the atoms in the table, the next ionization energy is always higher than the previous one. This is exactly what we would expect.

If we examine the size of the ionization energy increases, however, and put that information together with electron configuration of the atoms and the knowledge of what charge ions these atoms normally produce, we can gain a new insight. For each atom, there is one increase in ionization energies of succeeding ionizations where the next ionization energy is at least five times the previous one. In the case of sodium, this very large jump in ionization energy occurs between the first and second ionization energy. For magnesium, the huge jump occurs between the second and third ionization energies, and for aluminum, it is between the third and fourth ionization energies. If we combine this information with the fact that sodium always forms a +1 ion and never a +2 ion, magnesium always forms a +2 ion and never a +3 or +4, and aluminum always forms a +3 ion and never a +4 ion, we have a consistency in our observations that allows us to suggest an explanation.

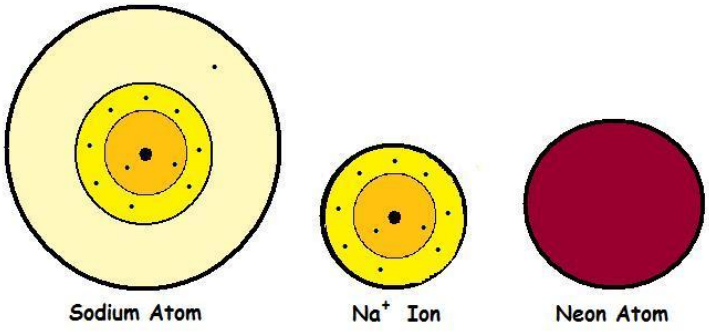

Figure 5: The electron distribution in energy levels for a sodium atom and an Na^+ ion.

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Looking at the electron distribution in energy levels for a sodium atom (Figure 3), we see that the first two energy levels are full and the third energy level contains only a single electron. When we remove the first electron from a sodium atom, it is the electron in the third energy level that is removed because it is the furthest from the nucleus and will have the lowest ionization energy. When that electron is removed, the entire third energy level is no longer available for electron removal. The sodium ion that remains has the same electron configuration as a neon atom. Neon atoms are very small atoms and have very large ionization energies. This Na^+ ion will have an even larger ionization energy than neon because while it has the same electron configuration, it has one more proton in the nucleus. The sodium ion will be slightly smaller than a neon atom. **When you have removed all the electrons in the outer energy level of an atom, the next ionization energy will take a huge jump because the next electron must be removed from a lower energy level (which is closer to the nucleus).**

Let’s consider the same picture for magnesium.

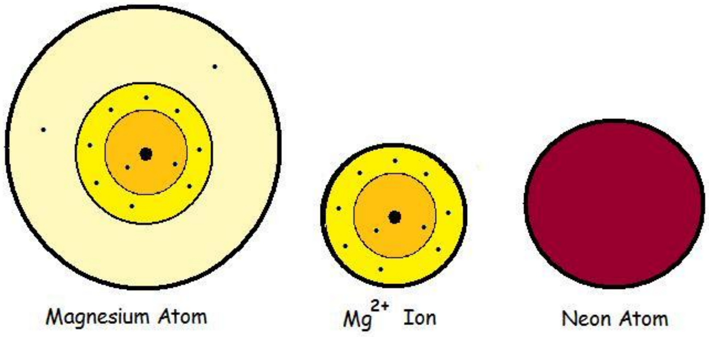

Figure 6: The electron distribution in energy levels for a magnesium atom and an Mg^{2+} ion.

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The magnesium atom has two electrons in the outermost energy level. When those two are removed, the Mg^{2+} ion that results has the same electron configuration as neon, but is smaller than neon because it has two more protons in the nucleus than neon. The first two ionization energies for magnesium are relatively small, but the third ionization is five times as great as the second. This is the reason that a magnesium atom loses two electrons relatively easily but does not lose a third.

The huge jump in ionization energies after the outermost energy level has been emptied is so consistent that we can identify the family of an unknown atom just by its successive ionization energies. If we had an unknown atom whose ionization energies were 1st: 500 kJ/mol, 2nd: 1000 kJ/mol, 3rd: 2000 kJ/mol, and 4th: 12,000 kJ/mol, we would immediately identify this atom as a member of family 3A. The reason for this is that the large jump occurs between the 3rd and 4th ionization energies so we know that three electrons can be easily removed from this atom but not a fourth.

The logic for the formation of anions is very similar to that for cations. A fluorine atom, for example, has a high electron affinity and an available space for one electron in its outer energy level. When a fluorine atom takes on an electron, the potential energy of the fluorine ion is less than the potential energy of a fluorine atom. The potential energy of the system decreases because we are moving objects that attract each other closer together. The energy is given off to the surroundings. The fluoride ion that is formed has the same electron configuration as neon. The fluoride ion will be slightly larger than a neon atom because while it has the same electron configuration, it has one less proton in its nucleus than neon so the energy levels will not be pulled in as tightly. The electron affinity of a fluoride ion is essentially zero – there is no potential energy lowering if another electron is added. As a result, fluorine will take on one and only one extra electron.

An oxygen atom has a high electron affinity and has two spaces available for electrons in its outermost energy level. When oxygen takes on one electron, the potential energy of the system is lowered and energy is given off, but this oxygen ion has not filled its outer energy level; therefore, another electron can penetrate that electron shell. The oxygen ion (O^{-1}) can accept another electron to produce the O^{2-} ion. This ion has the same electron configuration as the neon atom and it will require an input of energy to force this ion to accept another electron.

Common Ions that Form

All the metals in family 1A have electron configurations ending with an s^1 electron in the outer energy level. For that reason, all family 1A members will tend to lose exactly one electron when they are ionized. The entire family forms +1 ions: Li^+, Na^+, K^+, Rb^+, Cs^+, Fr^+. We need to note that while hydrogen (H) is in this same column, it is not considered to be an metal. There are times that hydrogen acts as if it is a metal and forms +1 ions; however, most of the time it bonds with other atoms as a nonmetal. In other words, hydrogen doesn't easily fit into any chemical family.

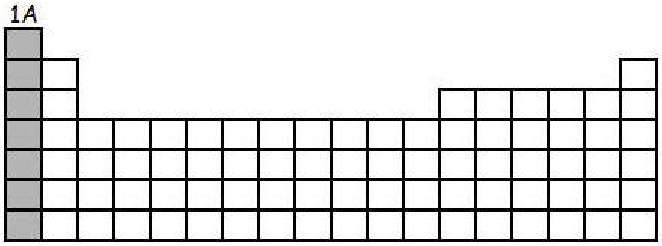
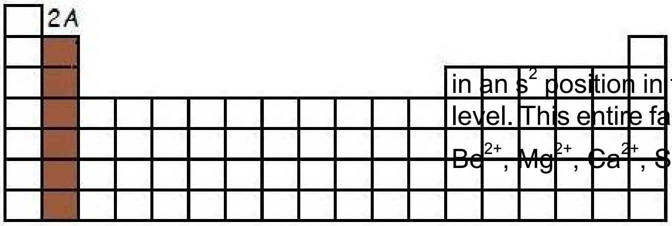


Figure 7: All members of family 1A form ions with 1+ charge. (*Created by:* Richard Parsons, *License:* CC-BY-SA)



2A all have electron ng with two electrons in an s^2 position in the outermost energy level. This entire family will form +2 ions; Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, and Ra^{2+}.

Figure 8: All members of family 2A form ions with 2+ charge. (*Created by:* Richard Parsons, *License:* CC-BY-SA)

Family 3A members have electron configurations ending in s^2p^1. When these atoms form ions, they will almost always form 3+ ions; Al^{3+}, Ga^{3+}, In^{3+}, and Tl^{3+}. You probably noticed that boron was omitted from this list. That's because boron falls on the non-metal side of the metal/non-metal dividing line. Boron doesn't form ions during chemical reactions.

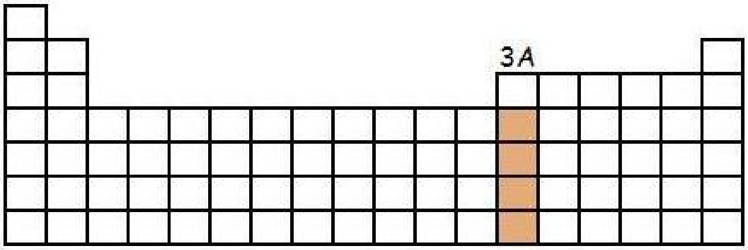


Figure 9: Most members of family 3A form ions with 3+ charge. (*Created by:* Richard Parsons, *License:* CC-BY-SA)

Family 4A is about evenly split as metals and non-metals. The larger atoms in the family, germanium, tin, and lead fall on the metal side. Since these atoms have electron configurations that end in s^2p^2, they are expected to form ions with charges of +4. All three of the atoms do form such ions, Ge^{4+}, Sn^{4+}, and Pb^{4+}, but you will learn later than some atoms have the ability to form ions of different charges. Tin and lead both have the ability to also form +2 ions. The reasons for this will be examined later. Family 5A is also divided by the metal/non-metal line. The smaller atoms in this family behave as non-metals and the larger atoms behave as metals. Since bismuth and arsenic both have electron configurations that end with s^2p^3, they will form +5 ions when they form ions. Family 6A are almost all non-metals with electron configurations ending with s^2p^4. These small atoms have enough electron affinity to take on electrons and will generally take on two electrons to fill their outermost energy level. They form -2 ions; O^{-2}, S^{-2}, Se^{-2}, Te^{-2}.

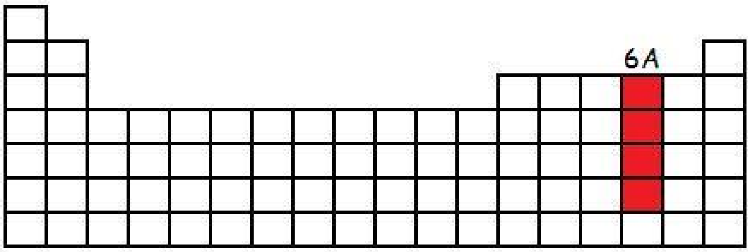


Figure 10: All members of family 6A form ions with a -2 charge.

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Family 7A are all non-metals with high electron affinities and electron configurations that end with s^2p^5. When these atoms form ions, they will form -1 ions; F^{-1}, Cl^{-1}, Br^{-1}, I^{-1}. Family 8A, of course, is the noble gases and has no tendency to either gain or lose electrons so they do not form ions.

Lesson Summary

- Ions are atoms or groups of atoms that carry electrical charge.
- When an atom gains one or more extra electrons, it becomes a negative ion.
- When an atom loses one or more of its electrons, it becomes a positive ion.

- Atoms with low ionization energy and low electron affinity (metals) tend to lose electrons and become positive ions.
- Atoms with high ionization energy and high electron affinity (non-metals) tend to gain electrons and become negative ions.
- Atoms with high ionization energy and low electron affinity (noble gases) tend to neither gain nor lose electrons.
- Atoms that tend to lose electrons will lose all the electrons in their outermost energy level.
- Atoms that tend to gain electrons will gain enough electrons to completely fill the s and p orbitals in their outermost energy level.

Review Questions

1. Define an ion. **(Beginning)**

2. In general, how does the ionization energy of metal compare to the ionization energy of a non-metal? **(Beginning)**

3. Will an iron atom form a positive or negative ion? Why? **(Beginning)**

4. Will a bromine atom form a positive or negative ion? Why? **(Beginning)**

5. How is the number of valence electrons of a metal atom related to the charge on the ion the metal will form? **(Intermediate)**

6. How is the number of valence electrons of a non-metal related to the charge on the ion the non-metal will form? **(Intermediate)**

7. If carbon were to behave like a metal and give up electrons, how many electrons would it give up? **(Intermediate)**

Further Reading / Supplemental Links

Website with lessons, worksheets, and quizzes on various high school chemistry topics.

- Lesson 4-1 is on Electronegativity.
- Lesson 4-2 is on Types of Bonds.

http://www.fordhamprep.org/gcurran/sho/sho/lessons/lesson31.htm

Vocabulary

ion	An atom or group of atoms with an excess positive or negative charge.
cation	positive ion
anion	negative ion

Review Answers

1. An ion is an atom or a group of atoms that carry an electrostatic charge. i.e. The atom of group of atoms has a different number of protons and electrons.

2. In general, the ionization energy of metals is less than the ionization energy of non-metals.

3. An iron atom is expected to form a positive ion. Iron is a metal atom and therefore, will have a low ionization energy (gives up electrons easily) and a low electron affinity (doesn't attract new electrons).

4. A bromine atom is expected to form a negative ion. Bromine is a non-metal and therefore, will have a high ionization energy (holds its electrons tightly) and a high electron affinity (attracts new electrons).

5. Metals tend to lose all their valence electrons when forming an ion and therefore, the ionic charge will be positive and equal to the number of valence electrons.

6. Non-metals tend to gain enough electrons to completely fill the s and p orbitals of their outermost energy level. Non-metals will gain a number of electrons equal to the difference between 8 and their number of valence electrons. If a non-metal has 5 electrons, it will tend to gain (8 - 5) = 3 electrons. Therefore, the charge on a non-metal ion will equal to the number of valence electrons minus 8.

7. Since carbon has four valence electrons, if it were to behave like a metal, it would give up four electrons.

Ionic Bonding

Objectives

- The student will describe how atoms from an ionic bond.
- The student will state why, in terms of energy, why atoms from ionic bonds.
- The student will state the octet rule.
- Given the symbol of a representative element, the student will indicate the most likely number of electrons the atom will gain or lose.
- Given the electron configuration of a representative element, the student will indicate the most likely number of electrons the atom will gain or lose.
- Given the successive ionization energies of a metallic atom, the student will indicate the most likely number of electrons the atom will lose during ionic bond formation.

Introduction

Molecular collisions between atoms that tend to lose electrons (metals) and atoms that tend to gain electrons (non=-metals) are sometime sufficient to remove electrons from the metal atom and add them to the non-metal atom. This transference of electrons from metals to non-metals forms positive and negative ions which in turn, attract each other due to opposite charges. The compounds formed by this electrostatic attraction are said to be ionically bonded.

Electron Transfer

When an atom with a low ionization energy encounters an atom with high electron affinity, it is possible for an electron transfer to occur. The ionization of the metal atom requires an input of energy. This energy input is often accomplished simply by the collision of atoms due to particle motion. Once electrons have been removed from the metal atoms, the electrons are taken on by the non-metal atoms and energy is released. The energy released by absorption of electrons by non-metal atoms provides sufficient energy for the reaction to continue. In some cases, a reaction of this sort must be heated in order to start the reaction but once the reaction begins, the reaction itself provides enough heat to continue.

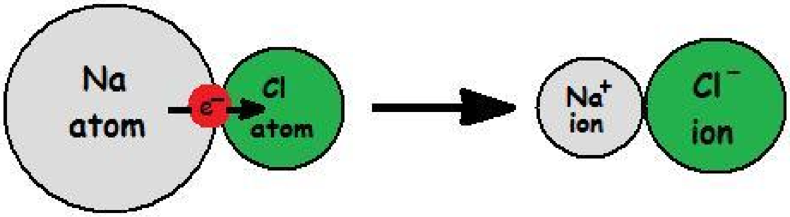

Figure 11: During a collision between sodium and chlorine atoms, an electron is transferred.

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The process of transferring an electron from a sodium atom to a chlorine atom as shown in Figure 9 produces oppositely charged ions which then stick together because of ***electrostatic attraction***. Electrostatic attraction is the attraction between opposite charges. In chemistry, the electrostatic attraction between oppositely charged ions is called an **ionic bond.** You should also note in Figure 11 that before the collision, the sodium atom is larger than the chlorine atom, but after the electron transfer the sodium ion is now smaller than the chloride ion. The sodium ion is smaller than a neon atom because it has the same electron configuration as neon, but it has one more proton in the nucleus than neon. The chloride ion is larger than an argon atom because while it has the same electron configuration as argon, it has one less proton in the nucleus than argon. The sodium ion now has high ionization energy and low electron affinity (just like a noble gas) so there is no reason for any further changes. The same is true for the chloride ion. These ions are chemically more stable than the atoms were.

Atoms that Gain or Lose More than One Electron

If we had been using sodium and sulfur atoms for the transfer discussion, the process would be only slightly different. Sodium atoms have a single electron in their outermost energy level and therefore can lose only one electron. Sulfur atoms, however, require two electrons to complete their outer energy level. In such a case, two sodium atoms would be required to collide with one sulfur atom. Each sodium atom would contribute one electron for a total of two electrons and the sulfur atom would take on both electrons. The two Na atoms would become Na^+ ions and the sulfur atom would become a S^{2-} ion. Electrostatic attractions would cause all three ions to stick together.

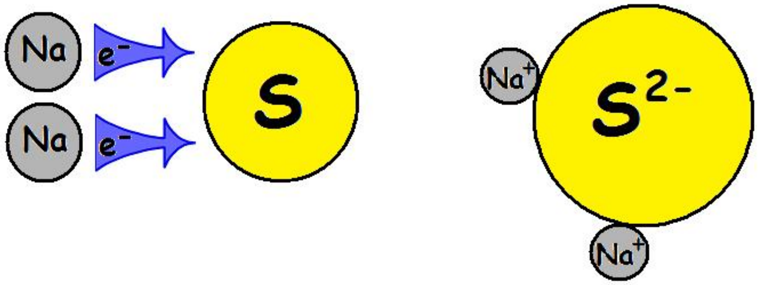

Figure 12: Two electrons are transferred from sodium atoms to a sulfur atom.

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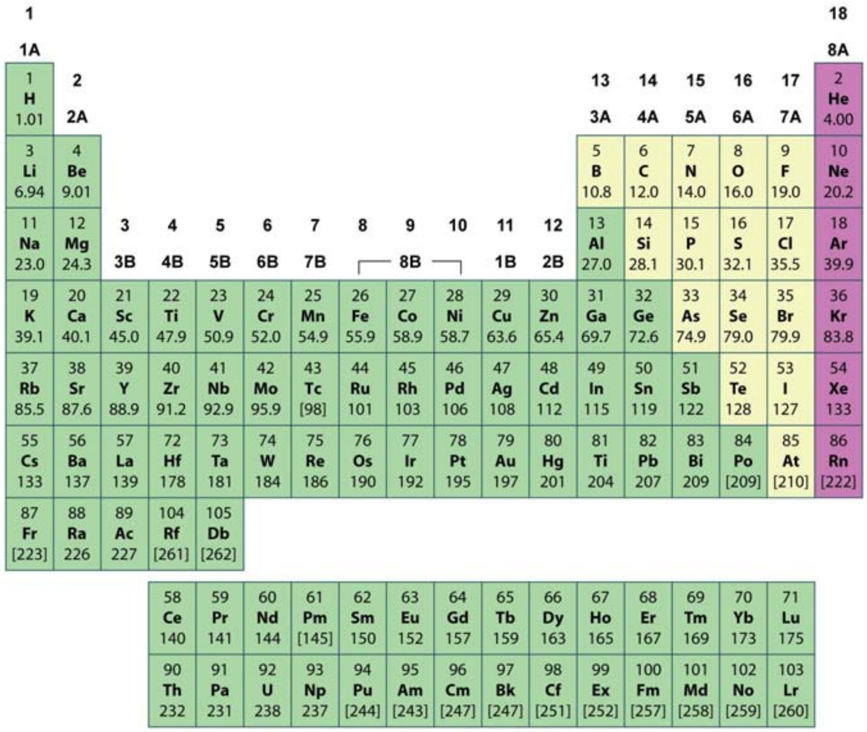
The Octet Rule

Depending on the source or age of your periodic table, you may see two different systems of referring to the families on the periodic table.



1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9	10	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1 **H** 1.01																	2 **He** 4.00
3 **Li** 6.94	4 **Be** 9.01											5 **B** 10.8	6 **C** 12.0	7 **N** 14.0	8 **O** 16.0	9 **F** 19.0	10 **Ne** 20.2
11 **Na** 23.0	12 **Mg** 24.3											13 **Al** 27.0	14 **Si** 28.1	15 **P** 30.1	16 **S** 32.1	17 **Cl** 35.5	18 **Ar** 39.9
19 **K** 39.1	20 **Ca** 40.1	21 **Sc** 45.0	22 **Ti** 47.9	23 **V** 50.9	24 **Cr** 52.0	25 **Mn** 54.9	26 **Fe** 55.9	27 **Co** 58.9	28 **Ni** 58.7	29 **Cu** 63.6	30 **Zn** 65.4	31 **Ga** 69.7	32 **Ge** 72.6	33 **As** 74.9	34 **Se** 79.0	35 **Br** 79.9	36 **Kr** 83.8
37 **Rb** 85.5	38 **Sr** 87.6	39 **Y** 88.9	40 **Zr** 91.2	41 **Nb** 92.9	42 **Mo** 95.9	43 **Tc** [98]	44 **Ru** 101	45 **Rh** 103	46 **Pd** 106	47 **Ag** 108	48 **Cd** 112	49 **In** 115	50 **Sn** 119	51 **Sb** 122	52 **Te** 128	53 **I** 127	54 **Xe** 133
55 **Cs** 133	56 **Ba** 137	57 **La** 139	72 **Hf** 178	73 **Ta** 181	74 **W** 184	75 **Re** 186	76 **Os** 190	77 **Ir** 192	78 **Pt** 195	79 **Au** 197	80 **Hg** 201	81 **Ti** 204	82 **Pb** 207	83 **Bi** 209	84 **Po** [209]	85 **At** [210]	86 **Rn** [222]
87 **Fr** [223]	88 **Ra** 226	89 **Ac** 227	104 **Rf** [261]	105 **Db** [262]													
			58 **Ce** 140	59 **Pr** 141	60 **Nd** 144	61 **Pm** [145]	62 **Sm** 150	63 **Eu** 152	64 **Gd** 157	65 **Tb** 159	66 **Dy** 163	67 **Ho** 165	68 **Er** 167	69 **Tm** 169	70 **Yb** 173	71 **Lu** 175	
			90 **Th** 232	91 **Pa** 231	92 **U** 238	93 **Np** 237	94 **Pu** [244]	95 **Am** [243]	96 **Cm** [247]	97 **Bk** [247]	98 **Cf** [251]	99 **Ex** [252]	100 **Fm** [257]	101 **Md** [258]	102 **No** [259]	103 **Lr** [260]	

Figure 13: The periodic table with both numbering systems.

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The older system refers to the families with numbers and letters, 1A, 2A, 3A etc. The newer system numbers the columns in the table consecutively from left to right as 1, 2, 3, . . . , 18. Using the old system, the "A" groups were referred to as the representative elements.

In the representative elements, all the valence electrons are in ***s*** and ***p*** orbitals. Therefore, for the representative elements, all electron dot formulas have somewhere between one and eight electrons. The cation forming elements lose all valence electrons so the electron dot formula for the ions formed will have the eight electrons of the previous noble gas. (Those whose electron dot formula matches helium, of course, will have only two.) The anion forming elements will gain enough electrons so the electron dot formulas of their ions will match those of the following noble gas. In all cases, for the "A" groups elements, the ions will have eight electrons in their electron dot formula. The **octet rule** is an expression of this end result of eight electrons in the outer most energy level.

Lesson Summary

- Ionic bonds are formed by a transfer of electrons from metal atoms to non-metal atoms with the resulting electrostatic attraction holding the ions together.
- The octet rule is an expression of the tendency for atoms gain or lose the appropriate number of electrons so that the resulting ion has either completely filled or completely empty outer energy levels.

Review Questions

1. What takes place during the formation of an ionic bond? **(Beginning)**

2. What effect does the transfer of electrons have on the nuclei of the atoms involved? **(Beginning)**

3. Explain why chlorine is a small atom and tends to take on an extra electron but argon is an even smaller atom and does not tend to take on electrons. **(Intermediate)**

4. If an atom had the following successive ionization energies, to which family would it belong? Why did you chose this family? **(Challenging)**

1st ionization energy = 75 kJ/mol

2nd ionization energy = 125 kJ/mol

3rd ionization energy = 1225 kJ/mol

4th ionization energy = 1750 kJ/mol

Vocabulary

ionic bond	A bond between ions resulting from the transfer of electrons from one of the bonding atoms to the other and the resulting electrostatic attraction between the ions.
electrostatic attraction	The force of attraction between opposite electric charges.

Review Answers

1. Electrons are transferred from metallic atoms to non-metallic atoms forming oppositely charged ions which are then attracted to each other.

2. no effect

3. The outer energy level of chlorine is not full and so a new electron can penetrate the outer energy level and get close enough to the nucleus to be attracted. The outer energy level of argon is filled and so a new electron cannot penetrate this outer energy level and cannot get close enough to the nucleus to be attracted.

4. This atom would most likely belong to family 3A. A large jump in energy occurs between the 2nd and 3rd ionization energies which indicates the outer energy level is empty after the 2nd ionization.

Properties of Ionic Compounds

Objectives

- The student will give a short, generic description of a lattice structure.
- The student will identify distinctive properties of ionic compounds.

Introduction

When ionic compounds are formed, we are almost never dealing with just a single positive ion and a single negative ion. When ionic compounds are formed in laboratory conditions, many cations and anions are formed at the same time. The positive and negative ions are not just attracted to a single oppositely charged ion. The ions are attracted to several of the oppositely charged ions. The ions arrange themselves into organized patterns where each ion is surrounded by several ions of the opposite charge.

Lattice Structures

The organized patterns of positive and negative ions are called **lattice structures**. There are a number of different ionic lattice structures. Which lattice structure forms for particular ionic compounds is determined by the relative sizes of the ions and by the charge on the ions. The lattice structure for sodium chloride, shown in Figure 14 is called *hexagonal closest packing*. There are many other lattice structures that may form. Because ionic compounds form these large lattice structures in the solid phase, they are not referred to as "molecules" but rather as lattice structures or crystals.

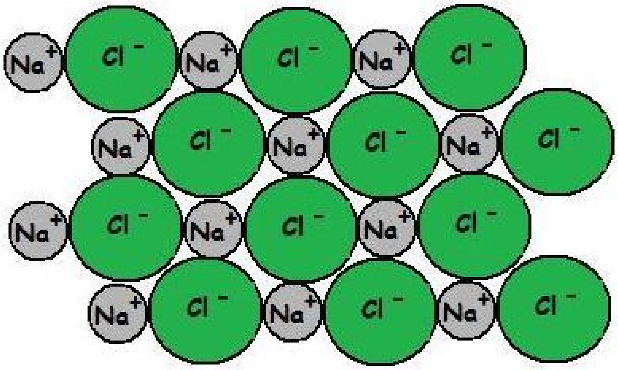

Figure 14: NaCl lattice structure.

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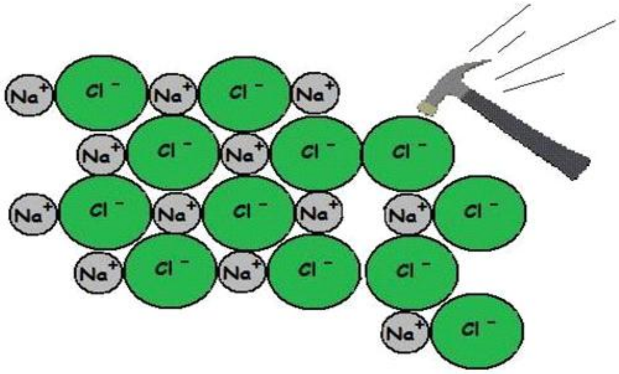
Figure 14 shows the solid structure of sodium chloride. Only one layer is shown. When layers are placed above and below this one, each sodium ion would be touching six chloride ions – the four surrounding ones and one above and one below. Each chloride ion will be touching six sodium ions in the same way.

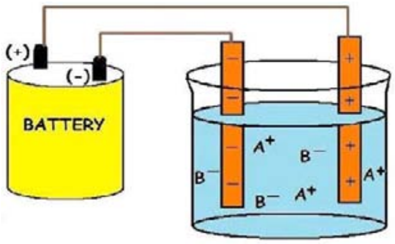
Ionic Properties

When electrons are transferred from metallic atoms to non-metallic atoms during the formation of an ionic bond, the electron transfer is permanent. That is, the electrons now belong to the non-metallic ion. If the ionic lattice structure is taken apart by melting it to a liquid, or vaporizing it to a gas, or dissolving it in water, the particles come apart in the form of ions. The electrons that were transferred go with the negative ion when the ions separate.

The electrostatic attraction between the oppositely charge ions is quite strong and therefore, ionic compounds have very high melting and boiling points. Sodium chloride (table salt), for example, must be heated to around 800°C to melt and around 1500°C to boil. There is only one type of solid that has higher melting points and boiling points, in general, than ionic compounds.

If you look again at Figure 14, you can see that negative ions are surrounded by positive ions and vice versa. If part of the lattice is pushed downward, negative ions will then be next to negative ions and the structure will break up. If you attempt to hammer on ionic substances, they will shatter. This is very different from metals which can be hammered into different shapes without the metal atoms separating from each other.





Ionic substances generally dissolve readily in water. In an ionic compound that has been melted or an ionic compound dissolved in water, ions are present that have the ability to move around in the liquid. The presence of the mobile ions in liquid or solution allow the solution to conduct electric current. The liquid forms of non-ionic compounds and non-ionic compounds dissolved in water do not conduct electric current. It is specifically the presence of the mobile ions that allow electric current to be conducted by ionic liquids and ionic solutions.

Ionization Changes Chemical Properties

The process of gaining and/or losing electrons completely changes the chemical properties of the substances. The chemical and physical properties of an ionic compound will bear no resemblance to the properties of the elements which formed the ions. For example, sodium is a metal that is shiny, an excellent conductor of electric current, and reacts violently with water. Chlorine is a poisonous gas. When sodium and chlorine are chemically combined to form sodium chloride (table salt), the product has an entirely new set of properties. Sometimes, we sprinkle sodium chloride on our food. This is not something we would do if we expected it to explode when contacted by water or if we expected it to poison us.

Lesson Summary

- Ionic compounds form ionic crystal lattices rather than molecules.
- Ionic compounds are generally soluble in water and their water solutions will conduct electricity.
- Ionic compounds have chemical properties that are unrelated to the chemical properties of the elements from which they were formed.

Review Questions

1. Hydrogen gas is not an acid and chlorine gas is not an acid but when hydrogen and chlorine combine to form hydrogen chloride, the compound is an acid. How do you explain that? **(Intermediate)**

2. Why do we not refer to molecules of sodium chloride? **(Intermediate)**

3. Which is larger, a fluorine atom or a fluoride ion? **(Challenging)**

Further Reading / Supplemental Links

Chemistry, A Modern Course, Chapter 10: Periodic Properties, Robert C. Smoot, Jack Price, and Richard G. Smith, Merrill Publishing Co., 1987.

http://www.kanescience.com/_chemistry/5Ionic.htm

http://visionlearning/library/module_viewer.php?mid=55

Vocabulary

Crystal lattice	A systematic, symmetrical network of atoms forming an ionic solid.

Review Answers

1. The properties of a compound formed from elements have no relationship to the properties of the elements.

2. Sodium chloride is an ionic compound and ionic compounds form crystal lattices rather than molecules.

3. The fluoride ion is larger because it has one more electron in the electron cloud but the same number of protons to pull on the electrons.

12. Writing and Naming Ionic Formulas

Predicting Formulas of Ionic Compounds

Lesson Objectives

- Given the elements to be combined, the student will write correct formulas for binary ionic compounds, compounds containing metals with variable oxidation numbers, and compounds containing polyatomic ions.

Introduction

Ionic compounds do not exist as molecules. In the solid state, ionic compounds are in crystal lattices containing many ions each of the cation and anion. An ionic formula, like NaCl, is an empirical formula. This formula merely indicates that sodium chloride is made of an equal number of sodium and chloride ions.

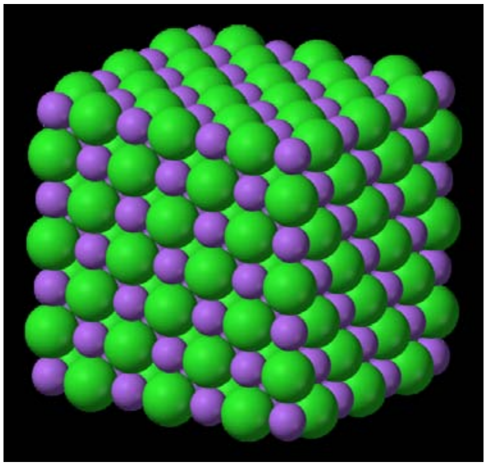


Figure 1: The three-dimensional crystal lattice structure of sodium chloride.

(*Source:* http://en.wikipedia.org/wiki/Image:Sodium-chloride-3D-ionic.png, *License:* Public Domain)

Sodium sulfide, another ionic compound, has the formula Na_2S. This formula indicates that this compound is made up of twice as many sodium ions as sulfide ions. Na_2S will also form a crystal lattice but it won't be the same as the NaCl lattice because the organization has to have two sodium ions per sulfide ion instead of one to one.

Determining Ionic Charge

The charge that will be on an ion can be predicted for most of the monatomic ions. Many of these ionic charges can be predicted for entire families of elements. There are a few ions whose charge must simply be memorized and there are also a few that have the ability to form two or more ions with different charges so the exact charge on the ion can only be determined by analyzing the ionic formula of the compound.

All of the elements in family 1A have the same outer energy level electron configuration, the same number of valence electrons (one), and they are all metals with low first ionization energies. Therefore, these atoms will lose their one valence electron and form ions with a 1+ charge. This allows us to predict the ionic charges on all the 1A ions; Li^+, Na^+, K^+, Rb^+, Cs^+, Fr^+.

Hydrogen is a special case that is usually considered by itself rather than as a member of a family. Hydrogen has the ability to form a positive ion by losing its single valence electron just as the 1A metals do. In those cases, hydrogen forms the 1+ ion, H^+. In rare cases, hydrogen can take on one electron to complete its outer energy level. The compounds where this occurs are called hydrides, NaH, KH, LiH. Hydrogen also has the ability to form compounds without losing or gaining electrons and that process will be discussed in the next chapter.

All of the elements in family 2A have the same outer energy level electron configuration and the same number of valence electrons (two).

Be : $1s^22s^2$

Mg : $1s^22s^22p^63s^2$

Ca : $1s^22s^22p^63s^23p^64s^2$

Sr : $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^2$

Ba : $[Xe]6s^2$

Ra : $[Rn]7s^2$

Each of these atoms is a metal with a low first and second ionization energies and will therefore lose both of its valence electrons forming an ion with a 2+ charge. The ions formed in family 2A are Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, and Ra^{2+}.

There is a slight variation in family 3A. The line separating metals from non-metals on the periodic table cuts through family 3A between boron and aluminum. In family 3A, boron, $1s^22s^22p^1$, behaves as a non-metal due to its higher ionization energy and higher electron affinity. In the periodic table, it is on the non-metal side of the metal/non-metal dividing line.

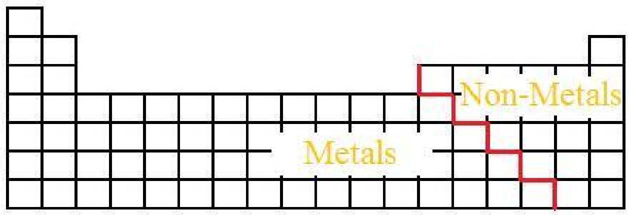


Figure 2: The red line divides metals from non-metals on the periodic table.

(*Created by*: Richard Parsons, *License:* CC-BY-SA)

Aluminum, on the other hand, is on the metallic side of the line and behaves as an electron donor. Aluminum, $1s^22s^22p^63s^23p^1$, always loses all three of its valence electrons and forms an Al^{3+} ion. Gallium and indium have the same outer energy level configuration as aluminum except they are in the next higher periods (4 and 5) and they also lose all three of their valence electrons and form the 3+ ions, Ga^{3+} and In^{3+}. Thallium, whose electron configuration ends with $6s^26p^1$ should also form a 3+ ion, but for reasons not yet determined, is more stable as a 1+ ion, Tl^+.

The electron configurations for the members of family 6A are as follows:

O : $1s^22s^22p^4$

S : $1s^22s^22p^63s^23p^4$

Se : $1s^22s^22p^63s^23p^64s^23d^{10}4p^4$

Te : $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^4$

Each of these atoms has six valence electrons and they all have high electron affinities. These atoms will, therefore, take on additional electrons to complete the octet of electrons in their outer energy levels. Since each atom will take on two electrons to complete their octet, they will form 2- ions. The ions formed will be O^{2-}, S^{2-}, Se^{2-}, and Te^{2-}.

Family 7A elements have the outer energy level electron configuration ns^2np^5. These atoms have the highest electron affinities in their periods and will each take on one more electron to complete the octet of electrons in their outer energy levels. Therefore, these atoms will form 1- ions; F^-, Cl^-, Br^-, I^-, and At^-.

Family 8A elements have exactly filled outer energy levels, have very high ionization energy, and very low electron affinities. Therefore, these atoms do not give up electrons and do not take on electrons. The atoms of family 8A do not form ions.

Transition Elements with Fixed Oxidation Numbers

Many of the transition elements have variable oxidation states so they can form ions with different charges. We will consider some of those later in this chapter. There are also some transition elements that only form one ion and you will need to know a few of those. The electron configuration of silver, Ag, is $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^14d^{10}$. You should note that this electron configuration does not follow the regular rules for the filling of orbitals. A lower energy level, the 5s orbital, is not full and yet electrons are placed in the 4d orbital. It happens that the electron configuration is slightly lower in energy when the d orbitals are exactly half full (5 electrons) or completely full (10 electrons). This also happens with chromium, copper, molybdenum, and gold. There are a few anomalies like this in the electron configurations of the transition elements and chemists do not agree as to why they occur. Whatever the reason, it gives silver an outer energy level that contains only one electron, and therefore, the silver ion is Ag^+.

The electron configuration for Zn is $[Ar]4s^23d^{10}$. Like most metals, zinc loses all of its valence electrons when it forms an ion and therefore, Zn forms a Zn^{2+} ion. Cadmium is similar. The electron configuration for Cd is $[Kr]5s^23d^{10}$ and so it will form a Cd^{2+} ion.

Writing Basic Ionic Formulas

In writing formulas for binary ionic compounds (binary refers to two elements, NOT two single atoms), the more electropositive element is always written first.

[Even though the rule above states that the more electropositive element is always written first, there are a couple of compounds that have been commonly known and used for several decades before the rules were established. These compounds continue to be known by their common name and have their formulas written as they were for many years. Ammonia, NH_3, for example, continues to be written as NH_3 rather than H_3N, even though hydrogen is the more electropositive of the two elements.]

Chemists use subscripts following the symbol of each element to indicate the number of atoms of that element present in the formula. For example, the formula Na_2O indicates that the formula for the compound that forms between sodium and oxygen contains two atoms of sodium for each one of oxygen. When the subscript for an element is "1," the subscript is omitted. The number of atoms of an element with no indicated subscript is always read as "1." When an ionic compound forms, the number of electrons given off by the cations must be exactly the same as the number of electrons taken on by the anions. Therefore, if calcium, which gives off two electrons, is to combine with fluorine, which takes on one electron, then one calcium atom must combine with two fluorine atoms. The formula would be CaF_2.

Suppose we wish to write the formula for the compound that forms between aluminum and chlorine. To write the formula, we must first determine the oxidation numbers of the ions that would be formed.

$$\overset{3+}{Al} \quad \overset{1-}{Cl}$$

Then, we determine the simplest whole numbers with which to multiply these charges so they will balance (add to zero). In this case, we would multiply the 3+ by 1 and the 1- by 3.

$$\underset{(3+)(1) = 3+}{\overset{3+}{Al}} \qquad \underset{(1-)(3) = 3-}{\overset{1-}{Cl}}$$

You should note that we could multiply the 3+ by 2 and the 1- by 6 and get 6+ and 6- which would also balance, but this is NOT acceptable because we are writing empirical formulas and empirical formulas must have the lowest whole number multipliers. Once we have the *lowest* whole number multipliers, those multipliers become the subscripts for the symbols.

$$AlCl_3$$

Here's the process for writing the formula for the compound formed between aluminum and sulfur.

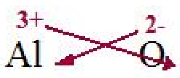
$$\underset{(3+)(2) = 6+}{\overset{3+}{Al}} \qquad \underset{(2-)(3) = 6-}{\overset{2-}{S}}$$

Therefore, the formula for this compound would be Al_2S_3.

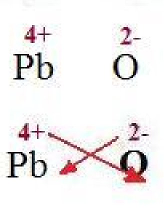
Another method used to write formulas is called the criss-cross method. It is a quick method but it often produces errors if the user doesn't pay attention to the results. Here's the criss-cross method for writing the formula for the compound formed between aluminum and oxygen. In the criss-cross method, the oxidation numbers are placed over the symbols for the elements just as before.

$$\overset{3+}{Al} \qquad \overset{2-}{O}$$

But in this method, the oxidation numbers are then criss-crossed and used as the subscripts for the other atom (ignoring sign).



This produces the formula Al_2O_3 for the compound and this is the correct formula. The errors that occur with this method would occur when you are writing the formula for a compound in which the two atoms have oxidation numbers of 2+ and 2-. Obviously, the two subscripts should both be "1," but the criss-cross method would produce subscripts of 2 for each atom. Here's another example of a criss-cross error.



Pb_2O_4

PbO_2

If you used the original method of finding the lowest multipliers to balance the charges, you would get the correct formula PbO_2, but the criss-cross method produces an incorrect formula Pb_2O_4 (both subscripts could be divided by 2 to produce the lowest whole number ratio). If you are alert to the final result and check you make sure you do not have double or triple the correct value, then the criss-cross method works. Otherwise, stick to the original method of writing formulas.

Metals with Variable Oxidation Number

There are a few metals that form ions with different charges. For some of them, the reason is apparent from their electron configuration but for others, the reason is not yet determined. It is necessary for you to memorize some of these metals and their different oxidation numbers. When writing formulas, you are given the oxidation number, so there is no problem if a metal forms more than one ion. When we get to naming ionic compounds, however, it is absolutely vital that you recognize metals that can have more than one oxidation number. A partial list of variable oxidation number metals includes iron, copper, tin, lead, nickel, and gold.

We find, in the case of iron, that it can form both Fe^{2+} and Fe^{3+} ions. The electron configuration for neutral Fe is $1s^22s^22p^63s^23p^64s^23d^6$. It is fairly obvious why iron forms the 2+ ion, it simply loses all its valence electrons just as other metals do. The electron configuration for the Fe^{2+} ion is $[Ar]3d^6$. What is it about this electron configuration that would allow the iron ion to lose one more electron? Just a few paragraphs back, we were talking about the electron configuration for silver and it was mentioned that the ***d*** orbitals have slightly lower energy when they are exactly half full or completely full. If this Fe^{2+} ion were to lose one more electron, the ***3d*** orbitals would be exactly half full with five electrons. When iron reacts, if there is normal pull on its electrons from the non-metal, it will form Fe^{2+} and if the pull on its electrons is particularly strong, it will form Fe^{3+}.

Copper can form ions with either a +1 or a +2 charge, Cu^+ and Cu^{2+}. The Cu^{2+} is more common and more stable. Tin forms both Sn^{2+} and Sn^{4+}. Lead also forms both Pb^{2+} and Pb^{4+}. Nickel forms both Ni^+ and Ni^{2+} and finally, gold forms both Au^+ and Au^{3+} ions. There are more variable oxidation number metals and you will meet some of them but you should memorize iron, copper, tin, lead, nickel, and gold.

Polyatomic Ions

Thus far, we have been dealing with ions made from single atoms. Such ions are called monatomic ions. There also exists a group of polyatomic ions, ions composed of a group of atoms that are covalently bonded and behave as if they were a single ion. Almost all the common polyatomic ions are negative ions. The only common positive polyatomic ion is ammonium, NH_4^+. The name and formula of ammonium ion is similar to ammonia, BUT it is not ammonia and you should not confuse the two. These polyatomic ions are another group of names and formulas that you need to memorize.

Ammonium ion, NH_4^+

Acetate ion, $C_2H_3O_2^{\;-}$

Carbonate ion, $CO_3^{\;2-}$

Chromate ion, $CrO_4^{\;2-}$

Dichromate ion, $Cr_2O_7^{\;2-}$

Hydroxide ion, OH^-

Nitrate ion, $NO_3^{\;-}$

Phosphate ion, $PO_4^{\;3-}$

Sulfate ion, $SO_4^{\;2-}$

Sulfite ion, $SO_3^{\;2-}$

You should know these well enough that when someone says the name, you can respond with the formula and charge, and if someone shows you the formula and charge, you can respond with the name.

These polyatomic ions require additional consideration when you write formulas involving them. Suppose we are asked to write the formula for the compound that would form between calcium and the nitrate ion. We begin by putting the charges above the symbols just as before.

$$\underset{(2+)(1) = 2+}{\overset{2+}{Ca}} \qquad \underset{(1-)(2) = 2-}{NO_3^{\;1-}}$$

The multipliers needed to balance these ions are "1" for calcium and "2" for nitrate. We wish to write a formula that tells our readers that there are two nitrate ions in the formula for every calcium ion. When we put the subscript "2" beside the nitrate ion in the same fashion as before, we get something strange - $CaNO_{32}$. With this formula, we are indicating 32 oxygen atoms which is VERY wrong. Chemists decided that the solution to this problem is to put parentheses around the nitrate ion before the subscript is added. Therefore, the correct formula looks like this, $Ca(NO_3)_2$. Calcium phosphate would look like this $Ca_3(PO_4)_2$. Please note that parentheses are only used when they are needed! If a polyatomic ion does not need a subscript other than an omitted "1," then parentheses are not needed. When students make an error with parentheses, it is almost never a case of leaving off parentheses when they are needed. The most common errors with parentheses is students put them around everything. The goal is to have every single chemist in the world write exactly the same formula for the same compound. If you put parentheses around something where they are not needed, the reader of your formula knows you made a mistake but he doesn't know whether you put on parentheses you didn't need or whether you left off a subscript.

Practicing with Parentheses 1

Write the formula for the compound that will form from aluminum and acetate.

The charge on an aluminum ion is 3+ and the charge on an acetate ion is 1-. Therefore, three acetate ions are required to combine with one aluminum ion. This is also apparent by the criss-cross method. However, we cannot place a subscript of 3 beside the oxygen subscript of 2 without inserting parentheses first. Therefore, the formula will be

$$Al(C_2H_3O_2)_3$$

Practicing with Parentheses 2

Write the formula for the compound that will form from ammonium and phosphate.

The charge on an ammonium ion is 1+ and the charge on a phosphate ion is 3-. Therefore, three ammonium ions are required to combine with one phosphate ion. The criss-cross procedure will place a subscript of 3 next to the subscript 4. This can only be carried out if the ammonium ion is first placed in parentheses. Therefore, the proper formula is

$$(NH_4)_3PO_4$$

Practicing with Parentheses 3

Write the formula for the compound that will form from aluminum and phophate.

$$Al^{3+} \quad PO_4^{3-}$$

Since the charge on an aluminum ion is 3+ and the charge on a phosphate ion is 3-, these ions will combine in a one-to-one ratio. In this case, the criss-cross method would produce an incorrect answer. Since it is not necessary to write the subscripts of one, no parentheses are needed in this formula. Since parentheses are not needed, is is actually INCORRECT to use them.

$$AlPO_4$$

More Examples

Magnesium and hydroxide . . . . $Mg(OH)_2$

Sodium carbonate . . . . Na_2CO_3

Barium acetate . . . . $Ba(C_2H_3O_2)_2$

Hydrogen phosphate . . . . H_3PO_4
.

Ammonium dichromate . . . . $(NH_4)_2Cr_2O_7$
.

Practice!

Lesson Summary

- The oxidation number for ions of the representative elements can usually be determined by the number of valence electrons.
- The number of valence electrons for the representative elements is equal to the number in the family name.
- Some transition elements have fixed oxidation numbers and some have variable oxidation numbers.
- Some metals, such as iron, copper, tin, lead, nickel, and gold, have variable oxidation numbers.
- There are groups of atoms formed into an ion and called polyatomic ions that behave as if they were a single ion.
- Formulas for ionic compounds contain the lowest whole number ratio of subscripts such that the sum of the subscript of the more electropositive element times its oxidation number plus the subscripts of the more electronegative element times its oxidation number equals zero.

Review Questions

1. Fill in the chart by writing formulas for the compounds that might form between the ions in the columns and rows. Some of these compounds don't exist but you can still write formulas for them. **(Intermediate)**

	Na^+	Ca^{2+}	Fe^{3+}	NH_4^+	Sn^{4+}
NO_3^-					
SO_4^{2-}					
Cl^-					
S^{2-}					
PO_4^{3-}					
OH^-					
$Cr_2O_7^{2-}$					
CO_3^{2-}					

Further Reading / Supplemental Links

Website with lessons, worksheets, and quizzes on various high school chemistry topics.

- Lesson 5-3 is on Writing Chemical Formulas.

http://www.fordhamprep.org/gcurran/sho/sho/lessons/lesson31.htm

Vocabulary

oxidation number	The charge or apparent charge that an atom in a compound or ion would have if all the electrons in its bonds belonged entirely to the more electropositive atom.
polyatomic ion	An electrically charged species formed by covalent bonding of atoms of two or more different elements, usually non-metals.

Review Answers

1.

	Na^+	Ca^{2+}	Fe^{3+}	NH_4^+	Sn^{4+}
NO_3^-	$NaNO_3$	$Ca(NO_3)_2$	$Fe(NO_3)_3$	NH_4NO_3	$Sn(NO_3)_4$
SO_4^{2-}	Na_2SO_4	$CaSO_4$	$Fe_2(SO_4)_3$	$(NH_4)_2SO_4$	$Sn(SO_4)_2$
Cl^-	$NaCl$	$CaCl_2$	$FeCl_3$	NH_4Cl	$SnCl_4$
S^{2-}	Na_2S	CaS	Fe_2S_3	$(NH_4)_2S$	SnS_2
PO_4^{3-}	Na_3PO_4	$Ca_3(PO_4)_2$	$FePO_4$	$(NH_4)_3PO_4$	$Sn_3(PO_4)_4$
OH^-	$NaOH$	$Ca(OH)_2$	$Fe(OH)_3$	NH_4OH	$Sn(OH)_4$
$Cr_2O_7^{2-}$	$Na_2Cr_2O_7$	$CaCr_2O_7$	$Fe_2(Cr_2O_7)_3$	$(NH_4)_2Cr_2O_7$	$Sn(Cr_2O_7)_2$
CO_3^{2-}	Na_2CO_3	$CaCO_3$	$Fe_2(CO_3)_3$	$(NH_4)_2CO_3$	$Sn(CO_3)_2$

Inorganic Nomenclature

Lesson Objectives

- Given the formulas, the student will correctly name binary ionic compounds, compounds containing metals with variable oxidation numbers, and compounds containing polyatomic ions.
- Given the names, the student will provide formulas for binary ionic compounds, compounds containing metals with variable oxidation numbers, and compounds containing polyatomic ions.

Naming Binary Ionic Compounds

Binary ionic compounds are compounds that contain only two kinds of ions regardless of how many of each ion is present. To name such compounds, you name the metal first and then you name the non-metal except you drop the ending off the non-metal and add "ide".

Examples

$MgCl_2$	magnesium chloride
NaBr	sodium bromide

AlF_3	aluminum fluoride
K_2S	potassium sulfide
CaI_2	calcium iodide
Rb_2O	rubidium oxide
H_3N	hydrogen nitride

There is no need to attempt to indicate how many of each ion is present because all these ions have only one oxidation number and therefore these are the only possible compounds between the two ions.

Naming Compounds Containing Polyatomic Ions

When naming a compound containing a polyatomic ion, the name of the polyatomic ion is not changed in any way regardless of whether it is written first or last in the formula. If the formula contains a positive polyatomic ion in place of the metal and a regular non-metal, the polyatomic ion is named with no change in its name and the non-metal is named with its ending replaced by "ide." If the compound contains a regular metal and the non-metal is a polyatomic ion, both the metal and the polyatomic ion are named with no changes. If both the metal and the non-metal are replaced with polyatomic ions, the polyatomic ions are named with no changes in either name.

Examples

$NaC_2H_3O_2$	sodium acetate
$Mg(NO_3)_2$	magnesium nitrate
$(NH_4)_2CrO_4$	ammonium chromate
$(NH_4)_2S$	ammonium sulfide
$Ca(OH)_2$	calcium hydroxide
$BaCr_2O_7$	barium dichromate
H_3PO_4	hydrogen phosphate

Once again, no effort is made to indicate how many of each ion is present because these are the only possible compounds between these substances.

Naming Compounds Containing Variable Oxidation Number Metals

Metals with variable oxidation numbers may form different compounds with the same non-metal. Iron, for example, may form FeO and Fe_2O_3. These are very different compounds with different properties. When we name these compounds, it is absolutely vital that we clearly distinguish between them. They are both iron oxides but in FeO, iron is exhibiting an oxidation number of 2+ and in Fe_2O_3, it is exhibiting an oxidation number of 3+. The rule for naming these compounds is to insert the oxidation number of the iron with Roman numerals in parentheses after the name iron. These two compounds would be named iron (II) oxide and iron (III) oxide. When you see that the compound involves any of the variable oxidation number metals (iron, copper, tin, lead, nickel, and gold), you must determine the oxidation number of the metal from the formula and insert Roman numerals indicating that oxidation number.

Suppose we wish to name the compound $CuSO_4$. Because we have memorized the six metals that have variable oxidation numbers, we immediately recognize that copper is one of them and that we must indicate the oxidation number in the name of this compound. We also have memorized the polyatomic ion sulfate and recognize that its oxidation number is 2-. Since this compound formed with one ion of copper and one sulfate ion, the copper ion in this compound must have an oxidation number of 2+ (they reacted one to one). Therefore, the name of the compound is copper (II) sulfate.

How about SnS_2? Tin is a variable oxidation number metal. We need a Roman numeral in the name of this compound. The oxidation number of sulfur is 2-. Two sulfide ions were necessary to combine with one tin ion. Therefore, the oxidation number of the tin must be 4+ and the name of this compound is tin (IV) sulfide.

Examples:

PbO	lead (II) oxide
NiCl	nickel (I) chloride
FeI_2	iron (II) iodide
$Fe_2(SO_4)_3$	iron (III) sulfate
$AuCl_3$	gold (III) chloride
CuO	copper (II) oxide
PbS_2	lead (IV) sulfide

The most common error made by students in naming these compounds is to choose the Roman numeral based on the number of atoms of the metal. The Roman numeral in these names is the oxidation number of the metal and the oxidation number is used as explained previously. For example, in PbS_2, the oxidation state of lead (Pb) is +4 so the Roman numeral following the name lead is "IV." Notice that there is no four in the formula. As in previous examples, the empirical formula is always the lowest whole number ratio of the ions involved. Think carefully when you encounter variable oxidation number metals. Make note that the Roman numeral does not appear in the formula but does appear in the name.

Lesson Summary

- Ionic charge is determined by electron configuration, ionization energy, and electron affinity. Atoms with low ionization energy and high electron affinity tend to lose electrons. Atoms with high ionization energy and high electron affinity tend to gain electrons. Atoms with high ionization energy and low electron affinity tend to neither gain nor lose electrons.
- The number of electrons gained or lost is determined by the electron configuration. Metals tend to lose all of their valence electrons. Non-metals tend to gain enough electrons to complete their outermost energy level.
- Ionic bonds are formed by transferring electrons from metals to non-metals after which the oppositely charged ions are attracted to each other.
- Ionic compounds form crystal lattice structures rather than molecules.
- Binary ionic compounds are named by naming the metal first followed by the non-metal with the ending of the non-metal changed to "ide."
- Compounds containing polyatomic ions are named with the name of the polyatomic ion in the place of the metal or non-metal or both with no changes in the name of the polyatomic ion.

- Compounds containing variable oxidation number metals are named with Roman numerals in parentheses following the name of the metal and indicating the oxidation number of the metal.

Review Questions

1. Name the following compounds. **(Intermediate)**

CaF_2 ____

$(NH_4)_2CrO_4$ ____

K_2CO_3 ____

$NaCl$ ____

PbO ____

$CuSO_4$ ____

H_2CO_3 ____

$Ca(NO_3)_2$ ____

$Mg(OH)_2$ ____

SnO_2 ____

2. Write the formulas from the names of the following compounds. **(Intermediate)**

Sodium carbonate ____

Calcium hydroxide ____

Iron (III) nitrate ____

Magnesium oxide ____

Aluminum sulfide ____

Copper (I) dichromate ____

Ammonium sulfate ____

Iron (II) phosphate ____

Hydrogen nitride ____

Lead (IV) sulfate ____

Further Reading / Supplemental Links

Website with lessons, worksheets, and quizzes on various high school chemistry topics.

- Lesson 5-4 is on Naming Compounds.

http://www.fordhamprep.org/gcurran/sho/sho/lessons/lesson54.htm

Vocabulary

anion	An ion with a negative charge.
cation	An ion with a positive charge.
chemical nomenclature	The system for naming chemical compounds.

ionic bond	The electrostatic attraction between ions of opposite charge.
polyatomic ion	A group of atoms bonded to each other covalently but possessing an overall charge.

Review Answers

1.

Calcium fluoride

Ammonium chromate

Potassium carbonate

Sodium chloride

Lead (II) oxide

Copper (II) sulfate

Hydrogen carbonate

Calcium nitrate

Magnesium hydroxide

Tin (IV) oxide

2.

Na_2CO_3

$Ca(OH)_2$

$Fe(NO_3)_3$

MgO

Al_2S_3

$Cu_2Cr_2O_7$

$(NH_4)_2SO_4$

$Fe_3(PO_4)_2$

H_3N

$Pb(SO_4)_2$

13. Covalent Bonding

The Covalent Bond

Lesson Objectives

- The student will describe the basic nature of covalent bond formation.
- The student will explain the difference between ionic and covalent bonding.
- The student will state the relationship between molecular stability and bond strength.

Introduction

In ionic bonding, electrons leave metallic atoms and enter non-metallic atoms. This complete transfer of electrons changes both of the atoms into ions. Often, however, two atoms combine in a way that no complete transfer of electrons occurs. Instead, electrons are held in overlapping orbitals of the two atoms, so that the atoms are sharing the electrons. The shared electrons occupy the valence orbitals of both atoms at the same time. The nuclei of both atoms are attracted to this shared pair of electrons and the atoms are held together by this attractive force. The attractive force produced by sharing electrons is called a **covalent bond.**

Sharing Electrons

In covalent bonding, the atoms acquire a stable octet of electrons by sharing electrons. The covalent bonding process produces molecular substances as opposed to the lattice structures of ionic bonding. The covalent bond, in general, is much stronger than ionic bonds and there are far more covalently bonded substances than ionic substances.

The diatomic hydrogen molecule, H_2, is one of the many molecules that are covalently bonded. Each hydrogen atom has a ***1s*** electron cloud containing one electron. These ***1s*** electron clouds overlap and produce a common volume which the two electrons occupy.

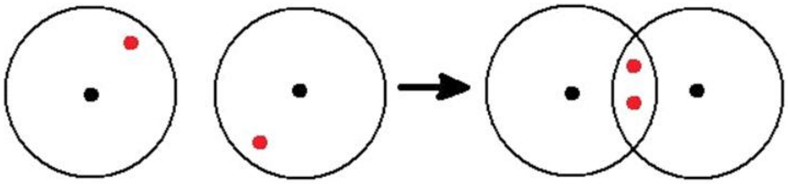


Figure 1: The 1s orbitals of two hydrogen atoms overlap and share the two valence electrons.

(*Created by:* Richard Parsons, *License:* CC-BY-SA)

The shared pair of electrons spend more time between the two atoms than they do in other parts of the two 1s orbitals but the shared pair of electrons occupies all of the 1s orbitals of both atoms. In the simulated probability pattern for the overlapped ***1s*** orbitals in an H_2 molecule, we see the electrons are still more likely to be found close to the nucleus than far away, but we also see that they spend more time between the two nuclei than they do on the far sides of the atoms. The extra time spent between the two nuclei is the source of the attraction that holds the atoms together in a covalent bond.

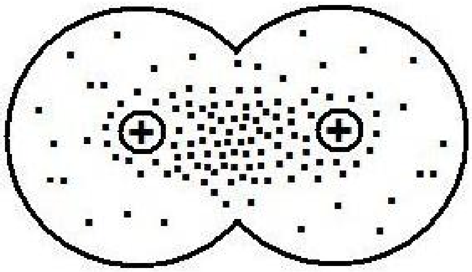


Figure 2: Simulated probability pattern for the overlapped orbitals in H_2. (*Created by:* Richard Parsons, *License:* CC-BY-SA)

The diatomic fluorine molecule is also a covalently bonded atom. In the case of fluorine atoms, the atoms have filled ***1s*** orbitals, filled ***2s*** orbitals, and two of the three ***2p*** orbitals are full. Each atom has a half-filled ***2p*** orbital that is available to be overlapped.

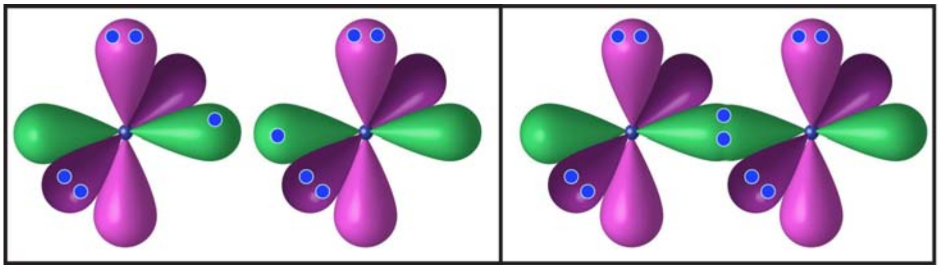


Figure 3: Showing the 2p orbitals of fluorine with two orbitals full and one orbital half-full and then showing the half-filled orbital of each atom overlapping.

(*Source:* CK-12 Foundation, *License:* CC-BY-SA)

Figure 3 shows the available (half-filled) ***2p*** orbitals of two fluorine atoms overlapping to form a covalent bond. We use several methods to represent a covalent bond so that we don't have to spend all our time drawing orbitals. We can represent the bond in the F_2 molecule with an electron dot formula.

Figure 4: We can also show a covalent bond between atoms with an electron dot formula where the shared pair of electrons are the bonding electrons or with the bond represented by a dash.

(*Created by:* Richard Parsons, *License:* CC-BY-SA)

Bond Strength

When atoms that attract each other move closer together, the potential energy of the system (the two atoms) decreases. When a covalent bond is formed, the atoms move so close together that the atoms overlap their electron clouds. As the atoms continue to move closer yet, the potential energy of the system continues to decrease . . . to a point. If you continue to move atoms closer and closer together, eventually the two nuclei will begin to repel each other. If you push the nuclei closer together at this point, the repulsion causes the potential energy to increase. Each pair of covalently bonding atoms will have a distance between their nuclei that is the lowest potential energy distance. This position has the atoms close enough that the attraction between the nucleus of each one and the electrons of the other is maximum but the nuclei have not begun to repel each other strongly. For bonding atoms, this distance occurs somewhere after the electron clouds have overlapped. At this position, the atoms are at lowest potential energy. If the atoms are pushed closer, the potential energy goes up because you are crowding the nuclei together and if the atoms are pulled apart, potential energy goes up because you are separating particles that attract each other. Since this is the lowest potential energy position, the atoms will remain at the distance, bonded together. This distance is called the bond length. The more potential energy that was given up as this bond formed, the stronger the bond will be. If you want to break this bond, you must input all the potential energy that was given up as the bond was formed.

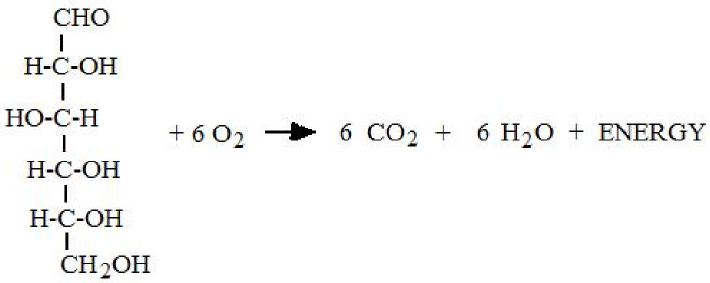
The strength of a diatomic covalent bond can be expressed by the amount of energy necessary to break the bond and produce separate atoms. The energy needed to break a covalent bond is called **bond energy** and is measured in kilojoules per mole. Bond energy is used as a measure of bond strength. The bond strength of HBr is 365 kilojoules per mole. i.e. It would take 365 kilojoules to break all the chemical bonds in 6.02×10^{23} molecules of HBr and produce separate hydrogen and bromine atoms. The bond strength of HCl is 431 kilojoules per mole. Consequently, the bond in HCl is stronger than the bond in HBr.

Molecular Stability

Compounds with high bond strengths are difficult to break up and therefore are stable compounds. When stable compounds are formed, large amounts of energy are given off so these molecules are in a relatively low energy state. In order to break the molecule apart, all the energy that was given off must be put back in. Low energy state bonds are stable and have high bond strength.

Molecules with high bond energy have weak bonds. They did not release much energy when they formed and so not much energy is needed to the break the molecules back apart. High bond energy means low bond strength.

Atoms of carbon, hydrogen, and oxygen can be chemically bonded in more than one way. In the molecule shown below, these atoms are bonded in a way that produces a molecule of glucose.



The molecule of glucose can be reacted with six oxygen atoms to produce six molecules of carbon dioxide and six molecules of water. During the reaction, the atoms of the glucose molecule are rearranged into the structure of carbon dioxide and water molecules. The bonds in the glucose are broken and new bonds are formed. As this occurs, potential energy is released because the new bonds have lower potential energy that the original bonds. The bonds in the products are lower energy bonds and therefore, the product molecules are more stable.

Some Compounds Have Both Covalent and Ionic Bonds

If you recall the introduction of polyatomic ions, you will remember that the bonds that hold the polyatomic ions together are covalent bonds. Once the polyatomic ion is constructed with covalent bonds, it reacts with other substances as an ion. The bond between a polyatomic ion and another ion will be ionic. An example of this type of situation is in the compound sodium nitrate. Sodium nitrate is composed of a sodium ion and a nitrate ion. The nitrate ion is held together by covalent bonds and the nitrate ion is attached to the sodium ion by an ionic bond.

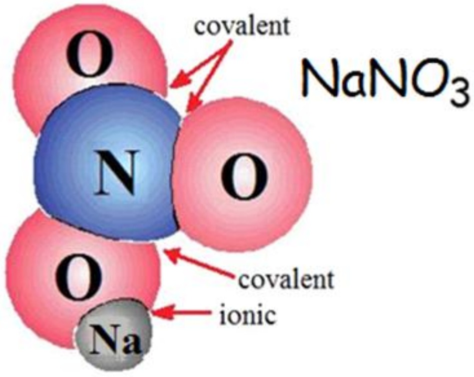


Figure 5: The bonding in sodium nitrate, $NaNO_3$.

(*Created by:* Richard Parsons, *License:* CC-BY-SA)

Lesson Summary

- Covalent bonds are formed by electrons being shared between two atoms.
- Half-filled orbitals of two atoms are overlapped and the valence electrons shared by the atoms.
- Bond energy is the amount of energy necessary to break the covalent bond.
- The strength of a covalent bond is measured by the bond energy.
- Stable compounds have high bond energy and unstable compounds have low bond energy.

Review Questions

1. Describe the characteristics of two atoms that would be expected to form an ionic bond. **(Beginning)**

2. Describe the characteristics of two atoms that would be expected to form a covalent bond. **(Beginning)**

3. If an atom had a very high bond energy, would you expect it to be stable or unstable? **(Intermediate)**

4. When gaseous potassium ions and gaseous fluoride ions join together to form a crystal lattice, the amount of energy released is 821 kJ/mol. When gaseous potassium ions and gaseous chloride ions join together to form a crystal lattice, the amount of energy released is 715 kJ/mol. Which is the strong bond, KF or KCl? It these two compounds were increasingly heated, which compound would break apart at the lower temperature? **(Challenging)**

Further Reading / Supplemental Links

Website with lessons, worksheets, and quizzes on various high school chemistry topics.

- Lesson 4-3 is on Ionic vs. Covalent Bonds.

http://www.fordhamprep.org/gcurran/sho/sho/lessons/lesson43.htm

Vocabulary

covalent bond	A type of chemical bond where two atoms are connected to each other by the sharing of two or more electrons in overlapped orbitals.
covalent bond strength	The strength of a covalent bond is measured by the amount of energy required to break the bond.

Review Answers

1. The two atoms will have very different ionization energies and electron affinities.

2. The two atoms will have similar ionization energies and electron affinities.

3. Stable because bond energy is the energy necessary to break a molecules bonds – a high bond energy would mean it takes a great deal of energy to break up the molecule.

4. Since the formation of KF gives off greater energy, greater energy would be required to break that bond. Therefore, KF is the stronger bond and KF would require a higher temperature to break the bond.

Atoms that Form Covalent Bonds

Lesson Objectives

- The student identify pairs of atoms that will form covalent bonds.
- The student will draw Lewis structures for simple covalent molecules.
- The student will identify sigma and pi bonds in a Lewis structure.

Introduction

A great deal of importance seems to have been attached to the electron configurations of noble gases or to the *octet of electrons*. These structures have been made in some way to seem to be a "desirable" thing for an atom to have. It is hoped that you do not see atoms and electrons as behaving the way they do because of "wants" and "desires". The bonding of atoms is directly by the laws of nature relating to the tendency toward minimum potential energy, electrical attraction and repulsion, and the arrangement of electrons in atoms. As it happens, these laws of nature and energy conditions do favor (in most cases) an octet of electrons for atoms. In ionic bonding, the atoms acquired this octet by gaining or losing electrons and, in covalent bonding, as you have seen, the atoms acquire the noble gas electron configuration by sharing electrons.

Non-Metals Bond with Non-Metals to Form Covalent Bonds

In the discussion of ionic bonds, it was clear that ionic bonds form between metals and non-metals because the high electron affinity non-metals are able to take electrons away from metals. Metals lose their electrons readily and have no attraction to add electrons. Since covalent bonds require that electrons be shared, it becomes apparent that metals will form few if any covalent bonds. Metals simply do not hold on to electrons with enough strength to form much in the way of covalent bonds. For a covalent bond to form, we need two atoms that both attract electrons with high electron affinity. Hence, the great majority of covalent bonds will be formed between two non-metals. When both atoms in a bond are from the right side of the periodic table, you can be sure that the bond is covalent. Here are some examples of molecules with covalent bonds. You should check to see where the atoms involved in these molecules appear in the periodic table. Covalent bonds form between atoms with relatively high electron affinity and they form individual, separate molecules.

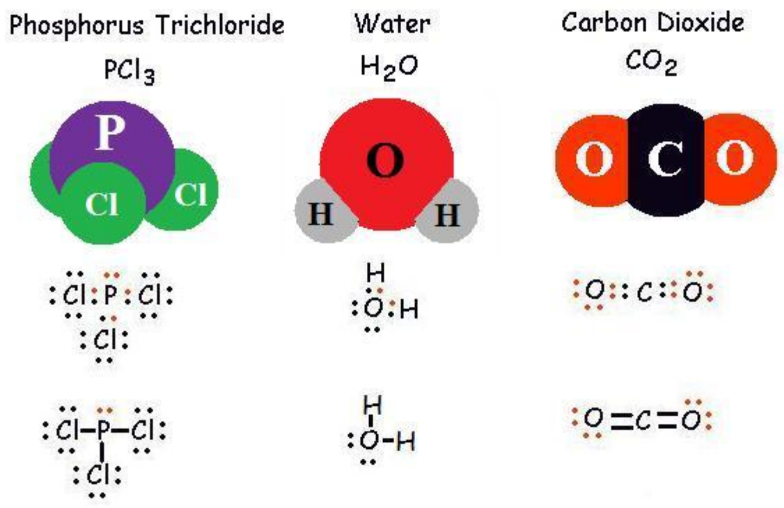


Figure 6: Various methods of showing a covalent bond.

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Multiple Bonds

So far, we have discussed covalent bonds in which one pair of electrons is shared. This type of bond is called a single bond. Some atoms can share more than one pair of electrons. When atoms share two pairs of electrons, it is called a **double bond** and when atoms share three pairs of electrons, it is called a **triple bond.**

Double bonds are formed when atoms overlap two orbitals at the same time. An example of the formation of a double bond is in the bonding in the O_2 molecule. Oxygen has six valence electrons and they are distributed in the outermost energy level as $2s^2 2p_x^{\ 2} 2p_y^{\ 1} 2p_z^{\ 1}$. Two of the ***p*** orbitals in the bonding shell of oxygen are only half-filled and therefore are available for overlap. One of these half-filled ***p*** orbitals from each oxygen atom will overlap end-to-end as shown in Figure 7.

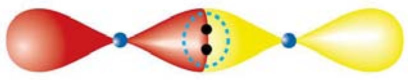


Figure 7: The end-to-end overlap of orbitals forms a sigma bond.

(*Source*: CK-12 Foundation, *License:* CC-BY-SA)

Bonds formed by end-to-end overlap are called sigma (σ) bonds. The first bond formed between two atoms is always a sigma bond. The second half-filled orbitals of the oxygen atoms will be oriented vertically and cannot overlap end-to-end but they can overlap side-to-side as shown in Figure 8.

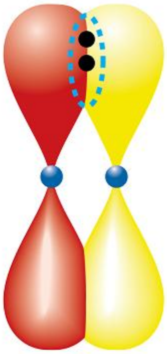


Figure 8: The side-to-side overlap of orbitals forms a pi bond.

(*Source*: CK-12 Foundation, *License:* CC-BY-SA)

The side-to-side overlap of orbitals forms a bond called a pi (π) bond. All the bonds formed between two atoms after the first bond are pi bonds. The electron dot formula for a double bond would show two pairs of electrons shared between atoms (See Figure 9).

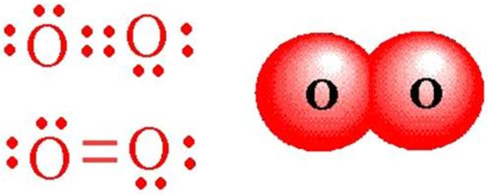


Figure 9: Oxygen is double bonded.

(*Created by:* Richard Parsons, *License:* CC-BY-SA)

Double bonds are stronger than single bonds. They are not exactly twice as strong; sometimes they are more than twice as strong and sometimes they are less than twice as strong. Oxygen is a reactive element and it is surprising that there is so much elemental oxygen in our atmosphere. The explanation for the existence of so much elemental oxygen is that the double bond is very strong and it takes a great deal of energy to break the double bond in oxygen so that the oxygen atoms could react with something else.

The nitrogen molecule, N_2, is triple bonded. That means that the two nitrogen atoms share three pairs of electrons. The first bond will be an end-to-end overlap (σ bond) and the other two bonds will be side-to-side overlaps (π bonds). If the end-to-end overlap are the p_x orbitals, then the side-to-side overlaps will be the p_y and p_z orbitals.

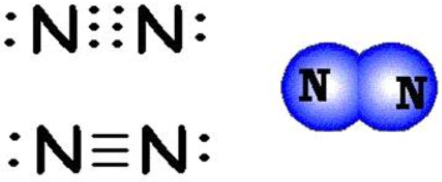


Figure 9: Nitrogen is triple bonded.

(*Created by:* Richard Parsons, *License:* CC-BY-SA)

Atomic nitrogen is quite reactive but molecular nitrogen is un-reactive. The reason nitrogen molecules not do react readily is that the molecule is held together by an unusually strong bond – namely a triple bond. Approximately 78% of our atmosphere is made up of nitrogen molecules.

Lewis Formulas

What was called "electron dot formulas" when drawing them for individual atoms become "Lewis dot formulas" or "Lewis structures" or "Lewis formulas" when drawing them for molecules. The Lewis structures of a molecule show how the valence electrons are arranged among the atoms of the molecule. These representations are named after G. N. Lewis. The rules for writing Lewis structures are based on observations of thousands of molecules. From experiment, chemists have learned that when a stable compound forms, the atoms usually have a noble gas electron configuration. Hydrogen forms stable molecules when it shares two electrons (sometimes called the duet rule). Other atoms involved in covalent bonding typically obey the octet rule. (Note: Of course, there will be exceptions.)

Rules for Writing Lewis Structures

- Decide which atoms are bonded.
- Count all the valence electrons of all the atoms.
- Place two electrons between each pair of bonded atoms.
- Complete all the octets (or duets) of the atoms attached to the central atom.
- Place any remaining electrons on the central atom.
- If the central atom does not have an octet, look for places to form double or triple bonds.

Example 1:

Write the Lewis structure for water, H_2O.

Step 1: Decide which atoms are bonded.

Begin by assuming the hydrogen atoms are bonded to the oxygen atom. i.e. Assume the oxygen atom is the central atom. H - O - H.

Step 2: Count all the valence electrons of all the atoms.

The oxygen atom has 6 valence electrons and each hydrogen has 1. The total is 8.

Step 3: Place two electrons between each pair of bonded atoms.

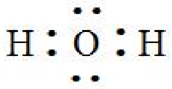
H : O : H

Step 4: Complete all the octets or duets of the atoms attached to the central atom.

The hydrogen atoms are attached to the central atom and hydrogen atoms require a duet of electrons and those duets are already present.

Step 5: Place any remaining electrons on the central atom.

The total number of valence electrons is 8 and we have already used 4 of them. The other 4 will fit around the central oxygen atom.



Is this structure correct?

Are the total number of valence electrons correct? Yes

Does each atom have the appropriate duet or octet of electrons? Yes

Example 2:

Write the Lewis structure for carbon dioxide, CO_2.

Step 1: Decide which atoms are bonded.

Begin by assuming the carbon is the central atom and that both oxygen atoms are attached to the carbon.

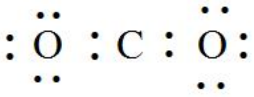
Step 2: Count all the valence electrons of all the atoms.

The oxygen atoms each have 6 valence electrons and the carbon atom has 4. The total is 16.

Step 3: Place two electrons between each pair of bonded atoms.

O : C : O

Step 4: Complete all the octets or duets of the atoms attached to the central atom.



Step 5: Place any remaining electrons on the central atom.

We have used all 16 of the valence electrons so there are no more to place around the central carbon atom.

Is this structure correct?

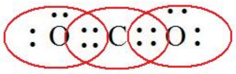
Is the total number of valence electrons correct? Yes

Does each atom have the appropriate duet or octet of electrons?

NO - each oxygen has the proper octet of electrons but the carbon atom only has 4 electrons. Therefore, this is NOT correct.

Step 6: If the central atom does not have an octet, look for places to form double or triple bonds.

Double bonds can be formed between carbon and each oxygen atom.



Notice this time, each atom is surrounded by 8 electrons.

Example 3:

Write the Lewis structure for ammonia, NH_3.

Solution

The most likely bonding for this molecule is nitrogen as the central atom and each hydrogen bonded to the nitrogen. Therefore, we can start by putting nitrogen in the center and put the three hydrogen atoms around it.

The nitrogen atom has five valence electrons and each hydrogen atom has one so the total number of valence electrons is 8.

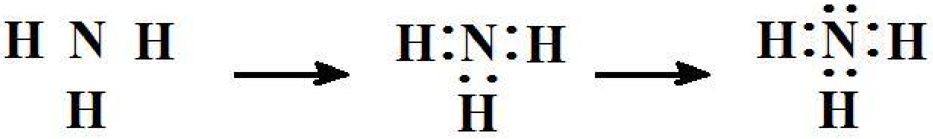


Figure 10: The process for writing Lewis structures.

The next step is to put a pair of electrons between every bonded pair of atoms so we put a pair of electrons between each of the hydrogen and nitrogen. The next step is to complete the octet or duet of each of the non-central atoms. In this case, all the non-central atoms are hydrogen and they already have a duet of electrons. The next step is to put all the left over electrons around the central atom. We have two electrons left over so they would complete the octet for nitrogen. If the central atom, at this point, does not have an octet of electrons, we would look for places to create a double or triple bond but in this case, the central atom does have an octet of electrons. The final drawing on the right is the Lewis structure for ammonia.

Example 4:

Given the skeleton structure for nitric acid, HNO_3, place the electrons into a proper Lewis structure.

Solution

The skeleton for nitric acid has the three oxygen atoms bonded to the nitrogen and the hydrogen bonded to one of the oxygen atoms. The total number of valence electrons is 5 + 6 + 6 + 6 + 1 = 24.

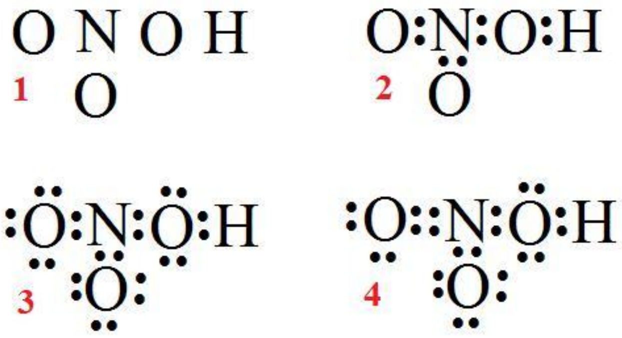


Figure 11: The process of writing the Lewis structure for nitric acid.

The skeleton structure is given in “1” in Figure 11. The next step is to put in a pair of electrons between each bonded pair – this is done in “2.” So far, we have accounted for 8 of the 24 valence electrons. The next step is to complete the octet or duet for each of the non-central atoms. This is completed in “3.” At that point, we have used all of the valence electrons and the central atom does not have an octet of electrons. The rules tell us to find a place to put a double or triple bond. For the amount of knowledge we have at this point, any of the three oxygen atoms is just as good as the others for a double bond, so we move two of the electrons around the far left oxygen atom and make a double bond between that oxygen and the nitrogen. Now every atom in the molecule has its appropriate octet or duet of electrons. We have a satisfactory Lewis structure for the nitric acid molecule.

Lesson Summary

- Covalent bonds are formed between atoms with relatively high electron affinity.
- Some atoms are capable of forming double or triple bonds.
- Multiple bonds between atoms require multiple half-filled orbitals.
- End-to-end orbital overlaps are called sigma bonds.
- Side-to-side orbital overlaps are called pi bonds.
- Lewis structures are commonly used to show the valence electron arrangement in covalently bonded molecules.

Review Questions

1. Which of the following compounds would you expect to be ionically bonded and which covalently bonded? **(Beginning)**

Compound	**Ionic or Covalent**
CS_2	
K_2S	
FeF_3	
PF_3	
BF_3	
AlF_3	
BaS	

2. How many sigma bonds and how many pi bonds are present in a triple bond? **(Beginning)**

3. Draw the Lewis structure for CCl_4. **(Intermediate)**

4. Draw the Lewis structure for SO_2. **(Challenging)**

Further Reading / Supplemental Links

http://learner.org/resources/series61.html'"

The ***learner.org*** website allows users to view streaming videos of the Annenberg series of chemistry videos. You are required to register before you can watch the videos but there is no charge. The website

has one video that relates to this lesson called ***Chemical Bonds*** .

Vocabulary

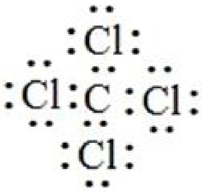
covalent bond	A type of bond in which electrons are shared by atoms.
diatomic molecule	A molecule containing exactly two atoms.
double bond	A bond in which two pairs of electrons are shared.
triple bond	A bond in which three pairs of electrons are shared.
sigma bond	A covalent bond in which the electron pair is shared in an area centered on a line running between the atoms.
pi bond	A covalent bond in which p orbitals share an electron pair occupying the space above and below the line joining the atoms.

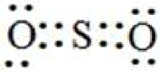
Review Answers

1.

|- |width="220px"| **Compound** |width="320px"| **Ionic or Covalent** |- | CS_2 | covalent |- | K_2S | ionic |- | FeF_3 | ionic |- | PF_3 | covalent |- | BF_3 | covalent |- | AlF_3 | ionic |- | BaS | covalent |}

2. A triple bond will contain one sigma bond and two pi bonds.

3. 

4. 

Naming Covalent Compounds

Lesson Objectives

- The student name covalent compounds using the IUPAC nomenclature system.
- The student will provide formulas for covalent compounds given the IUPAC name.

Introduction

The systematic procedure for naming chemical compounds uses a different approach for different types of compounds. In a previous chapter, we have discussed the procedures for naming binary ionic compounds, ionic compounds involving polyatomic ions, and ionic compounds involving metals with variable oxidation states. In this section, we will describe the system used for covalently bonded compounds. Because of the large numbers of covalent compounds that may form between the same two elements, the nomenclature system for covalent compounds is quite different.

The Number of Atoms in the Formulas Must be Indicated

In naming ionic compounds, there is no need to indicate the number of atoms of each element in a formula because, for most cases, there is only one possible compound that can form from the ions present. When aluminum combined with sulfur, the only possible compound is aluminum sulfide, Al_2S_3. The only exception to this is a few variable oxidation number metals and those are handled with Roman numerals for the oxidation number of the metal, as in iron (II) chloride, $FeCl_2$.

With covalent compounds, however, we have a very different situation. There are six different covalent compounds that can form between nitrogen and oxygen and in two of them, nitrogen has the same oxidation number. Therefore, the Roman numeral system will not work. Chemists devised a nomenclature system for covalent compounds that indicate how many atoms of each element is present in a molecule of the compound.

Greek Prefixes

In naming binary covalent compounds, four rules apply:

1. The first element in the formula is named first using the normal name of the element.

2. The second element is named as if it were an anion. Note: There are no ions in these compounds but we use the “-ide” ending on the second element as if it were an anion.

3. Greek prefixes are used for each element to indicate the number of atoms of that element present in the compound.

Greek Prefixes

Prefix	**Number Indicated**
Mono-	1
Di-	2
Tri-	3
Tetra-	4
Penta-	5
Hexa-	6
Hepta-	7
Octa-	8
Nona-	9
Deca-	10

4. The prefix "mono-" is never used for naming the first element. For example, CO is called carbon monoxide, *not* monocarbon monoxide.

Examples

N_2O	dinitrogen monoxide
NO	nitrogen monoxide
NO_2	nitrogen dioxide
N_2O_3	dinitrogen trioxide

N_2O_4	dinitrogen tetraoxide
N_2O_5	dinitrogen pentaoxide
SF_6	sulfur hexafluoride
CO_2	carbon dioxide
P_4O_{10}	tetraphosphorus decaoxide
P_2S_5	diphosphorus pentasulfide

Lesson Summary

- Covalently bonded molecules use Greek prefixes in their nomenclature.

Review Questions

1. Name the compound CO. **(Intermediate)**

2. Name the compound PCl_3. **(Intermediate)**

3. Name the compound PCl_5. **(Intermediate)**

4. Name the compound N_2O_3. **(Intermediate)**

5. Name the compound BCl_3. **(Intermediate)**

6. Name the compound SF_4. **(Intermediate)**

7. Name the compound Cl_2O. **(Intermediate)**

8. Write the formula for the compound sulfur trioxide. **(Intermediate)**

9. Write the formula for the compound dinitrogen tetrafluoride. **(Intermediate)**

10. Write the formula for the compound oxygen difluoride. **(Intermediate)**

11. Write the formula for the compound dinitrogen pentoxide. **(Intermediate)**

12. Write the formula for the compound sulfur hexafluoride. **(Intermediate)**

13. Write the formula for the compound tetraphosphorus decaoxide. **(Intermediate)**

Further Reading / Supplemental Links

http://www.mhhe.com/physsci/chemistry/animations/chang_7e_esp/bom1s2_11.swf

http://www.visionlearning.com/library/module_viewer.php?mid=55

Review Answers

1. carbon monoxide

2. phosphorus trichloride

3. phosphorus pentachloride

4. dinitrogen trioxide

5. boron trichloride

6. sulfur tetrafluoride

7. dichlorine monoxide

8. SO_3

9. N_2F_4

10. OF_2

11. N_2O_5

12. SF_6

13. P_4O_{10}

14. Molecular Architecture

Types of Bonds that Form Between Atoms

Lesson Objectives

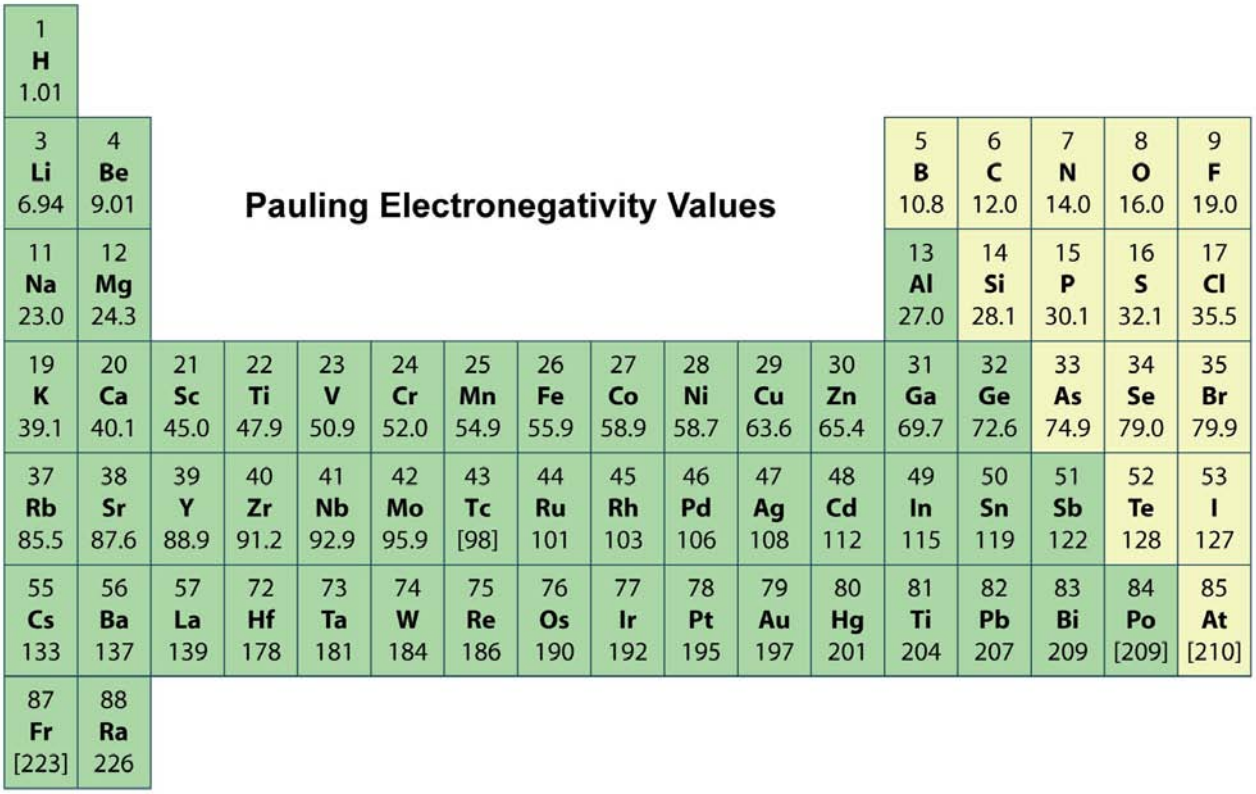
- Given binary formulas and an electronegativity chart, students will identify the most likely bonding type (ionic, covalent, or polar covalent) for each compound.
- The student will describe a polar covalent bond and explain why it forms.

Introduction

Around 1935, the American chemist Linus Pauling developed a scale of electronegativity to describe the attraction an element has for electrons in a chemical bond. You will see an electronegativity chart in the next section. The values of electronegativity are higher for elements that more strongly attract electrons. Differences in the electronegativity of bonded atoms can be used to predict whether the bond between the atoms will be ionic or covalent . . . *or something in-between*.

Electronegativity

The ability of an atom in a molecule to attract shared electrons is called **electronegativity.** The electronegativity of atoms have been measured by several methods. One method that is widely accepted is that of Linus Pauling.



Pauling Electronegativity Values

1 **H** 1.01																
3 **Li** 6.94	4 **Be** 9.01											5 **B** 10.8	6 **C** 12.0	7 **N** 14.0	8 **O** 16.0	9 **F** 19.0
11 **Na** 23.0	12 **Mg** 24.3											13 **Al** 27.0	14 **Si** 28.1	15 **P** 30.1	16 **S** 32.1	17 **Cl** 35.5
19 **K** 39.1	20 **Ca** 40.1	21 **Sc** 45.0	22 **Ti** 47.9	23 **V** 50.9	24 **Cr** 52.0	25 **Mn** 54.9	26 **Fe** 55.9	27 **Co** 58.9	28 **Ni** 58.7	29 **Cu** 63.6	30 **Zn** 65.4	31 **Ga** 69.7	32 **Ge** 72.6	33 **As** 74.9	34 **Se** 79.0	35 **Br** 79.9
37 **Rb** 85.5	38 **Sr** 87.6	39 **Y** 88.9	40 **Zr** 91.2	41 **Nb** 92.9	42 **Mo** 95.9	43 **Tc** [98]	44 **Ru** 101	45 **Rh** 103	46 **Pd** 106	47 **Ag** 108	48 **Cd** 112	49 **In** 115	50 **Sn** 119	51 **Sb** 122	52 **Te** 128	53 **I** 127
55 **Cs** 133	56 **Ba** 137	57 **La** 139	72 **Hf** 178	73 **Ta** 181	74 **W** 184	75 **Re** 186	76 **Os** 190	77 **Ir** 192	78 **Pt** 195	79 **Au** 197	80 **Hg** 201	81 **Ti** 204	82 **Pb** 207	83 **Bi** 209	84 **Po** [209]	85 **At** [210]
87 **Fr** [223]	88 **Ra** 226															

Figure 1: The Pauling Electronegativity Values.

(*Source*: CK-12 Foundation, *License :* CC-BY-SA)

When two atoms combine, the difference between their electronegativities is an indication of the type of bond that will form. If the difference between the electronegativities of the two atoms is small, neither atom can take the shared electrons completely away from the other atom and the bond will be covalent. If the difference between the electronegativities is large, the more electronegative atom will take the bonding electrons completely away from the other atom (electron transfer will occur) and the bond will be ionic. There is no exact number for the electronegativity difference that will produce an ionic bond but many chemists suggest 1.7 as the approximate difference that will produce an ionic bond.

If we compare a few electronegativities, we can see that 1.7 is a reasonable suggestion. The difference between the electronegativities of hydrogen and oxygen is 1.4 and we know the bonds in the water molecule are covalent. In magnesium chloride, the electronegativity difference is 1.8 and we know this molecule contains ionic bonds.

The Partial Ionic Character of Covalent Bonds

So far, we have discussed two extreme types of bonds. One case is when two identical atoms bond. They have exactly the same electronegativities, thus the two bonded atoms pull exactly equally on the shared electrons. The shared electrons will be shared exactly equally by the two atoms. The other case is when the bonded atoms have a very large difference in their electronegativities. In this case, the more electronegative atom will take the electrons completely away from the other atom and an ionic bond forms.

What about the molecules whose electronegativities are not the same but the difference is not as large as 1.7? For these molecules, the electrons remain shared by the two atoms but they are not shared equally. The shared electrons are pulled closer to the more electronegative atom. This results in an uneven distribution of electrons over the molecule and causes slight charges on opposite ends of the molecule. These charges are not full +1 and -1 charges, they are fractions of charges. For small fractions of charges, we use the symbols δ+ and δ- (See Figure 2). These molecules have slight opposite charges on opposite ends of the molecule. Such molecules are said to have a dipole or are called polar molecules.

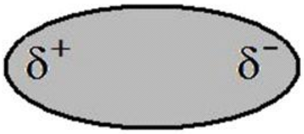


Figure 2: A polar molecule has partially positive and partially negative charges on opposite sides of the molecule.

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Atoms whose electronegativities are not the same but also do not have a difference of 1.7, will form **polar covalent bonds.** These polar covalent bonds will be discussed in more detail later in this chapter and again later in the course. With the introduction of the polar covalent bond, we now have three possibilities for types of bonds.

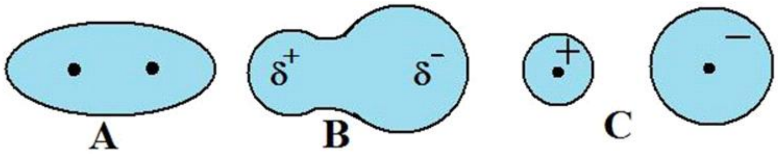

Figure 3: The three possible types of bonds.

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When atoms combine, there are three possible types of bonds that they can form. In Figure 3, molecule A represents a perfectly covalent bond that would be formed between identical atoms. Molecule B is a polar covalent bond formed between atoms whose electronegativities are not the same but whose electronegativity difference is less than 1.7 and molecule C is an ionic bond formed between atoms whose electronegativity difference is greater than 1.7.

Lesson Summary

- Bonds formed between atoms whose electronegativity difference exceeds 1.7 are most likely ionic bonds.
- Bonds formed between atoms whose electronegativity difference is between 0.4 and 1.7 are polar covalent bonds.

Review Questions

1. Explain the differences among a covalent bond, a polar covalent bond, and an ionic bond. **(Beginning)**

2. Explain why a pair of atoms form a covalent bond rather than an ionic bond. **(Beginning)**

3. Predict which of the following bonds will be more polar and explain why; P-Cl or S-Cl. **(Intermediate)**

Vocabulary

bonding electron pair	an electron pair found in the space between two molecules.
electronegativity	the tendency of an atom in a molecule to attract shared electrons to itself.
octet rule	the observation that atoms of non-metals tend to form the most stable molecules when they are surrounded by eight electrons (to fill their valence orbitals).
polar covalent bond	a covalent bond in which the electrons are not shared equally because one atom attracts them more strongly that the other.

Review Answers

1. In a covalent bond, the bonding electrons are shared equally. In a polar covalent bond, the bonding electrons are shared but not equally. In an ionic bond, the bonding electrons are transferred from the more electropositive atom to the more electronegative atom.

2. If the electronegativity difference between the bonding atoms is greater than 1.7, the atoms will form an ionic bond and if the difference is less than 1.7, the atoms will form a covalent bond.

3. P-Cl will be more polar because the electronegativity difference between P and Cl is greater than the difference between S and Cl.

The Covalent Molecules of Family 2A - 8A

Lesson Objectives

- Given binary formulas and an electronegativity chart, students will identify the most likely bonding type (ionic, covalent, or polar covalent) for each compound.
- The student will draw Lewis structures for simple molecules that violate the octet rule.

- Given a list of binary compounds, the student will identify those that require electron promotion in the explanation of their bonding.
- The student will identify the type of hybridization in various molecules.
- The student will explain the necessity for the concept of hybridized orbitals.

Introduction

In your study of chemistry, you may have noticed occasionally that shortly after you have learned a "rule" for the behavior of matter, you are introduced to the exceptions to the "rule." For example, shortly after you learned the filling order rule for electron configuration, you were introduced to the exceptions caused by the slightly lower potential energy when the ***d*** orbitals were exactly half-filled or completely filled. And, shortly after you learned that when metals form ions, they lose all their valence electrons, you were introduced to some variable oxidation number metals that sometimes give up a different number of electrons. There are more rules to come and more exceptions to the rules yet to come.

Now that you have learned the octet rule, you will be introduced to exceptions to the octet rule. Most of the exceptions to rules in chemistry are related to the fact that the behavior of matter is often controlled by the tendency toward lowest potential energy. Therefore, when some small variation produces slightly lower potential energy, matter will follow that path.

In this unit, you will learn that some very big ideas, such as the shape of molecules, are controlled by very small differences in potential energy.

First Exception to the Octet Rule

Consider the molecule formed by the combination of beryllium and hydrogen, beryllium hydride, BeH_2. The electronegativity difference between these two atoms is only 0.6 (2.1 – 1.5) with beryllium being the more electropositive. Therefore, the bonds in BeH_2 are polar covalent bonds. The Lewis structure for the molecule is:

Figure 4: The Lewis structure for beryllium hydride.

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The first thing we might notice about the BeH_2 molecule is that it does not obey the octet rule. Beryllium has two valence electrons and each hydrogen has one valence electron. There just are not enough valence electrons to produce an octet around the beryllium atom but BeH_2 is a relatively stable molecule anyway.

Electron Promotion

There are other unusual things about this molecule, BeH_2, which we must first recognize and then *explain.* The orbital representation for the electron configuration of beryllium shows the ***2s*** orbital is full. In previous discussions of covalent bonding, we have pointed out that the two atoms must each have a half-filled orbital available for overlap in order to form a bond. How can beryllium form two bonds when it has no half-filled orbitals? The explanation involves the theory of **electron promotion.** It is suggested that one of the electrons in the ***2s*** orbital is promoted to a ***2p*** orbital so that beryllium for short period of time has two half-filled orbitals (See figure 5).

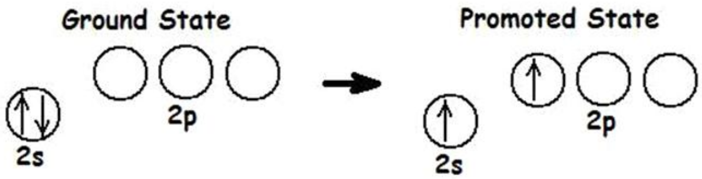

Figure 5: Electron promotion in beryllium.

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By promoting an electron from the ***2s*** orbital to one of the ***2p*** orbitals, beryllium acquires two half-filled orbitals available for overlap and therefore can form two covalent bonds. Is this concept of electron promotion reasonable? The amount of necessary to promote an electron from a ***2s*** orbital to a ***2p*** orbital is small and the amount of energy given off when beryllium forms two covalent bonds is relatively large. A small input of energy in return for a large output of energy seems quite reasonable especially when you consider that the double covalent bond in BeH_2 does, in fact, occur.

Orbital Hybridization

We are not yet finished with the theoretical developments necessary to explain this BeH_2 molecule. Chemists have the instrumentation now to measure the characteristics of bonds. They can measure bond length, bond strength, and even bond flexibility. Bonds formed by overlapping ***s*** orbitals, in general, are shorter, stronger, and more flexible that bonds formed by overlapping ***p*** orbitals in the same shell. Therefore, when considering the two bonds in BeH_2, it would be presumed that we could determine which one was formed by a hydrogen atom overlapping beryllium's half-filled ***2s*** orbital and which one was formed by a hydrogen atom overlapping beryllium's half-filled ***2p*** orbital. Examination of the two bonds, however, shows them to be identical in length, strength, and flexibility. Not only are they identical but the values for their length, strength, and flexibility fall in between the values expected for overlapping ***s*** and ***p*** orbitals. That is, the two bonds are the same and their lengths, strengths, and flexibilities appear to be intermediate between the values expected for an ***s*** orbital overlap and the values expected for a ***p*** orbital overlap. This might be likened to a biologist crossing a red rose plant with a white rose plant and producing a plant that has pink roses. This odd situation calls for yet another theory . . . this one is called **orbital hybridization.**

The concept involved in orbital hybridization is that all the orbitals involved in bonding are hybridized to orbitals that are identical and have properties intermediate to the properties of the orbitals that were hybridized.

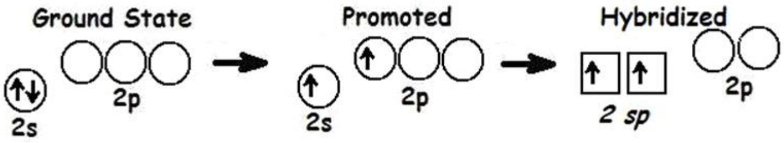

Figure 6: ***sp*** hybridized orbitals.

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The half-filled ***2s*** and ***2p*** orbitals hybridize to form two completely new orbitals named ***sp* hybridized orbitals.** These two new orbitals are identical in characteristics and those characteristics are somewhere between the characteristics of ***2s*** and ***2p*** orbitals. When these ***sp*** hybridized orbitals are overlapped by hydrogen atoms, two identical bonds are produced.

The Covalent Bonds of Family 3A

The only family member of family 3A that forms a significant number of covalent compounds is boron. Numerous boron compounds exist and in virtually all of them, boron forms three bonds. Since the ground state electron configuration of boron, $1s^22s^22p^1$, has a filled ***2s*** orbital and one half-filled ***2p*** orbital, it should be obvious that we are going to require electron promotion in order to explain boron forming three bonds.

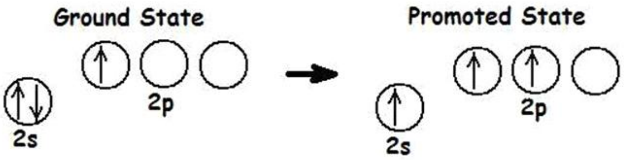

Figure 7: Electron promotion in boron.

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One of the electrons in the ***2s*** orbital is promoted to an empty ***2p*** orbital and this produces three half-filled orbitals for overlap allowing boron to form three covalent bonds. As with the two bonds in BeH_2, the three bonds in boron compounds such as BH_3 are found to be identical in length, strength, and flexibility. That means that orbital hybridization also occurs in family 3A covalent compounds. In the case of boron compounds, there is one ***2s*** orbital and two ***2p*** orbitals to hybridize. The hybridized orbitals are called ***sp^2*** hybridized orbitals.

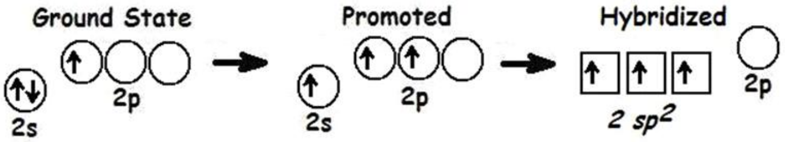

Figure 8: sp^2 hybridization.

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The three hybridized orbitals can now be overlapped and form three identical bonds, just as we find in boron compounds such as BH_3 and BCl_3. In these boron compounds, the central atom is surrounded by only six electrons and therefore this is another exception to the octet rule.

It should be recognized that the ***sp^2*** hybridized orbitals are not the same as ***sp*** hybridized orbitals. If you mix one bucket of blue paint with one bucket of yellow paint, you get green paint. If you mix two buckets of blue with one bucket of yellow, you will also get green paint but it will not be the same shade of green as before. Hybridizing one ***s*** and one ***p*** orbital does not produce the same orbitals as hybridizing one ***s*** and two ***p*** orbitals.

The Covalent Bonds of Family 4A

The members of family 4A that form covalent bonds are carbon and silicon. Their electron configurations are $1s^22s^22p^2$ and $1s^22s^22p^63s^23p^2$. In the outer energy level of both atoms, the ***s*** orbital is filled, two of the ***p*** orbitals are half-filled, and the third ***p*** orbital is empty. The huge majority of the covalent compounds of carbon and silicon show carbon and silicon to have four bonds. The two half-filled ***p*** orbitals available in the ground state for these atoms are not sufficient. Electron promotion must occur in these atoms also. If one of the electrons in the ***s*** orbital is promoted to the empty ***p*** orbital, four half-filled orbitals are produced as shown in Figure 9.

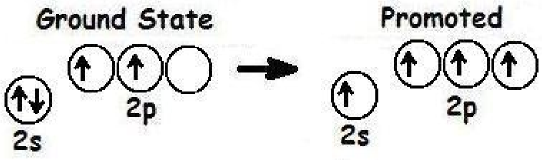

Figure 9: Electron promotion in family 4A.

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With four half-filled orbitals, carbon and silicon can form four covalent bonds as necessary for CH_4, CCl_4 and so on. As you already suspect before it is even mentioned, these four bonds in carbon and silicon compounds are all identical. Therefore, orbital hybridization also occurs in this family. The four hybridized orbitals are called ***sp***^{3} hybridized orbitals (See Figure 10).

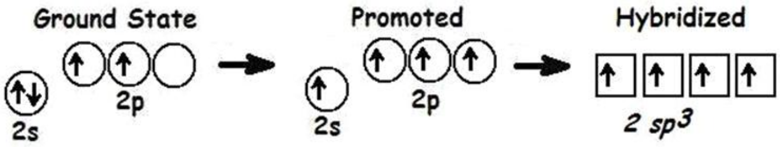

Figure 10: sp^3 hybridization in carbon.

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Since the ***sp***^{3} hybridized orbitals are a mix of one ***s*** and three ***p*** orbitals, their characteristics are not the same as ***sp***^{2} hybridized orbitals or ***sp*** hybridized orbitals. These four identical orbitals can be overlapped by four hydrogen atoms and form four identical bonds. The covalent compounds in family 4A do obey the octet rule.

The Covalent Bonds of Family 5A

In family 5A, the electron configuration of the outermost energy level is s^2p^3. These atoms have three half-filled ***p*** orbitals available for overlap and would appear to form three covalent bonds with no need of either electron promotion or hybridization. The first member of the family, nitrogen, does commonly form three bonds such as in the compounds NH_3, NCl_3, and N_2O_3. The second member of the family, phosphorus, also forms similar compounds with three bonds, PH_3 and PCl_3. Phosphorus, however, can also form compounds with five covalent bonds such as PCl_5. In order to explain five identical bonds for the phosphorus atom, we will need to invoke both electron promotion and orbital hybridization.

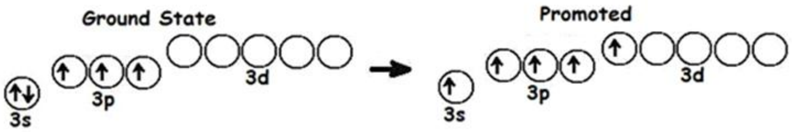

Figure 11: Electron promotion in phosphorus.

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As you can see in Figure 11, phosphorus promotes one of its ***3s*** electrons into an orbital in the ***3d*** sublevel. This gives phosphorus five half-filled orbitals and allows it to form the five bonds in PCl_5 and other phosphorus compounds with five covalent bonds. It also makes it clear why nitrogen does not form compounds with five bonds, because in the second period, there is no ***d*** sub-energy level available. The five bonds in these compounds are identical and require us to invoke orbital hybridization again. In this case, there is one ***s*** orbital, three ***p*** orbitals, and one ***d*** orbital to hybridize. These hybridized orbitals will be called sp^3d or dsp^3 hybridized orbitals. Of course, as you already guessed, these orbitals are different in length, strength, and flexibility from all the other hybridized orbitals. As you probably already noticed, molecules like PCl_5 and PF_5 will have the central atom surrounded by 10 electrons and so this electron promotion produces another group of molecules that do not obey the octet rule.

The Covalent Bonds of Family 6A

The outermost energy level of the members of family 6A has the electron configuration of s^2p^4. This outer energy level has a filled ***s*** orbital, one filled ***p*** orbital, and two half-filled ***p*** orbitals. With two half-filled orbitals available for overlap, all of the member of this family can and do form two covalent bonds. By far, the most common compounds formed by members of family 6A have two covalent bonds. There are, however, some compounds that form more covalent bonds. Oxygen is in the second period and therefore has no ***d*** orbitals so promotion into the d sub-energy level is not possible. But sulfur and larger members of family 6A do have ***d*** orbitals which allows for electron promotion. In the case of sulfur, two electrons can be promoted into ***d*** orbitals.

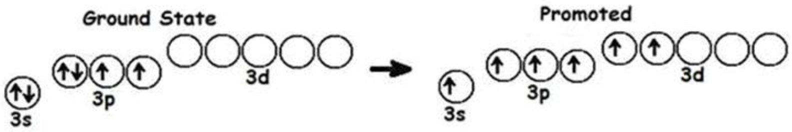

Figure 12: Electron promotion in sulfur.

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As you can see in Figure 12, sulfur can promote two electrons into the ***d*** orbitals and produce six half-filled orbitals available for overlap. The six orbitals are, of course, hybridized and form d^2sp^3 or sp^3d^2 hybridized orbitals. Such orbitals are necessary for the formation of compounds such as SF_6.

The Covalent Bonds of Family 7A

All of the members of family 7A have outermost energy level electron configurations of s^2p^5. This configuration has one half-filled ***p*** orbital which allows the members of this family to form one covalent bond. The majority of compounds formed by this family are compounds with one bond. Fluorine has no ***d*** orbitals and so electron promotion is not available for fluorine so fluorine only forms one bond. Chlorine and the larger members of the family have empty ***d*** orbitals allowing them to undergo electron promotion. Chlorine can promote one ***p*** electron to a ***d*** orbital producing three half-filled orbitals which provides for compounds like ClF_3. Chlorine can also promote two electrons producing five half-filled orbitals which provides for compounds like ClF_5.

The Covalent Bonds of Family 8A

Even members of the noble gases, under extreme conditions, can form some covalent compounds. Since the ground state electron configuration for these atoms has completely filled outer energy levels, we should expect that they form bonds by electron promotion and orbital hybridization.

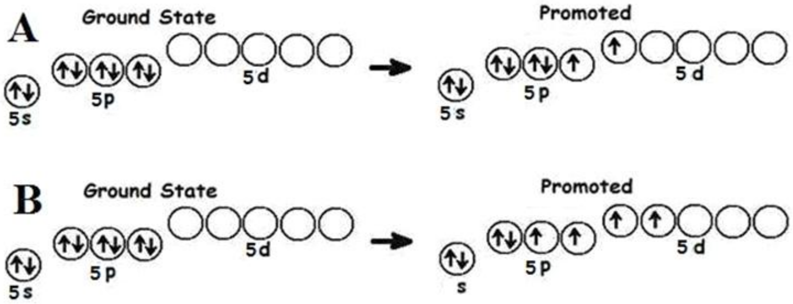

Figure 13: Two possible electron promotions in xenon.

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In Figure 13A above, xenon is promoting one electron from ***p*** to ***d*** orbitals. This allows xenon to form two covalent bonds as in XeF_2. In Figure 13B, xenon is promoting two electrons from ***p*** to ***d*** orbitals producing four orbitals available for overlap to provide for XeF_4. In both family 7A and 8A, when electrons are promoted and orbitals are hybridized, even though some of the orbitals are filled and some are half-filled, the hybridization is considered to involve ALL the outer energy level orbitals that contain any electrons. Therefore, in Figure 13A, the orbital hybridization would be sp^3d and in Figure 13B, the hybridization would be sp^3d^2 .

Summary of Hybridized Orbitals

Orbitals Hybridized	**Hybridized Orbital Names**	**Number of Orbitals**
1s and 1p	sp	2
1s and 2p	sp^2	3
1s and 3p	sp^3	4
1s, 3p, and 1d	sp^3d	5
1s, 3p, and 2d	sp^3d^2	6

Lesson Summary

- There are stable molecules that form whose central atom has less than an octet of electrons.
- There are stable molecules that form whose central atom has more than an octet of electrons.
- Atoms can promote electrons to produce electron configurations above ground state because when all the half-filled orbitals are overlapped, the energy output will be greater than the energy input required to promote the electrons.
- When more than one sub-level is involved in covalent bonding, the orbitals are hybridized to produce a group of identical orbitals which will be overlapped to produce identical bonds.
- The maximum number of hybridized orbitals is six.

Review Questions

1. What is the designation for the hybrid orbitals formed from each of the following combinations of atomic orbitals and what is the bond angle associated with the hybrid orbitals? **(Beginning)**

|- | width="150px" align="center"| **Orbitals Combined** | width="300px" align="center"| **Type of Hybridization** | width="150px" align="center"| **Bond Angles** |- | align="center"| one s and one p | | |- | align="center"|

one s and two p | | |- | align="center"| one s and three p | | |}

2. What laboratory evidence necessitates the theory of hybridized orbitals? **(Challenging)**

3. Fill in the type of hybridization necessary for the following molecules. **(Intermediate)**

|- | width="120px"| **Molecule** | width="300px"| **Type of Hybridization** |- | H_2O | |- | NH_3 | |- | $BeCl_2$ | |- | NaH | |- | BF_3 | |- | PCl_5 | |- | BrF_5 | |- | SF_6 | |- | XeF_2 | |}

Vocabulary

hybrid orbitals	a set of orbitals adopted by an atom in molecule different from those of the atom in the free state.
hybridization	a mixing of the native orbitals on a given atom to form special atomic orbitals for bonding.
VSEPR model	a model whose main postulate is that the structure around a given atom in a molecule is determined by minimizing electron-pair repulsion.

Review Answers

1.

|- | width="150px" align="center"| **Orbitals Combined** | width="300px" align="center"| **Type of Hybridization** | width="150px" align="center"| **Bond Angles** |- | align="center"| one s and one p | align="center"| *sp* | align="center"| 180^o |- | align="center"| one s and two p | align="center"| sp^2 | align="center"| 120^o |- | align="center"| one s and three p | align="center"| sp^3 | align="center"| 109.5^o |}

2. Bonds formed by overlapping half-filled s orbitals, p orbitals, and d orbitals would be expected to be different in terms of bond length, strength, flexibility, etc. But laboratory analysis determined that the bonds in molecules involving these various overlapped orbitals are all the same.

3.

|- | width="120px"| **Molecule** | width="270px" align="center"| **Type of Hybridization** |- | H_2O | align="center"| sp^3 |- | NH_3 | align="center"| sp^3 |- | $BeCl_2$ | align="center"| *sp* |- | NaH | align="center"| none |- | BF_3 | align="center"| sp^2 |- | PCl_5 | align="center"| sp^3d |- | BrF_5 | align="center"| sp^3d^2 |- | SF_6 | align="center"| sp^3d^2 |- | XeF_2 | align="center"| sp^3d |}

Resonance

Lesson Objectives

- The student will describe (chemistry) resonance.
- The student will explain the equivalent bond strengths in a resonance situation.

Introduction

When drawing Lewis structures for molecules, there are a number of cases in which the Lewis structure appears to indicate that the bonds between the central atom and the attached atoms are different. That is, in order to satisfy the requirements for Lewis structures, one of the bonds must be drawn as a double bond while the other bonds are single bonds. This would indicate that the bonds between the central atom and the attached atoms are not the same in length, strength, and so on. The double bond would be expected to be stronger and different in other ways when compared to the single bonds. When the characteristics of the bonds are measured in the laboratory, however, it is determined that the bonds are actually equal in length and strength. ***Resonance*** is the theory used to explain this data.

Resonance Structures

Sometimes, more than one valid Lewis structure is possible for the same molecule. Consider the Lewis structure for the nitrite ion, NO_2^-. The charge on the ion indicates an electron has been gained, that is, the ion contains an electron that did not originally belong to either the nitrogen or oxygen atoms in the ion. In this case, the -1 charge indicates that the valence electron count will need one electron added to account for the electron that came from outside the ion. The total number of valence electrons for this ion is 5 + 6 + 6 + 1 = 18. We can then draw the Lewis structure for this ion following the normal rules. Before we apply the last rule of creating double or triple bonds to produce an octet for the central atom, the Lewis structure will look like that in Figure 14.

Figure 14: Unfinished Lewis structure for NO_2^-.

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We placed a pair of electrons between bonded atoms, completed the octet of all the non-central atoms, and placed the left over electrons around the central atom. We have used all 18 of the valence electrons available. The final rule for writing Lewis structures is that if the central atom does not have an octet of electrons, create a double or triple bond to generate an octet of electrons for the central atom. In this case, either one of the nitrogen-oxygen bonds can be made into a double bond (See Figure 15).

Figure 15: Equally likely Lewis structures for NO_2^-.

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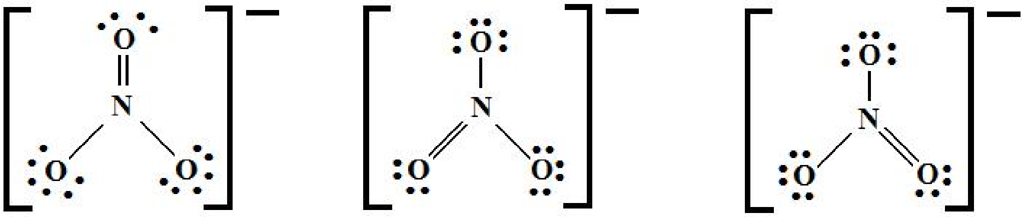
Let's look at the proposed Lewis structures for the nitrate ion, NO_3^-.



There is no reason to choose one of these structures above another. All of these are valid structures that fit the information. The question is, are any of them a correct description of the bonding in the nitrate ion? The answer is NO. The nitrate ion does NOT contain two singly bonded oxygen atoms and one double bonded oxygen atom. Laboratory data shows that the three oxygen bonds in this ion are all the same . . . they have the same length, the same strength, and the same flexibility. The three bonds in this ion are the same in every way. The nitrate ion does not exist as any one of these forms but rather the ***average*** of all three. Each bond in this ion is equivalent to 1.33 single bonds. **Resonance** occurs when more than one valid Lewis structure can be written for a particular molecule or ion. The actual structure of the molecule or ion is the average of the resonance structures. It is suggested that the fourth bond (drawn as part of a double bond) is actually a pi bond that exists in the plane above and below the molecule and is shared equally by the three oxygen atoms.

Resonance Suggests a Composite Structure

Both of the structures in Figure 15 suggest that one of the nitrogen-oxygen bonds should be shorter and stronger than the other one. Experiment, however, shows that they are identical. In fact, the carbon-oxygen bond lengths are about halfway between the expected values for a single bond and a double bond. Neither of the Lewis structures in Figure 15 matches the experimental evidence and there is no way to write one that does. The perfect Lewis structure would show 1.5 pairs of electrons in each bond. The solution to this problem is the use of a concept called **resonance.** We view the actual structure of the molecule or ion, which cannot be drawn properly, as a composite, or average, of all the Lewis structures we can draw. In the case of the nitrite ion in Figure 15, the proper view is that the second bond in the double bond is actually shared between both bonds, giving each bond the strength of about 1.5 bonds. Each of the Lewis structures that is drawn is called a resonance structure or a contributing structure and the actual structure is a resonance hybrid of all the contributing structures. *At one time, it was thought that the resonance structures took turns, that is, that the double bond vibrated between all the possible positions. That is why the name "resonance" was chosen. That concept has been completely rejected but unfortunately the name resonance was retained for the new concept. The term resonance as used in chemistry now has absolutely no relation to the normal use of the word resonance in English.*

Lesson Summary

- Resonance is a condition occurring when more than one valid Lewis structure can be written for a particular molecule. The actual electronic structure is not represented by any one of the Lewis structures but by the average of all of them.

Review Questions

1. Write a Lewis structure for CO_3^{2-}. Explain why all three carbon-oxygen bonds have the same length. **(Challenging)**

Further Reading / Supplemental Links

Website with lessons, worksheets, and quizzes on various high school chemistry topics.

- Lesson 4-7 is on Resonance.

http://www.fordhamprep.org/gcurran/sho/sho/lessons/lesson47.htm

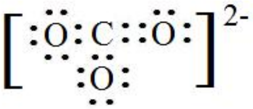
Vocabulary

bond energy	the energy required to break a given chemical bond.
bond length	the distance between the nuclei of the two atoms connected by a bond.
resonance	a condition occurring when more than one valid Lewis structure can be written for a particular molecule. The actual elec-

tronic structure is not represented by any one of the Lewis structures but by the average of all of them.

Review Answers

1.



The pi bond (one of the bonds in the double bond) is distributed evenly over all three bonds. The Lewis structure pictured is only one of three resonance structures for this ion. Each of the bonds is approximately one and one-third bonds and the three bonds are identical.

Electronic and Molecular Geometry

Lesson Objectives

- The student will state the main postulate in VSEPR theory.
- The student will identify both the electronic and the molecular geometry for simple binary compounds.

Introduction

Many accurate methods now exist for determining molecular structure, the three-dimensional arrangement of the atoms in a molecule. These methods must be used if precise information about structure is needed. However, it is often useful to be able to predict the approximate molecular structure of a molecule. A simple model that allows us to do this is called the **valence shell electron pair repulsion (VSEPR) theory.** This model is useful in predicting the geometries of molecules formed in the covalent bonding of non-metals. The main postulate of this theory is that in order to minimize electron-pair repulsion, the electron pairs around the central atom in a molecule will get as far away from each other as possible.

Electronic Geometry for a Central Atom with Two Pairs of Electrons

Consider first the covalent compounds formed by family 2A. An example of these compounds is $BeCl_2$. The central beryllium atom has two pairs of electrons in its valence shell. VSEPR theory tells us that these two pairs of electrons will move in the valence shell to get as far away from each other as possible. The greatest distance these two pairs of electrons can get from each other is 180° across from each on opposite sides of the nucleus. If both of these pairs of electrons were overlapped by a chlorine atom, the two chlorine atoms would also be on opposite sides of the nucleus. The electronic geometry in this case is **linear** and if the electron pairs are shared, the molecule will also be linear. A "linear molecule" means that a straight line would pass through all the nuclei in the molecule.

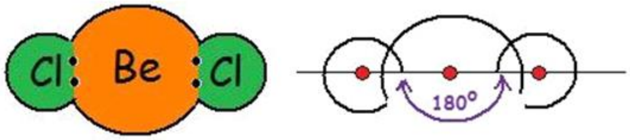


Figure 16: The electronic geometry of $BeCl_2$ is linear and if both pairs of electrons are shared, the molecule is also linear.

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Electronic Geometry for a Central Atom with Three Pairs of Electrons

We will look at boron trichloride, BCl_3, as an example molecule for the covalent molecules in family 3A. Boron has three valence electrons and each chlorine that overlaps a boron orbital contributes one more electron to boron's valence shell. Therefore, boron will have six electrons or three pairs of electrons in its valence shell. The farthest away from each other that three pairs of electrons can get is at the points of a planar triangle in the valence shell. Each bond angle will be 120°. This shape is known as **trigonal planar.**

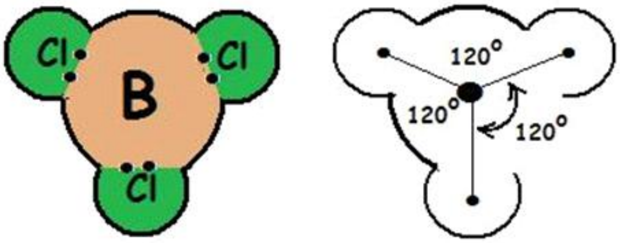

Figure 17: The trigonal planar electronic geometry of BH_3. If all electron pairs are shared, the molecule will also be trigonal planar.

(*Created by:* Richard Parsons, *License :* CC-BY-SA)

In the trigonal planar shape, all four atoms are in a single plane. None of the atoms project above or below the plane of the paper. You should note that if one of the pairs of electrons is not shared, so there is only two attached chlorine atoms, the shape of the molecule will **angular** or **bent.**

Electronic Geometry for a Central Atom with Four Pairs of Electrons

We will use methane, CH_4, as an example of the covalent bonding in family 4A. Carbon has four valence electrons and each hydrogen adds one more so the central atom in methane has four pairs of electrons in its valence shell. Those four pairs of electrons get as far away from each other as possible which forms a shape called **tetrahedral.** In the tetrahedral shape, the bond angle between any two hydrogen atoms is 109.5°.

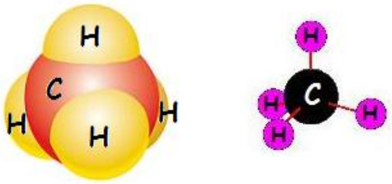

Figure 18: The electronic geometry of carbon's four pairs of electrons is tetrahedral and if all four pairs of electrons are shared, the molecule shape is also tetrahedral.

(*Source*: CK-12 Foundation, *Altered by:* Richard Parsons, *License:* CC-BY-SA)

Electronic Geometry for a Central Atom with Five Pairs of Electrons

We will consider the molecules PCl_3 and PCl_5 as reference molecules for family 5A. In the PCl_3 molecule, the central phosphorus atom has five valence electrons and each chlorine atom contributes one more electron so that the central atom has four pairs of electrons in its valence shell. These four pairs of electrons will form the tetrahedral shape in the effort to maximize the distance between them. Therefore, the electronic geometry for this molecule is tetrahedral. When the molecule is formed, however, one of the pairs of electrons is not shared. The resulting molecular geometry is called **pyramidal.**

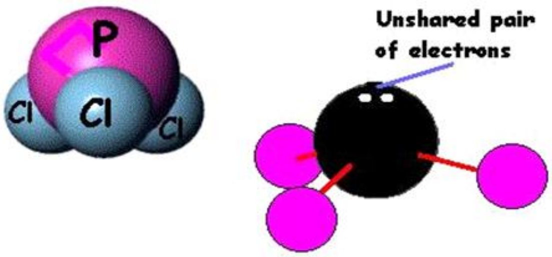

Figure 19: The tetrahedral electronic geometry forms a pyramidal molecule when one pair of electrons is unshared.

(*Source*: CK-12 Foundation, *Modified by:* Richard Parsons, *License:* CC-BY-SA)

It is important to note the difference between the pyramidal molecule in Figure 19 and the trigonal planar molecule discussed earlier. In the trigonal planar molecule, none of the attached atoms is below or above the plane of the central atom. In this pyramidal molecule, however, all three of the attached atoms are below the plane of the central atom.

In the PCl_5 molecule, the phosphorus has five valence electrons and each chlorine adds one more so the central atom will be surrounded by five pairs of electrons in its valence shell. When these five pairs of electrons maximize the distance between them, the shape is called **trigonal bipyramidal.** This shape has three attached atoms in a plane with the central atom and then has atoms attached to the two ends of the molecule.

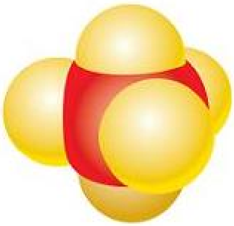

Figure 20: The trigonal bipyramidal electronic geometry of PCl_5.

(*Source*: CK-12 Foundation, *License*: CC-BY-SA)

The bond angles between the three atoms in the plane with the central atom are all 120° and the bond angles between the two end atoms and the other three are all 90°.

Electronic Geometry for a Central Atom with Six Pairs of Electrons

The two types of electronic geometry in family 6A can be seen in the molecules SF_2 and SF_6. In SF_2, the central sulfur atom has six valence electrons and each fluorine adds one more so that the central atom is surrounded by four pairs of electrons. The resultant electronic geometry is the tetrahedral shape we have seen twice before. However, when the compound SF_2 is formed, two of the pairs of electrons are unshared. The resultant molecular shape is called **angular** or **bent.**

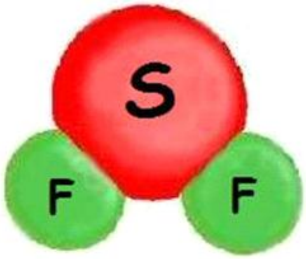

Figure 21: SF_2 has tetrahedral electronic geometry but two of the pairs of electrons are not shared so the resultant molecular geometry is angular.

(*Created by:* Richard Parsons, *License :* CC-BY-SA)

In the molecule SF_6, sulfur has six valence electrons and each fluorine contributes another electron so the central atom is surrounded by six pairs of electrons. The maximum distance six pairs of electrons can separate produces a geometry called **octahedral.**

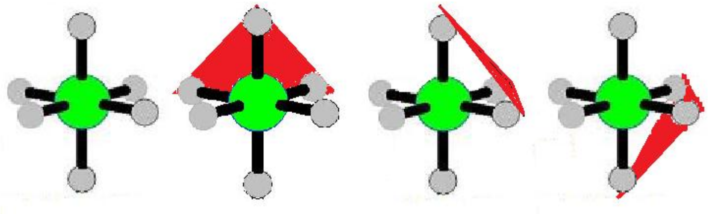

Figure 22: The octahedral electronic shape of six electron pairs.

(*Created by:* Richard Parsons, *License :* CC-BY-SA)

The bond angle between any two adjacent attached atoms is 90°. The shape name is based on the number of triangular plates that can be placed on the surface of the molecule and if you count carefully, you will see that it is eight, hence octahedral.

Summary of Electronic Geometry

Electron Pairs	Hybridization	Electronic Geometry
1	None	Linear
2	sp	Linear
3	sp^2	Trigonal Planar
4	sp^3	Tetrahedral
5	sp^3d	Trigonal Bipyramidal
6	sp^3d^2	Octahedral

Examples of Molecular Shapes

The electronic geometry for a given number of electron pairs surrounding a central atom is always the same. That number of electron pairs will distribute themselves in the same way to maximize their separation. The same thing cannot be said for molecular geometry. The molecular shape depends not only on the electronic geometry but also on the number of the electron pairs that are shared. In this section, we will go through a number of examples of molecules where some number of the pairs of electrons are not shared.

Beginning with members of family 3A, there are very few options. We will consider the shapes of the BH_3 molecule and the BH_2^- ion. In BH_3 molecules, the central atom is surrounded by three pairs of electrons, so the electronic geometry is trigonal planar, and when all three electron pairs are shared, the molecular geometry is also trigonal planar. In the case of the BH_2^- ion, there are still three pairs of electrons around the central atom (3 from boron, 1 each from the two hydrogens, and 1 electron that came from outside the ion), so the electronic geometry remains trigonal planar. The shape of the ion, however, will be a shape known as **bent** or **angular.**

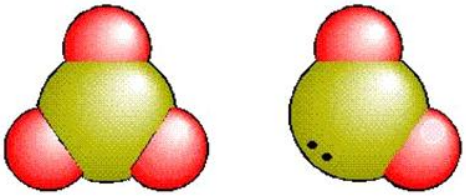

Figure 23: Trigonal planar molecular shape and angular shape when one pair of electrons is unshared.

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When the central atom is surrounded by four pairs of electrons, the electronic geometry will always be tetrahedral. When all four electron pairs are shared, such as with CH_4, the molecular shape will also be tetrahedral. In the case of ammonia, NH_3, however, three of the four pairs of electrons are shared but the fourth pair is unshared. This results in a molecular shape called pyramidal. If a second pair of electrons is unshared, such as with the NH_2^- ion, the shape is angular again.

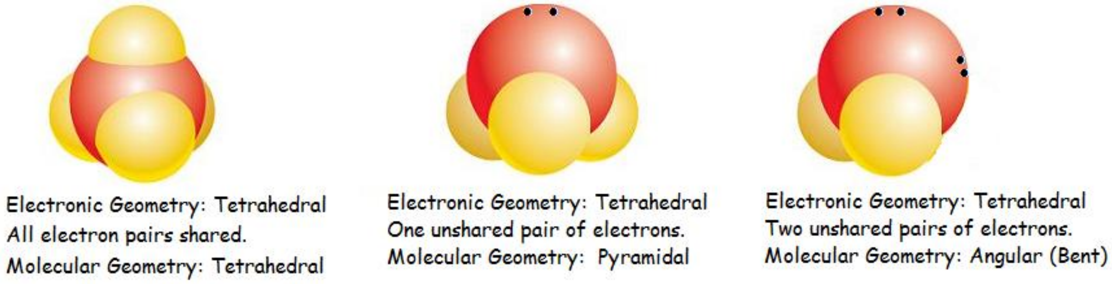


Figure 24: Four pairs of electrons shared and none unshared produces tetrahedral molecular shape, three pairs shared and one pair unshared produces pyramidal, and two pairs shared with two pairs unshared produces angular.

(*Source*: CK-12 Foundation, *Modified by*: Richard Parsons, *License*: CC-BY-SA)

When the central atom is surrounded with five pairs of electrons, the electronic geometry is trigonal bipyramidal. If all the electron pairs are shared, the molecular geometry will also be trigonal bipyramidal. An example of such a molecule is PF_5. If one of the pairs of electrons is not shared, the molecular shape is called a **distorted tetrahedron** which is sometimes called **seesaw.** An example of a molecule with trigonal bipyramidal electronic geometry and a molecular shape of a distorted tetrahedron is SF_4 (see Figure 25B). This molecule has five electron pairs around the central atom but only four of them are shared. When the electronic geometry is trigonal bipyramidal and two of the pairs of electrons are unshared, the shape is called **T-shaped.** An example of a T-shaped molecule is ClF_3 (Figure 25C). ClF_3 has five pairs of electrons around the central atom and only three of them are shared. When the trigonal bipyramidal electronic geometry has only two of the pairs of electrons shared, the molecular geometry produced is linear as in I_3^- (Figure 25D).

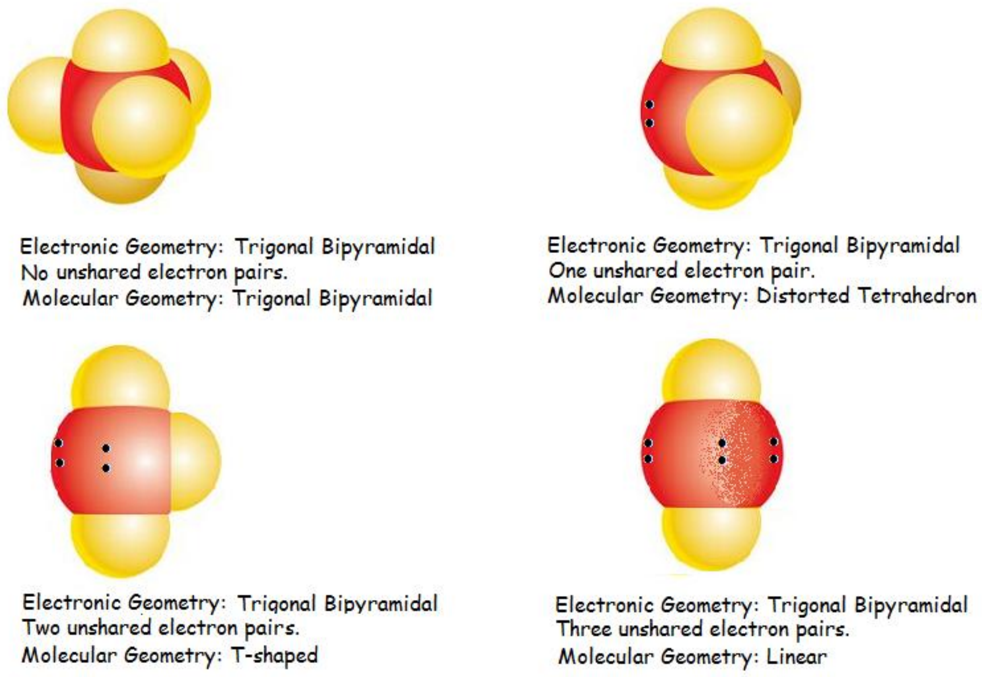


Figure 25: Trigonal bipyramidal electronic geometry produces all these molecular shapes depending on how many electron pairs are shared and unshared.

(*Source*: CK-12 Foundation, *Modified by*: Richard Parsons, *License*: CC-BY-SA)

Figure 25A shows a molecule whose central atom is surrounded by five pairs of electrons and all five pairs are shared. The result is trigonal bipyramidal electronic geometry and trigonal bipyramidal molecular geometry. Figure 25B shows a molecule whose central atom is surrounded by five pairs of electrons, one of which is unshared. The resultant molecular shape is a distorted tetrahedron. Figure 25C represents a molecule like ClF_3. The chlorine central atom has seven valence electrons and each fluorine atom contributes one more. The total number of electrons is ten or five pairs. With only three attached atoms, two of the electron pairs are left unshared. The first pairs of electrons that are left unshared in trigonal bipyramidal electronic geometry are the pairs around the middle of the molecule. The resultant molecular shape is called T-shape. In the ion, I_3^-, the central iodine atom has seven valence electrons, two more are contributed by the attached iodine atoms, and one more electron comes from outside the ion. The total electron pairs around the central atom is five pairs and three of the pairs are unshared. The resultant shape of the ion is linear.

Beginning with octahedral electronic geometry (six pairs of electrons), a number of molecular shapes can be produced depending on the number of electron pairs that are shared and unshared (see Figure 26).

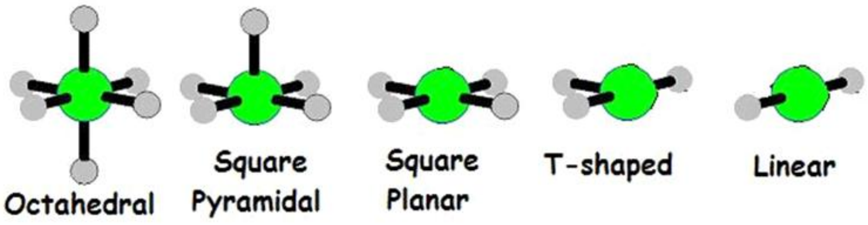


Figure 26: Octahedral electronic geometry produces all these molecular shapes depending on how many electron pairs are shared and unshared.

(*Source*: CK-12 Foundation, *Modified by*: Richard Parsons, *License*: CC-BY-SA)

When electron pairs are unshared in trigonal bipyramidal electronic geometry, the first pairs that are unshared are the pairs around the center. When electron pairs are unshared in octahedral electronic geometry, the first pairs that are unshared are the ones on the ends of the molecule.

Summary of Molecular Geometry

Valence Shell Electron Pairs Total	**Valence Shell Electron Pairs Shared**	**Valence Shell Electron Pairs Unshared**	**Molecular Geometry**
1	1	0	Linear
2	2	0	Linear
2	1	1	Linear
3	3	0	Trigonal Planar
3	2	1	Angular
3	1	2	Linear
4	4	0	Tetrahedral
4	3	1	Pyramidal
4	2	2	Angular
4	1	3	Linear
5	5	0	Trigonal Bipyramidal
5	4	1	Distorted Tetrahedron
5	3	2	T-shaped
5	2	3	Linear
5	1	4	Linear
6	6	0	Octahedral
6	5	1	Square Pyramidal
6	4	2	Square Planar
6	3	3	T-shaped
6	2	4	Linear
6	1	5	Linear

Only Sigma Bonds Affect Electronic and Molecular Geometry

In the process of determining the number of electron pairs around the central atom for the purpose of predicting electronic or molecular geometry, double bonds and triple bonds should be counted as one effective pair. The electron pairs, in order to repel other electron pairs, must be placed between the nuclei of the two atoms. In pi bonds, the electron density is above and below the plane of the bond and therefore, do not contribute to electron pair repulsion. ***For the VSEPR model, multiple bonds count as only one effective pair of electrons.*** We can use the nitrate ion,

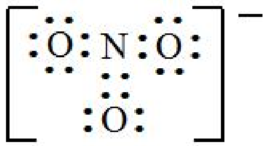
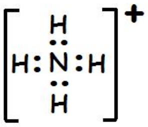


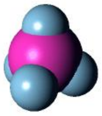
Figure 27: One of the resonance Lewis structure for the nitrate ion. (*Created by*: Richard

NO_3^-, as an example. In order to determine the shape of the nitrate ion, we count the number of electron pairs that are surrounding the central nitrogen atom. Since double bonds count as a single electron pair for the VSEPR model, we would count three pairs of electrons in the central atom valence shell and therefore, the shape would be determined as trigonal planar.

Parsons, *License*: CC-BY-SA)

Examples of Determining Molecular Geometry





Example 1

Determine the shape of the ammonium ion, NH_4^+.

Solution

Step one is to determine the number of electron pairs around the central nitrogen atom.

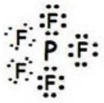
Electrons = 5 (from nitrogen) + 4 (one from each hydrogen) – 1 (the positive charge on the ion indicates this ion has lost one electron to the outside) = 8 electrons = 4 electron pairs

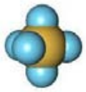
Step two is to choose the electronic geometry based on the number of electron pairs.

The electronic geometry of a central atom with four pairs of electrons = tetrahedral.

Step three is to determine the number of valence shell electron pairs that are shared and unshared and choose the molecular geometry.

Since all four pairs of electrons are shared in this ion, the ionic shape will be tetrahedral.



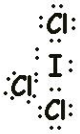


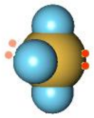
Example 2

Determine the molecular shape of the PF_5 molecule.

Electrons in the valence shell of phosphorus = 5 (phosphorus) + 5 (one from each fluorine) = 10 electrons = 5 pairs of electrons.

The electronic geometry is trigonal bipyramidal and because all five pairs of electrons are shared, the molecular geometry will also be trigonal bipyramidal.





Example 3

Determine the shape of the ICl_3 molecule.

Solution

The number of electrons surrounding the central iodine atom is 7 electrons from the iodine atom plus 1 from each chlorine atom yielding a total of 10 electrons which is 5 pairs. Therefore, the electronic geometry is trigonal bipyramidal. Since only three of the electron pairs are shared, the molecular geometry is T-shaped.

Example 4

Determine the shape of the CO_2 molecule.

Solution

Since there are multiple bonds involved in this molecule, we need to write the Lewis structure for the molecule to make sure we do not count any double or triple bonds for VSEPR model determinations.

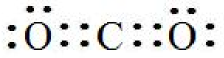


Figure 28: The Lewis structure for carbon dioxide.

(*Created by*: Richard Parsons, *License*: CC-BY-SA)

Only the sigma bonds count in determining the electron pairs surrounding the central carbon atom. This molecule, therefore, has two electron pairs in the valence shell of the central atom and that produces linear electronic geometry and since both pairs are shared, the molecular geometry will also be linear.

Example 5

Determine the shape of the SO_2 molecule.

Solution

We will write the Lewis structure to check for multiple bonds.

Figure 29: The Lewis structure for sulfur dioxide.

(*Created by*: Richard Parsons, *License*: CC-BY-SA)

In writing the Lewis structure for SO_2, we determine a double bond is necessary to provide an octet of electrons for the central sulfur atom. Therefore, this molecule has three pairs of electrons around the central atom and its electronic geometry will be trigonal planar. Since only two of the electron pairs are shared, the molecular geometry is angular.

Example 6

Determine the molecular shape of the XeF_4 molecule.

Solution

The number of electrons surrounding the central atom in XeF_4 is eight from the Xe and one each from the four fluorine atoms for a total of 12 electrons or 6 pairs of electrons. Six pairs of electrons around the central atom produces octahedral electronic geometry and since two pairs are unshared, the molecular geometry will be square planar.

Lesson Summary

- VSEPR theory suggests that the valence shell electron pairs due to electrostatic repulsion will spread themselves around the central atom in an attempt to maximize the distance between them.
- The electronic geometry of a molecule is dependent only on the number of electron pairs in the valence shell of the central atom.
- Molecular geometry is dependent on the electronic geometry and on the number of electron pairs that are unshared.

- Only sigma bonds contribute to electronic and molecular geometry.

Review Questions

1. Write a Lewis structure for OF_2 that obeys the octet rule. **(Beginning)**

2. Write a Lewis structure for H_2CO that obeys the octet rule. (C is the central atom.) **(Intermediate)**

3. What is the geometrical shape of the H_2CO molecule? **(Challenging)**

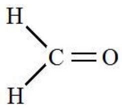
4. What is the bond angle in SCl_2? **(Challenging)**

5. What is the molecular shape of ICl_3? **(Challenging)**

6. What is the molecular shape of $XeCl_4$? **(Challenging)**

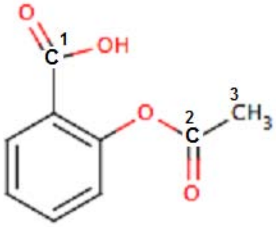
7. The ion I_3^- molecule has been produced in the lab but the molecule F_3^- has not. Offer an explanation as to why F_3^- cannot be produced in the lab. **(Challenging)**

8.



The molecule shown here is methanal. What is the hybridization of the carbon atom in this molecule? **(Intermediate)**

9.



The molecule shown here is acetylsalicylic acid, better known as aspirin.

A. What is the hybridization of carbon 1? **(Intermediate)**

B. What is the hybridization of carbon 2? **(Intermediate)**

C. What is the hybridization of carbon 3? **(Intermediate)**

D. What is the total number of pi bonds in the molecule? **(Intermediate)**

Further Reading / Supplemental Links

Website with lessons, worksheets, and quizzes on various high school chemistry topics.

- Lesson 4-4 is on Geometry of Molecules.

- Lesson 4-5 is on Polarity.

http://www.fordhamprep.org/gcurran/sho/sho/lessons/lesson31.htm

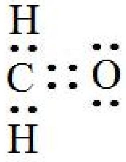
Vocabulary

unshared electron pair	An unshared electron pair, also known as a non-bonding pair of electrons or as a lone pair of electrons, is two electrons in the same orbital in the outer shell of an atom that are not used in the formation of a covalent bond.
electronic geometry	The geometric arrangement of orbitals containing the shared and unshared electron pairs surrounding the central atom of a molecule or polyatomic ion.
molecular geometry	The specific three-dimensional arrangement of atoms in molecules.

Review Answers

1.

2.



3. From the Lewis structure for this molecule drawn in problem 2, the number of shape contributing electron pairs around the central atom is three. Therefore, the electronic geometry would be trigonal planar and since all three electron pairs are shared, the molecular geometry would also be trigonal planar.

4. The electronic geometry for SCl_2 is tetrahedral and because only two of the electron pairs are shared, the molecular shape is angular or bent.

5. The electronic geometry for ICl_3 is trigonal bipyramidal and with only three of the electron pairs shared, the molecular geometry is T-shaped.

6. The electron geometry for $XeCl_4$ is octahedral and with only four of the electron pairs shared, the molecular geometry is square planar.

7. The I_3^- molecule is produced by having an electron in the central atom promoted into a ***d*** orbital. Fluorine cannot do this because it doesn't have any ***d*** orbitals.

8. Since only sigma bonds are involved in hybridization, this carbon atom has sp^2 hybridization.

9.

A. sp^2

B. sp^2

C. sp^3

D. 5 pi bonds

Molecular Polarity

Lesson Objectives

- The student will determine whether bonds are polar or non-polar.
- The student will determine whether simple molecules are polar or non-polar.

Introduction

Two atoms of the same electronegativity will share electrons equally in a pure covalent bond. Any molecule that contains atoms of only one element, like H_2 or F_2, has pure covalent bonding. Two atoms with different electronegativities will have either the distorted electron distribution of a polar bond or the complete electron transfer of an ionic bond. Table 1 interprets the bonding between two elements in terms of the difference in their electronegativities.

Table 1: Electronegativity Difference and Type of Bond

Electronegativity Difference	Ionic Character (%)	Covalent Character (%)	Bond Type
0.0	0	100	Covalent
0.5	5	95	Covalent
1.0	20	80	Covalent
1.5	40	60	Polar
2.0	60	40	Polar
2.5	75	25	Ionic
3.0	90	10	Ionic

The Cause of Polar Bonds

When covalent bonds form between identical atoms such as in H_2, N_2, O_2, and so on, the electrons shared in the bonds are shared exactly equally. The two atoms have the same electronegativity and therefore, the same pull on the shared electrons. The center of negative charge for the entire molecule will be in the exact center of the molecule. This will coincide with the center of positive charge for the molecule. When the center of negative charge and the center of positive charge coincide, there is no charge separation and no dipole.

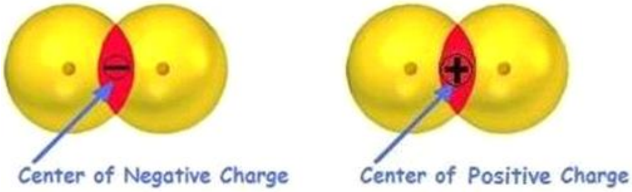


Figure 30: The center of positive and negative charge in a molecule.

(*Created by*: Richard Parsons, *License*: CC-BY-SA)

If the two atoms sharing the bonding pair of electrons are not of the same element, the atom with the greater electronegativity will pull the shared electrons closer to it. Because of the resulting uneven distribution of electrons, the center of negative charge will not coincide with the center of positive charge and a dipole is created on the molecule. When the centers of positive and negative charge do not coincide, a charge separation exists and a dipole is present.

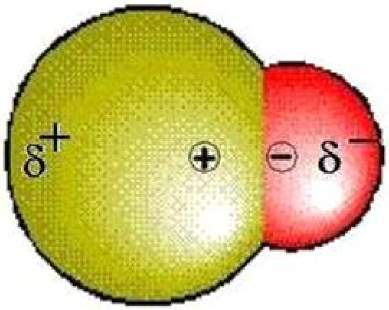


Figure 31: Sketch of a polar molecule showing the separation of the centers of positive and negative charge.

(*Created by*: Richard Parsons, *License*: CC-BY-SA)

The end of the molecule with the more electronegative atom will have a partial negative charge and the end of the molecule with the more electropositive atom will have a slight positive charge. The symbols δ+ and δ- are used because these are not full 1+ and 1- charges. This polarity is much less of a charge separation than in an ionic bond. These charges are only fractions of full 1+ and 1- charges. How much polarity a bond will experience depends on the difference in the electronegativities of the atoms.

No Dipole is Present on Symmetrical Molecules

In the case of a symmetrical molecule with polar bonds, the symmetry of the electron displacements of two or more electron pairs will keep the center of negative charge in the center of the molecule coincident with the center of positive charge. When the centers of positive and negative charge are coincident, no dipole will occur.

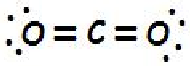


Figure 32: The Lewis structure for carbon dioxide.

(*Created by*: Richard Parsons, *License*: CC-BY-SA)

For example, in the CO_2 molecule, both carbon-oxygen bonds are polar but the shift of bonding electrons toward the oxygen is the same on both sides of the carbon atom and the center of negative charge remains in the center.

All bonds between non-metallic atoms that are not the same atom will be polar bonds. However, having polar bonds is not enough to guarantee than the molecule will be polar. If the molecule has those polar bonds in a symmetrical shape, the center of negative charge does not move away from the center of positive charge, and the molecule will not be polar. For a particular molecule to be symmetrical, all the attached atoms must be the same atom. For example, CH_4 is a symmetrical molecule but CH_3Cl is not symmetrical.

Symmetrical Molecular Shapes

Molecular Geometry	Example Molecule	Symmetry
Linear	F_2	Symmetrical
Linear	BeH_2	Symmetrical
Trigonal Planar	BH_3	Symmetrical
Angular	H_2O	Not Symmetrical
Pyramidal	NH_3	Not Symmetrical
Tetrahedral	CH_4	Symmetrical
Trigonal Bipyramidal	PCl_5	Symmetrical
Distorted Tetrahedron	SF_4	Not Symmetrical
T-shaped	ClF_3	Not Symmetrical
Octahedral	SF_6	Symmetrical
Square Pyramidal	ClF_5	Not Symmetrical
Square Planar	XeF_4	Symmetrical

All molecules that have polar bonds and are not symmetrical will have a dipole on the molecule.

Lesson Summary

- Covalent bonds between atoms that are not identical will produce polar bonds.
- Molecules with polar bonds and non-symmetrical shapes will have a dipole.

Review Questions

1. What two requirements should be satisfied for a molecule to be polar? **(Beginning)**

2. BF_3 contains polar bonds but the molecule is not polar. Why not? **(Intermediate)**

3. Which of the following molecules will be polar: ICl_5, $XeCl_4$, $SeCl_6$? **(Challenging)**

4. Which of the following molecules will be polar: PCl_3, SCl_2, SiF_4? **(Challenging)**

5. Which of the following molecules will have the largest dipole moment? **(Intermediate)**

A. C_2H_2

B. CH_2Cl_2

C. BF_3

D. CH_3CH_2OH

E. HF

6. Which of the following molecules will have a triple bond? **(Intermediate)**

A. C_2H_2

B. CH_2Cl_2

C. BF_3

D. CH_3CH_2OH

E. HF

7. Which of the following molecules has a central atom with sp^2 hydridized orbitals? **(Intermediate)**

A. C_2H_2

B. CH_2Cl_2

C. BF_3

D. CH_3CH_2OH

E. HF

Further Reading / Supplemental Links

http://learner.org/resources/series61.html'"

The ***learner.org*** website allows users to view streaming videos of the Annenberg series of chemistry videos. You are required to register before you can watch the videos but there is no charge. The website has one video that relates to this lesson called ***Molecular Architecture*** .

http://www.sparknotes.com/testprep/books/sat2/chemistry/section4section8.rhtml

http://www.up.ac.za/academic/chem/mol_geom/mol_geometry.htm

http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch8/lewis.html#step

http://en.wikipedia.org/wiki/Molecular_geometry

Vocabulary

polar bond	A covalent bond in which the shared pair of electrons are not shared equally owing to a difference in the electronegativity of the two atoms.
molecular symmetry	The property of a molecule that enables it to undergo inversion through a line, a point, or a plane, and its new state is indistinguishable from its original state.
dipole	A pair of equal and opposite charges separated by a small distance; a molecular dipole is produced when the centers of positive and negative charge do not coincide.

Review Answers

1. A molecule will be polar if 1) it contains at least one polar bond, and 2) if the molecule is not symmetrical.

2. The molecular shapes for these three molecules are, respectively, square pyramidal, square planar, and octahedral. Square planar and octahedral are symmetrical and therefore, neither of those molecules will be

polar. The square pyramidal molecule, ICl_5, will be polar.

3. The molecular shapes for these three molecules are, respectively, T-shaped, angular, and tetrahedral. T-shaped and angular molecules are not symmetrical and therefore are always polar.

4. The molecular shapes for these three molecules are, respectively, pyramidal, angular, and tetrahedral. Pyramidal and angular molecules are not symmetrical and are always polar. SiF_4 is symmetrical and will not be polar.

5. E

6. A

7. C

15. The Mathematics of Compounds

Determining Formula and Molar Masses

Lesson Objectives

- Given the formula or name of a compound and a periodic table, the student will calculate the formula mass.

Introduction

When atoms of one element chemically combine with atoms of another element, a compound is formed. Compounds have names and they have formulas. Previously, you have learned to properly write formulas and name compounds. The formula of a compound contains chemical symbols that tell us what elements are in the compound and the formula also contains subscripts that tell us the ratios of the atoms of the elements that combined. For example, the formula $MgCl_2$ tells us that this compound is composed of the elements magnesium and chlorine and that they combined in the ratio of two atoms of chlorine for each atom of magnesium. Using the relative masses of elements from the periodic table and the formula, we will calculate the relative formula mass for the compound.

Formula Mass

We have, on the periodic table, the relative masses of all the elements. By looking at the squares for carbon and helium, we can see that a carbon atom has about three times the mass of a helium atom. In this way, we can compare the relative masses of any two atoms in the table. We will now be looking at many chemical formulas and we wish to compare their masses in the same way. We can use the relative atomic masses to do exactly that. The **formula mass** of a compound is the sum of all the atomic masses in the formula. The formula for water, for example, is H_2O. This formula tells us that water is composed of hydrogen and oxygen and that their ratio is two hydrogen atoms for each oxygen atom. We can determine the formula mass for water by adding up the atomic masses of its components.

Example 1

What is the formula mass of H_2O?

Solution

Element	Atomic Mass	Number of Atoms per Formula	Product
H	1.0 Dalton	2	2.0 Dalton
O	16.0 Dalton	1	16.0 Dalton
			18.0 Dalton

The formula mass of H_2O = 18.0 Dalton.

Example 2

What is the formula mass of $Ca(NO_3)_2$?

Solution

Element	**Atomic Mass**	**Number of Atoms per Formula**	**Product**
Ca	40.0 Dalton	1	40.0 Dalton
N	14.0 Dalton	2	28.0 Dalton
O	16.0 Dalton	6	96.0 Dalton
			164.0 Dalton

The formula mass of $Ca(NO_3)_2$ = 164.0 Dalton.

These formula masses are in the same units as atomic masses and therefore are exactly comparable. That is, the atomic mass of an oxygen atom is 16 Dalton, the atomic mass of a fluorine atom is 19 amu, and the formula mass of a water molecule is 18 Dalton – that means that a water molecule is slightly more massive than an oxygen atom and slightly less massive than a fluorine atom.

Terminology

Since ionic compounds do not form molecules, the term formula mass is the only proper term for this relative mass. For covalent compounds, since they do form molecules, the formula mass may also be called the molecular mass. On the other hand, there are professional chemists who occasionally refer to the “molecular mass” of NaCl and so far no degrees in chemistry have been recalled due to such a slip of the tongue.

Lesson Summary

- The molecular mass of a molecule is found by adding the atomic masses of all the atoms in one molecule.
- Not all substances exist as molecules and therefore, the term molecular mass is not used for all substances. The masses of ionic compounds and empirical formulas are called formula mass.

Review Questions

1. Calculate the formula mass for each of the following. **(Beginning)**

A. K_2SO_4

B. CuO

C. $Mg_3(AsO_4)_2$

D. $Ca_3(PO_4)_2$

E. Fe_2O_3

F. $Al(OH)_3$

G. $(NH_4)_2S$

H. $C_{12}H_{22}O_{11}$

2. How many times heavier are bromine atoms on the average than neon atoms? **(Beginning)**

3. An unknown element, M, combines with oxygen to form a compound with a formula of MO_2. If 25.0 grams of the unknown element combines with 4.50 grams of oxygen, what is the atomic mass of M? **(Challenging)**

Vocabulary

formula mass	The sum of the atomic masses of the atoms in a formula.
molecular mass	The mass of a molecule found by adding the atomic masses of the atoms comprising the molecule.

Review Answers

1.

A. 174 g/mol

B. 79.5 g/mol

C. 351 g/mol

D. 310. g/mol

E. 160. g/mol

F. 78.0 g/mol

G. 68.0 g/mol

H. 342 g/mol

2. $\frac{\text{mass of Br}}{\text{mass of Ne}} = \frac{79.9}{20.2}$ = 3.96 times

3. The compound contains twice as many oxygen atoms as it does M atoms. Therefore, the mass ratio of an equal number of atoms of M to and atoms of oxygen would be $\frac{25.0\text{ g}}{2.25\text{ g}}$. This means that one atom of M is 11.1 times as heavy as an oxygen atom.

atomic mass of M = (11.1)(16.0 daltons) = 178 daltons

The Mole

Lesson Objectives

- Given the number of particles of a substance, the student will use Avogadro's number to convert to moles and vice versa.
- Given the number of moles of a substance, the student will use the molar mass to convert to grams and vice versa.

Introduction

When objects are very small, it is often inconvenient or inefficient, or even impossible to deal with the objects one at a time. For these reasons, we often deal with very small objects in groups, and have even invented names for various numbers of objects. The most common of these is “dozen” which refers to 12 objects.

We frequently buy objects in groups of 12, like doughnuts or pencils. Even smaller objects such as straight pins or staples are usually sold in boxes of 144, or a dozen dozen. A group of 144 is called a "gross."

This problem of dealing with things that are too small to operate with as single items also occurs in chemistry. Atoms and molecules too small to see, let alone to count or measure. Chemists needed to select a group of atoms or molecules that would be convenient to operate with.

Origin of the Mole

In chemistry, it is impossible to deal with a single atom or molecule because we can't see them or count them or weigh them. Chemists have selected a number of particles with which to work that is convenient. Since molecules are extremely small, you may suspect that this number is going to be very large and you are right. The number of particles in this group is 6.02×10^{23} particles and the name of this group is the **mole** (the abbreviation for ***mole*** is ***mol***). One mole of any object is 6.02×10^{23} of those objects. There is a very particular reason that this number was chosen and we hope to make that reason clear to you.

When chemists are carrying out chemical reactions, it is important that the relationship between the numbers of particles of each reactant is known. Chemists looked at the atomic masses on the periodic table and understood that the mass ratio of one carbon atom to one sulfur atom was 12 amu to 32 amu. They realized that if they massed out 12 grams of carbon and 32 grams of sulfur, they would have the same number of atoms of each element. They didn't know how many atoms were in each pile but they knew the number in each pile had to be the same. This is the same logic as knowing that if a basketball has twice the mass of a soccer ball and you massed out 100 lbs of basketballs and 50 lbs of soccer balls, you would have the same number of each ball.

The technique of taking one atomic mass or molecular mass in grams of substances for reactions was used to get equal numbers of particles. This amount of substance (its molecular mass in grams) became known as a gram-molecular mass. One gram-molecular mass of any substance had the same number of particles in it. Many years later, when it became possible to count particles using electrochemical reactions, the number of particles in a gram-molecular mass was counted. That number turned out to be 6.02×10^{23} particles. That group of particles continued to be called a gram-molecular mass for many years, but eventually chemists decided to call that number of particles a mole.

In present day, 1.00 mole of carbon-12 atoms has a mass of 12.0 grams and contains 6.02×10^{23} atoms. Likewise, 1.00 mole of water has a mass of 18.0 grams and contains 6.02×10^{23} molecules. 1.00 mole of any element or compound has a mass equal to its molecular mass in grams and contains 6.02×10^{23} particles. The mass in grams of 6.02×10^{23} particles of a substance is now called the **molar mass** (mass of 1.00 mole).

Converting Molecules to Moles and Vice Versa

The number 6.02×10^{23} is called Avogadro's number and is symbolized as N (the capital letter N). Avogadro, of course, had no hand in determining this number, rather it was named in honor of Avogadro. The mass of a single molecule of H_2SO_4 is 98 Dalton and the mass of an Avogadro number of molecules of H_2SO_4 is 98 grams. We can use this information to find the mass in grams of a single H_2SO_4 molecule because we know that 98 grams contains 6.02×10^{23} molecules. If we divide 6.02×10^{23} molecules into 98 grams, we will get the mass of a single molecule of H_2SO_4 in grams. The answer is 1.6×10^{-22} grams/molecule – tiny, indeed. If we are given a number of molecules of a substance, we can convert it into moles by dividing by Avogadro's number and vice versa.

Example 3

How many moles are present in 1,000,000,000 (1 trillion or 1×10^9) molecules of water?

Solution

$$\text{moles} = (1{,}000{,}000{,}000 \text{ molecules})\left(\frac{1 \text{ mole}}{6.02 \times 10^{23} \text{ molecules}}\right) = 1.7 \times 10^{-15} \text{ moles}$$

You should note that this amount of water is too small for even our most delicate balances to determine the mass. A *very* large number of molecules must be present before the mass is large enough to detect with our balances.

Example 4

How many molecules are present in 0.00100 mole?

Solution

molecules = (moles)(6.02 x 10^{23} molecules/mole)

molecules = (0.00100 mole)(6.02 x 10^{23} molecules/mole) = 6.02 x 10^{20} molecules

This is a number of water molecules whose mass we can measure with a balance, 602,000,000,000,000,000,000.

Converting Grams to Moles and Vice Versa

We can also convert back and forth between grams of substance and moles. The conversion factor for this is the molar mass of the substance. To convert the grams of a substance into moles, we divide by the molar mass and to convert the moles of a substance into grams, we multiply by the molar mass.

Example 5

How many moles are present in 108 grams of water?

Solution

$$\text{moles} = \frac{\text{grams}}{\text{molar mass}} = \frac{108 \text{ grams}}{18.0 \text{ grams/mole}} = 6.00 \text{ moles}$$

Example 6

What is the mass of 7.50 moles of CaO?

Solution

Grams = (moles)(molar mass) = (7.50 moles)(56.0 grams/mole) = 420. Grams

Lesson Summary

- There are 6.02 x 10^{23} particles in 1.00 mole. This number is called Avogadro's number.
- The number of moles in a given number of molecules of a substance can be found by dividing the number of molecules by Avogadro's number.
- The number of moles in a given mass of substance can be found by dividing the mass by the formula mass expressed in g/mol.

Review Questions

1. Convert the following to moles. **(Intermediate)**

A. 60.0 grams of NaOH

B. 2.73 grams of NH_4Cl

C. 5.70 grams of ZrF_4

D. 10.0 grams of PbO_2

2. Convert the following to grams. **(Intermediate)**

A. 0.100 moles of CO_2

B. 0.437 moles of NaOH

C. 0.500 moles of $(NH_4)_2CO_3$

D. 3.00 moles of $ZnCl_2$

3. How many molecules are present in the following quantities? **(Intermediate)**

A. 0.250 mole of H_2O

B. 6.00 moles of H_2SO_4

C. 0.00450 mole of $Al_2(CO_3)_3$

4. How many moles are present in the following quantities? **(Intermediate)**

A. 1.00×10^{20} molecules of H_2O

B. 1.00×10^{25} molecules of H_2

C. 5,000,000,000,000 atoms of carbon

5. How many molecules (or atoms) are present in the following masses? **(Challenging)**

A. 1.00 gram of Na_2CO_3

B. 8.00 grams of helium

C. 1000. grams of H_2O

6. Convert the following to grams. **(Challenging)**

A. 1.00×10^{23} molecules of H_2

B. 1.00×10^{24} molecules of $AlPO_4$

C. 1.00×10^{22} molecules of NaOH

7. What is the mass of a single atom of silver, Ag, in grams? **(Intermediate)**

8. If you had a silver bar that exactly fit inside a 100. mL graduated cylinder and filled it precisely to the 100. mL mark, how many atoms of silver would be in the bar? The density of silver is 10.5 g/mL. **(Challenging)**

Further Reading / Supplemental Links

- http://learner.org/resources/series61.html
- The ***learner.org*** website allows users to view streaming videos of the Annenberg series of chemistry videos. You are required to register before you can watch the videos but there is no charge. The website has one video that relates to this lesson called ***The Mole*** .
- Website with lessons, worksheets, and quizzes on various high school chemistry topics.
- Lesson 5-5 is on Molar Mass.
- Lesson 9-1 is on The Mole.
- http://www.fordhamprep.org/gcurran/sho/sho/lessons/lesson31.htm

Vocabulary

Avogadro's number:	The number of objects in a mole; equal to 6.02 x 10^{23}.
mole	An Avogadro's number of objects.

Answers for Review Questions

1.

A. $\frac{60.0\ \text{g}}{40.0\ \text{g/mol}}$ = 1.50 mole

B. $\frac{2.73\ \text{g}}{53.5\ \text{g/mol}}$ = 0.0510 mole

C. $\frac{5.70\ \text{g}}{167.2\ \text{g/mol}}$ = 0.0341 mole

D. $\frac{10.0\ \text{g}}{239\ \text{g/mol}}$ = 0.0418 mole

2.

A. (0.100 mol)(44.0 g/mol) = 4.40 grams

B. (0.437 mol)(40.0 g/mol) = 17.5 grams

C. (0.500 mol)(96.0 g/mol) = 48.0 grams

D. (3.00 mols)(136.4 g/mol) = 409 grams

3.

A. (0.250 mol)(6.02 x 10^{23} molecules/mol) = 1.51 x 10^{23} molecules

B. (6.00 mol)(6.02 x 10^{23} molecules/mol) = 3.61 x 10^{24} molecules

C. (0.00450 mol)(6.02 x 10^{23} molecules/mol) = 2.71 x 10^{21} molecules

4.

A. $(1.00 \times 10^{20}$ molecules$)\left(\frac{1.00 \text{ mol}}{6.02 \times 10^{23} \text{ molecules}}\right) = 1.66 \times 10^{-4}$ mole

B. $(1.00 \times 10^{25}$ molecules$)\left(\frac{1.00 \text{ mol}}{6.02 \times 10^{23} \text{ molecules}}\right) = 16.6$ moles

B. $(5 \times 10^{12}$ molecules$)\left(\frac{1.00 \text{ mol}}{6.02 \times 10^{23} \text{ molecules}}\right) = 8.31 \times 10^{-12}$ mole

5.

A. moles $Na_2CO_3 = \frac{1.00 \text{ g}}{106 \text{ g/mol}} = 0.00943$ mole

molecules = (0.00943 mole)(6.02×10^{23} molecules/mole) = 5.68×10^{21} molecules

B. moles He = $\frac{8.00 \text{ g}}{4.00 \text{ g/mol}} = 2.00$ mole

atoms = (2.00 mole)(6.02×10^{23} molecules/mole) = 1.20×10^{24} molecules

C. moles $H_2O = \frac{1000. \text{ g}}{18.0 \text{ g/mol}} = 55.6$ mole

molecules = (55.6 mole)(6.02×10^{23} molecules/mole) = 3.35×10^{25} molecules

6.

A. moles $H_2 = \frac{1.00 \times 10^{23}}{6.02 \times 10^{23}} = 0.166$ mol

grams H_2 = (0.166 mol)(2.00 g/mol) = 0.664 grams

B. moles $AlPO_4 = \frac{1.00 \times 10^{24}}{6.02 \times 10^{23}} = 1.66$ mol

grams $AlPO_4$ = (1.66 mol)(122 g/mol) = 203 grams

C. moles NaOH = $\frac{1.00 \times 10^{22}}{6.02 \times 10^{23}} = 0.0166$ mol

grams NaOH = (0.0166 mol)(40.0 g/mol) = 0.664 grams

7. 6.02×20^{23} atoms of silver have a mass of 108 grams. Therefore, one atom of Ag would have a mass of $\frac{108 \text{ g}}{6.02 \times 10^{23} \text{ atoms}} = 1.79 \times 10^{-22}$ grams/atom.

8. mass of silver = (100. mL)(10.5 g/mL) = 1050 g

moles of silver = $\frac{1050 \text{ g}}{108 \text{ g/mol}} = 9.72$ moles

number of silver atoms = (9.72 moles)($6.02 \times 10^{23} = 5.85 \times 10^{24}$ atoms

Percent Composition

Lesson Objectives

- Given either masses of elements in a compound, the student will calculate the percent composition by mass.
- Given the formula or name of a compound, the student will calculate the percent composition by mass.

Introduction

Metals that are useful to man usually begin as ore in a mine. The ore is removed from the mine and partially purified by simply washing away the dirt and other non-chemically combined materials. This partially purified ore is then treated chemically in smelters or other purifying processes to separate pure metal from the other elements. The value of the original ore is very dependent on how much pure metal can eventually be separated from it. High grade ore and low grade ore command a significantly different price. The ore can be evaluated before it is mined or smelted to determine what percent of the ore can eventually become pure metal. The process involves determining what percent of the ore is metal compounds and then determining what percent of the metal compounds is pure metal.

Percent Composition from Masses

Compounds are made up of two or more elements. The Law of Definite Proportions tells us that the proportion, by mass, of the elements in a compound is always the same. Water, for example, is always 11% hydrogen and 89% oxygen by mass. The **percentage composition** of a compound is the percentage by mass of each of the elements in the compound.

Percentage composition can be determined by experiment. To do this, a known quantity of a compound is decomposed in the laboratory and the mass of each of the elements is measured. Then the mass of each element is divided by the total mass of the original compound. This tells us what fraction of the compound is made up of that element. This fraction can then be multiplied by 100 to convert it to a percent.

Example 7

Laboratory procedures show that 50.0 grams of ammonia, NH_3, yields 41.0 grams of nitrogen and 9.00 grams of hydrogen upon decomposition. What is the percent composition of ammonia?

Solution

$$\%\ \text{Nitrogen} = \left(\frac{41.0\ grams}{50.0\ grams}\right)(100) = 82\%$$

$$\%\ \text{Hydrogen} = \left(\frac{9.00\ grams}{50.0\ grams}\right)(100) = 18\%$$

Example 8

The decomposition of 25.0 grams of $Ca(OH)_2$ in the lab produces 13.5 grams of calcium, 10.8 grams of oxygen and 0.68 grams of hydrogen. What is the percent composition of calcium hydroxide?

Solution

$$\%\ \text{Calcium} = \left(\frac{13.5\ grams}{25.0\ grams}\right)(100) = 54.0\%$$

$$\%\ \text{Oxygen} = \left(\frac{10.8\ grams}{25.0\ grams}\right)(100) = 43.2\%$$

% Hydrogen = $\left(\frac{0.68\ grams}{25.0\ grams}\right)$ (100) = 2.8%

You should note that the sum of the percentages always adds to 100%. Sometimes, it may total 99 % or 101 % due to rounding, but if it totals to 96 % or 103%, you have an error.

Percent Composition from the Formula

Percent composition can also be calculated from the formula of a compound. Consider the formula for the compound, iron (III) oxide, Fe_2O_3. The percent composition of the elements in this compound can be calculated by dividing the total atomic mass of the atoms of each element in the formula by the formula mass

Example 9

What is the percent composition of iron (III) oxide, Fe_2O_3?

Solution

Element	Atomic Mass	Number of Atoms per Formula	Product
Fe	55.8 daltons	2	111.6 daltons
O	16.0 daltons	3	48.0 daltons
		The formula mass of Fe_2O_3 =	159.6 daltons

% iron = $\left(\frac{111.6}{159.6}\right)$ (100) = 69.9%

% oxygen = $\left(\frac{48.0}{159.6}\right)$ (100) = 30.1%

Example 10

What is the percent composition of aluminum sulfate, $Al_2(SO_4)_3$?

Solution

Adding up the formula mass = 2(27.0 daltons) + 3(32.0 daltons) + 12(16.0 daltons) = 342.0 daltons

% aluminum = $\left(\frac{54.0}{342}\right)$ (100) = 15.8%

% sulfur = $\left(\frac{96.0}{342}\right)$ (100) = 28.1%

% oxygen = $\left(\frac{192}{342}\right)$ (100) = 56.1%

Lesson Summary

- The percent composition of a compound is the percent of the total mass contributed by each of the elements in the compound.

- Percent composition can be determined either from the masses of each element in the compound or from the formula of the compound.

Further Reading / Supplemental Links

- Website with lessons, worksheets, and quizzes on various high school chemistry topics.
- Lesson 5-8 is on Percent Composition.

http://www.fordhamprep.org/gcurran/sho/sho/lessons/lesson31.htm

- The following website has solved example problems for a number of topics including:
- Calculating percent composition by mass.
- Empirical formulas from mass.
- Empirical formulas from percent composition.
- Molecular formulas from empirical formulas and molar mass.
- The website also has material applicable to topics in later chapters . . . so you may want to remember this website for later use.
- http://www.sciencejoywagon.com/chemzone/05chemical-reactions/

Review Questions

Determine the percent composition of the following compounds. **(Intermediate)**

1. BF_3

2. $Ca(C_2H_3O_2)_2$

3. FeF_3

4. $CrCl_3$

5. $(NH_4)_3PO_4$

Vocabulary

percent composition: The proportion of an element present in a compound found by dividing the mass of the element by the mass of the whole compound and multiplying by 100.

Answers for Review Questions

1. molar mass of BF_3 = 67.81 g/mol

$$\% \text{ B} = \frac{10.81}{67.81} \times 100 = 15.9\%$$

$$\% \text{ F} = \frac{57.00}{67.81} \times 100 = 84.1\%$$

2. molar mass of = 153.17 g/mol

$\% \text{ Ca} = \frac{40.08}{153.17} \times 100 = 26.2\%$

$\% \text{ C} = \frac{48.04}{153.17} \times 100 = 31.4\%$

$\% \text{ H} = \frac{1.05}{153.17} \times 100 = 0.69\%$

$\% \text{ O} = \frac{64.00}{153.17} \times 100 = 41.8\%$

3. 49.5 % iron and 50.5 % fluorine

4. 32.8 % chromium and 67.2 % chlorine

5. 28.2 % nitrogen, 8.1 % hydrogen, 20.8 % phosphorus, and 42.9 % oxygen

Empirical and Molecular Formulas

Lesson Objectives

- The student will reduce molecular formulas to empirical formulas.
- Given either masses or percent composition of a compound, the student will determine the empirical formula.
- Given either masses or percent composition of a compound and the molar mass, the student will determine the molecular formula.

Introduction

The empirical formula is the simplest ratio of atoms in a compound. Formulas for ionic compounds are always empirical formulas but for covalent compounds, the empirical formula is not always the actual formula for the molecule. Molecules such as benzene, C_6H_6, would have an empirical formula of CH.

Finding Empirical Formula from Experimental Data

Empirical formulas can be determined from experimental data or from percent composition. Consider the following example.

Example 11

We find that a 2.50 gram sample of a compound contains 0.900 grams of calcium and 1.60 grams of chlorine. The compound contains only these two elements. We can calculate the number of moles of calcium atoms and the number of moles of chlorine *atoms* in the compound. We can then find the ratio of moles of calcium atoms to moles of chlorine atoms and from this; we can determine the empirical formula.

Solution

First, we convert the mass of each element into moles.

$\text{moles of Ca} = \frac{0.900 \text{ g}}{40.1 \text{ g/mol}} = 0.0224 \text{ mole Ca}$

$\text{moles of Cl atoms} = \frac{1.60 \text{ g}}{35.5 \text{ g/mol}} = 0.0451 \text{ mole Cl}$

At this point, we have the correct ratio for the atoms in the compound, $Ca_{0.0224}Cl_{0.0451}$, except that this isn't an acceptable formula. We need to find the simplest *whole* number ratio. To find a simple whole number ratio for these numbers, we divide each of them by the smallest of them.

$$\text{moles of Ca} = \frac{0.0224}{0.0224} = 1.00\text{ Ca}$$

$$\text{moles of Cl} = \frac{0.0451}{0.0224} = 2.01\text{ Cl}$$

Now, we can see the correct empirical formula for this compound is $CaCl_2$.

It is important to note that when solving for empirical formulas, we are determining the number of atoms of each element in the compound. Therefore, those substances which occur in nature as diatomic molecules such as Cl_2, O_2, H_2, N_2, and so on, are dealt with as atoms in this procedure.

Finding Empirical Formula from Percent Composition

When finding the empirical formula from percent composition, the first thing we do is to convert the percentages into masses. For example, suppose we are given the percent composition of a compound as 40.0 % carbon, 6.71 % hydrogen, and 53.3 % oxygen. Since every sample of this compound regardless of size will have the same composition in terms of ratio of atoms, we could choose a sample of any size. Suppose we choose a sample size of 100. grams. The masses of each of the elements in this sample will be 40.0 grams of carbon, 6.71 grams of hydrogen, and 53.3 grams of oxygen. These masses can then be used to find the empirical formula. You should note that you could use any size sample. You could choose a sample size of 167.8 grams and take the percentages of this sample to get the masses of the individual elements. We choose a sample size of 100. grams because it makes the arithmetic simple.

Example 12

Find the empirical formula of a compound whose percent composition is 40.0 % carbon, 6.71 % hydrogen, and 53.3 % oxygen.

Solution

We choose a sample size of 100. grams and multiply this 100. gram sample by each of the percentages to get masses for each element. This would yield 40.0 grams of carbon, 6.71 grams of hydrogen, and 53.3 grams of oxygen. The next step is to convert the mass of each element into moles.

$$\text{moles of C} = \frac{40.0\text{ g}}{12.0\text{ g/mol}} = 3.33\text{ moles C}$$

$$\text{moles of H} = \frac{6.71\text{ g}}{1.01\text{ g/mol}} = 6.64\text{ moles H}$$

$$\text{moles of O} = \frac{53.3\text{ g}}{16.0\text{ g/mol}} = 3.33\text{ mole Ca}$$

Then, we divide all three numbers by the smallest one to get simple whole number ratios:

$$C = \frac{3.33}{3.33} = 1 \qquad H = \frac{6.64}{3.33} = 2 \qquad O = \frac{3.33}{3.33} = 1$$

and finally, we can write the empirical formula, CH_2O.

Sometimes, the technique of dividing each of the moles by the smallest to get a whole number ratio does not yield whole numbers. Whenever the subscript for any element in the empirical formula is "1," dividing each of the moles by the smallest will yield a simple whole number ratio but if none of the elements in the empirical formula has a subscript of "1," then this technique will not yield a simple whole number ratio. In those cases, a little more work is required.

Example 13

Determine the empirical formula for a compound that is 66.0 % calcium and 34.0 % phosphorus.

Solution

We choose a sample size of 100. grams and multiply the 100. grams by the percentage of each element to get masses. This yields 66.0 grams of calcium and 34.0 grams of phosphorus. We then divide each of these masses by their molar mass to convert to moles.

moles of Ca = $\frac{66.0\ \text{g}}{40.1\ \text{g/mol}}$ = 1.65 moles Ca

moles of P = $\frac{34.0\ \text{g}}{31.0\ \text{g/mol}}$ = 1.10 moles P

We then divide each of these moles by the smallest.

Ca = $\frac{1.65}{1.10}$ = 1.50 P = $\frac{1.10}{1.10}$ = 1.00

In this case, dividing each of the numbers by the smallest one does not yield a simple whole number ratio. In such a case, we must multiply both numbers by some factor that will produce a whole number ratio. If we multiply each of these by 2, we get a whole number ratio of 3 Ca to 2 P. Therefore, the empirical formula is Ca_3P_2.

Finding Molecular Formulas

Empirical formulas show the simplest whole number ratio of the atoms in a compound. Molecular formulas show the actual number of atoms of each element in a compound. When you find the empirical formula from either masses of elements or from percent composition, as demonstrated in the previous section, for the compound N_2H_4, you will get an empirical formula of NH_2 and for C_3H_6, you will get CH_2. If we want to determine the actual molecular formula, we need one additional piece of information. The molecular formula is always a whole number multiple of the empirical formula. That is, in order to get the molecular formula for N_2H_4, you must double each of the subscripts in the empirical formula. Since the molecular formula is a whole number multiple of the empirical formula, the molecular mass will be the same whole number multiple of the formula mass. The formula mass for NH_2 is 14 g/mol and the molecular mass for N_2H_4 is 28 g/mol. When we have the empirical formula and the molecular mass for a compound, we can divide the formula mass into the molecular mass and find the whole number that we need to multiply by each of the subscripts in the empirical formula.

Example 14

Suppose we have the same problem as in example 12 except that we are also given the molecular mass of the compound as 180 grams/mole and we are asked for the molecular formula. In example 12, we determined the empirical formula to be CH_2O. This empirical formula has a formula mass of 30.0 g/mol. In order to find the molecular formula for this compound, we divide the formula mass into the molecular mass (180 divided by 30) and find the multiplier for the empirical formula to be 6. As a result, the molecular formula for this compound will be $C_6H_{12}O_6$.

Example 15

Find the molecular formula for a compound with percent composition of 85.6 % carbon and 14.5% hydrogen. The molecular mass of the compound is 42.1 g/mol.

Solution

We choose a sample size of 100. g and multiply each element percentage to get masses for the elements in this sample.

This yields 85.6 g of C and 14.5 g of H.

Dividing each of these by their atomic mass yields 7.13 moles of C and 14.4 moles of H.

Dividing each of these by the smallest yields a whole number ratio of 1 carbon to 2 hydrogen.

Thus, the empirical formula will be CH_2.

The formula mass of CH_2 is 14 g/mol.

Dividing 14 g/mol into the molecular mass of 42.1 g/mol yields a multiplier of 3.

The molecular formula will be C_3H_6.

Lesson Summary

- The empirical formula of a compound indicates the simplest whole number ratio of atoms present in the compound.
- The empirical formula of a compound can be calculate from the masses of the elements in the compound or from the percent composition.
- The molecular formula of a compound is some whole number multiple of the empirical formula.

Review Questions

1. What is the empirical formula for C_8H_{18}? **(Beginning)**

2. What is the empirical formula for C_6H_6? **(Beginning)**

3. What is the empirical formula for WO_2? **(Beginning)**

4. A compound has the empirical formula C_2H_8N and a molar mass of 46 grams/mol. What is the molecular formula of this compound? **(Beginning)**

5. A compound has the empirical formula C_2H_4NO. If its molar mass is 116.1 grams/mole, what is the molecular formula of the compound? **(Beginning)**

6. A sample of pure indium chloride with a mass of 0.5000 grams is found to contain 0.2404 grams of chlorine. What is the empirical formula of this compound? **(Intermediate)**

7. Determine the empirical formula of a compound that contains 63.0 grams of rubidium and 5.90 grams of oxygen. **(Intermediate)**

8. Determine the empirical formula of a compound that contains 58.0% Rb, 9.50% N, and 32.5% O. **(Intermediate)**

9. Determine the empirical formula of a compound that contains 33.3% Ca, 40.0% O, and 26.7% S. **(Intermediate)**

10. Find the molecular formula of a compound with percent composition 26.7 % P, 12.1 % N, and 61.2 % Cl and with a molecular mass of 695 g/mol. **(Challenging)**

Further Reading / Supplemental Links

- Zumdahl, Steven S. and Zumdahl, Susan A., Chemistry, Fifth Edition, Chapter 3: Stoichiometry, Houghton Mifflin Company, New York, 2000.
- Website with lessons, worksheets, and quizzes on various high school chemistry topics.
- Lesson 5-5 is on Empirical Formulas.
- http://www.fordhamprep.org/gcurran/sho/sho/lessons/lesson55.htm
- http://misterguch.brinkster.net/molarmass.html
- http://www.ausetute.com.au/percentc.html
- http://www.chem.lsu.edu/lucid/tutorials/empiricalform.html

Vocabulary

empirical formula:	The formula giving the simplest ratio between the atoms of the elements present in a compound.
molecular formula	A formula indicating the actual number of each kind of atom contained in a molecule.

Review Answers

1. C_4H_9

2. CH

3. WO_2

4. C_2H_8N

5. $C_4H_8N_2O_2$

6.

moles of atoms of Cl = $\frac{0.2404\ \text{g}}{35.45\ \text{g/mol}}$ = 0.006781 mols

moles of atoms of In = $\frac{0.2596\ \text{g}}{114.82\ \text{g/mol}}$ = 0.002261 mols

Dividing each by the smallest yields

Cl = $\frac{0.006781}{0.002261}$ = 3.00

In = $\frac{0.002261}{0.002261}$ = 1.00

Therefore, the empirical formula is $InCl_3$.

7. Rb_2O

8. $RbNO_3$

9. $CaSO_3$

10. $P_6N_6Cl_{12}$

16. Chemical Reactions

Chemical Equations

Lesson Objectives

- The student will read chemical equations and provide requested information contained in the equation including information about substances, reactants, products, and physical states.
- The student will convert symbolic equations into word equations and vice versa.
- The student will use the common symbols, $\rightarrow$, +, (s) (l) (g) (aq), appropriately.
- The student will describe the roles of subscripts and coefficients in chemical equations.
- The student will balance chemical equations with the simplest whole number coefficients.

Introduction

A chemical change occurs when some substances (it could even be the same substance) come into contact, the chemical bonds of the substances break, and the atoms that compose the compounds separate and re-arrange themselves into new compounds with new chemical bonds. When this process occurs, we call it a **chemical reaction**. In order to describe a chemical reaction, we need to indicate what substances were present at the beginning and what substances were present at the end. The substances that were present at the beginning are called **reactants** and the substances present at the end are called **products**. In many chemical reactions, it is necessary not only to name the reactants and products but also to indicate the phase of each substance.

Molecules not only have a particular group of atoms arranged in an exact way, they also have a specific amount of potential energy associated with their chemical bonds. When reactants re-arrange the organization of their atoms and bonds, the amount of potential energy associated with the reactant bonds is almost never the same as the amount of energy associated with the product bonds. Therefore, energy must be absorbed or given off by the reaction. For some reactions, the potential energy difference between the reactant bonds and product bonds must be represented in the equation.

All of this information about a chemical reaction, reactants, products, phases, and energy changes can be described in words or it can be presented by a special shorthand notation devised precisely for communicating this information.

Some Interactions Represent Chemical Reactions

We know already that chemistry is the study of matter and that the Law of Conservation of Matter states that matter is conserved in a chemical reactions. But what does this really mean? When you place an ice cube on the counter and it melts, do you think the mass has changed? Of course you don't, but why not? The reason is because the mass before and after a (non-nuclear) change has to remain the same. Energy works the same way. The Law of Conservation of Energy states that total energy involved in a chemical reaction is conserved from reactants to products.

Energy cannot be created nor destroyed in a closed system. Think of it as balancing on a seesaw. If energy is absorbed by the reaction, it has to have come from somewhere in the closed system. Let's look at an example: $H_2O_{(s)} + 3312\ J \rightarrow H_2O_{(L)}$ Thus it takes 3312 Joules of energy to melt one ice cube of approximately 0.01kg. The 3312 Joules is an energy unit. Where did the energy come from? The energy came from the kinetic energy in the room where the ice cube was melting. So the energy was absorbed by the ice cube and released by the room. Therefore, the total amount of energy remained constant in the room. The mass of the ice cube is the same as the mass of the liquid puddle. Therefore mass was conserved. See how it works? We will go into further depth with this concept as we explore chemical reactions in detail through the remainder of this unit.

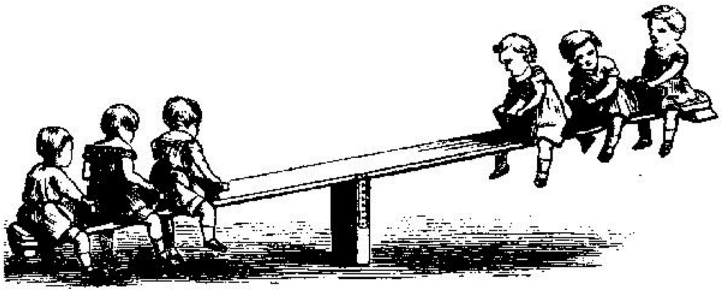


Image 1: Kids on a seesaw. (*Source:* http://commons.wikimedia.org/wiki/File:SeesawwithKids, *License:* Public Domain)

Reactants Change into Products

Sometimes when reactants are put into a reaction vessel, a reaction will take place to produce products. Reactants are the starting materials, that is, whatever we have as our initial ingredients. The products are just that, what is produced or the result of what happens to the reactants when we put them together in the reaction vessel. If we think about baking chocolate chip cookies, our reactants would be flour, butter, sugar, vanilla, some baking soda, salt, egg, and chocolate chips. What would be the products? Cookies! The reaction vessel would be our mixing bowl.

Flour + Butter + Sugar + Vanilla + Baking Soda + Eggs + Chocolate Chips → Cookies

Chemical reactions are similar. If sulfur dioxide is added to oxygen, sulfur trioxide is produced. Sulfur dioxide and oxygen ($SO_2 + O_2$) are reactants and sulfur trioxide (SO_3) is the product.

$$\underset{\text{Reactants}}{\underline{2\,SO_{2(g)} + O_{2(g)}}} \longrightarrow \underset{\text{Products}}{\underline{2\,SO_{3(g)}}}$$

In chemical reactions, the reactants are found before the symbol " → " and the products and found after the symbol " → ". The general equation for a reaction is:

Reactants → Products

We will explore more about this in the next section.

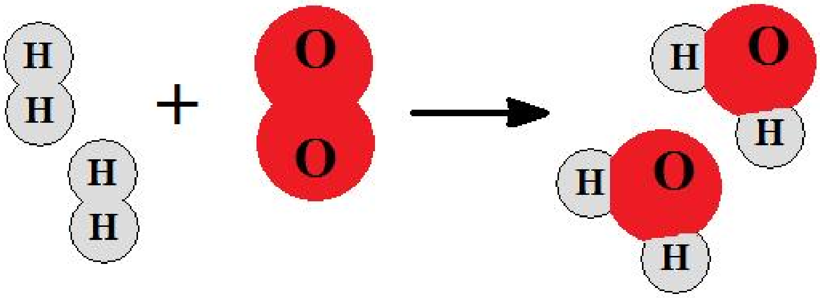
Symbol Equations are Shorthand for Word Equations

There are a few special symbols that we need to know in order to "talk" in chemical shorthand. Remember when you started learning pre-algebra and you learned the order of operations. We may have all learned the acronym **BEDMAS** for brackets, exponents, division, multiplication, addition, and subtraction. The acronym was a shorthand method or symbolic notation for the order of operations when we want to "talk" in mathematical equations. We have the same thing for chemistry when we want to "talk" in chemical equations. In the table below is the summary of the major symbols used in chemical equations. You will find there are others but these are the main ones that we need to memorize.

Table 16.1: Common Symbols

Symbol	Meaning
→	Symbol used to separate reactants and products; means "to produce", can be read as "yields" Ex: $2H_2 + O_2 \rightarrow 2H_2O$
+	Symbol used to separate reactants and/or products in a chemical reaction; means "is added to". $2H_2 + O_2 \rightarrow 2H_2O$ $AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$
(s)	In the solid state Sodium in the solid state: Na(s) Gold in the solid state: Au(s)
(l)	In the liquid state Water in the liquid state: $H_2O(l)$ Mercury in the liquid state: Hg(l)
(g)	In the gaseous state Helium in the gaseous state: He(g) Carbon dioxide in the gaseous state: $CO_2(g)$
(aq)	In the aqueous state, dissolved in water to make a solution Sodium chloride solution: NaCl(aq) Hydrochloric acid solution: HCl(aq)

Chemists have a choice of methods for describing a chemical reaction. They could draw a picture of the chemical reaction.



Or, they could write a word equation for the chemical reaction.

Two molecules of hydrogen gas react with one molecule of oxygen gas to produce two molecules of water vapor.

Or, they could write the equation in chemical shorthand.

$$2\,H_{2(g)} + O_{2(g)} \rightarrow 2\,H_2O_{(g)}$$

In the symbolic equation, chemical formulas are used instead of chemical names for reactants and products and symbols are used to indicate the phase of each substance. It should be apparent that the chemical shorthand method is the quickest and clearest method for writing chemical equations.

I could write that an aqueous solution of calcium nitrate is added to an aqueous solution of sodium hydroxide to produce solid calcium hydroxide and an aqueous solution of sodium nitrate. Or in shorthand I could write:

$$Ca(NO_3)_{2(aq)} + 2NaOH_{(aq)} \rightarrow Ca(OH)_{2(s)} + 2NaNO_{3(aq)}$$

How much easier is that to read? Let's try it in reverse? Look at the following reaction in shorthand notation and write the word equation for the reaction.

$$Cu_{(s)} + AgNO_{3(aq)} \rightarrow Cu(NO_3)_{2(aq)} + Ag_{(s)}$$

The word equation for this reaction might read something like "solid copper reacts with an aqueous solution of silver nitrate to produce a solution of copper (II) nitrate with solid silver".

Sample question: Transfer the following symbolic equations into word equations or word equations into symbolic equations.

(a) $HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(L)}$

(b) Gaseous propane (C_3H_8) burns in oxygen gas to produce gaseous carbon dioxide and liquid water.

(c) Hydrogen fluoride gas reacts with an aqueous solution of potassium carbonate to produce an aqueous solution of potassium fluoride, liquid water, and gaseous carbon dioxide.

Solution:

(a) An aqueous solution of hydrochloric acid reacts with an aqueous solution of sodium hydroxide to produce an aqueous solution of sodium chloride and liquid water.

(b) $C_3H_{8(g)} + O_{2(g)} \rightarrow CO_{2(g)} + H_2O_{(L)}$

(c) $HF_{(g)} + K_2CO_{3(aq)} \rightarrow KF_{(aq)} + H_2O_{(L)} + CO_{2(g)}$

Lesson Summary

- Chemical reactions can be represented by word equations or by formula equations.
- Formula equations have reactants on the left, an arrow that is read as "yields," and the products on the right.

Review Questions

1. Mothballs are commonly used to preserve clothing in “off-season.” We recognize mothballs due to its smell because of a chemical compound known as Naphthalene, $C_{10}H_8$. What are the different elements found in naphthalene and how many atoms of each are found in the formula? **(Beginning)**

2. Do you think a chemical reaction occurs every time two substances are placed together in a reaction vessel? **(Beginning)**

3. Transfer the following symbolic equations into word equations. **(Beginning)**

(a) $H_2SO_{4(aq)} + NaCN_{(aq)} \rightarrow HCN_{(aq)} + Na_2SO_{4(aq)}$

(b) $Cu(s) + AgNO_{3(aq)} \rightarrow Ag_{(s)} + Cu(NO_3)_{2(aq)}$

(c) $Fe_{(s)} + O_{2(g)} \rightarrow Fe_2O_{3(s)}$

4. Transfer the following equations from word equations into symbolic equations. **(Beginning)**

(a) Solid calcium metal is placed in liquid water to produce aqueous calcium hydroxide and hydrogen gas.

(b) Gaseous sodium hydroxide is mixed with gaseous chlorine to produce aqueous solutions of sodium chloride and sodium hypochlorite plus liquid water.

(c) Solid xenon hexafluoride is mixed with liquid water to produce solid xenon trioxide and gaseous hydrogen fluoride.

5. Did you know that you can simulate a volcanic eruption in a lab that looks like the real thing? A source of heat is gently placed it into a mound of ammonium dichromate. The ammonium dichromate decomposes to solid chromium (III) oxide, nitrogen monoxide gas, and water vapor. Write the symbolic reaction for the "volcanic eruption". **(Intermediate)**

Vocabulary

reactants	The starting materials in the reaction (i.e. $SO_3 + H_2O \rightarrow H_2SO_4$; $SO_3 + H_2O$ = reactants).
products	The materials present at the end of a reaction (i.e. $SO_3 + H_2O \rightarrow H_2SO_4$; H_2SO_4 = product).
$\rightarrow$	Symbol used to separate reactants and products; means to produce. Ex: $2H_2 + O_2 \rightarrow 2H_2O$.
$+$	Symbol used to separate reactants and/or products in a chemical reaction; means is added to. Examples: $2H_2+0_2 \rightarrow 2H_2O$; $AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$.
(s)	In the solid state. Examples: Sodium: Na(s); Gold: Au(s).
(l)	In the liquid state. Examples: Water: $H_2O(l)$; Mercury: Hg(l).
(g)	In the gaseous state. Examples: Helium: He(g); Carbon dioxide: $CO_2(g)$.
(aq)	In the aqueous state. Examples: Sodium chloride solution: NaCl(aq).

Review Answers

1. Carbon and hydrogen are present in the formula for naphthalene, 10 carbon atoms and 8 hydrogen atoms make up the formula for the compound. We can tell this by the subscripts present in the formula.

2. Not every combination of reactants result in a chemical reaction. Reactions occur when molecules bump into each other, break chemical bonds, and re-arrange the atoms to form new substances. Sometimes, the molecules bump into each other and simply bounce off (rebound).

3.

(a) An aqueous solution of sulfuric acid and an aqueous solution of sodium cyanide react to produce an aqueous solution of hydrogen cyanide and an aqueous solution of sodium sulfate.

(b) Solid copper and an aqueous solution of silver nitrate react to produce solid silver and an aqueous solution of copper (II) nitrate

(c) Solid iron and gaseous oxygen react to produce solid iron (III) oxide.

4.

(a) $Ca_{(s)} + H_2O_{(L)} \rightarrow Ca(OH)_{2(aq)} + H_{2(g)}$

(b) $NaOH_{(g)} + Cl_{2(g)} \rightarrow NaCl_{(aq)} + NaOCl_{(aq)} + H_2O_{(L)}$

(c) $XeF_{6(s)} + H_2O_{(L)} \rightarrow XeO_{3(s)} + HF_{(g)}$

5. $(NH_4)_2Cr_2O_{7(s)} \rightarrow Cr_2O_{3(s)} + NO_{(g)} + H_2O_{(g)}$

Balancing Equations

Lesson Objectives

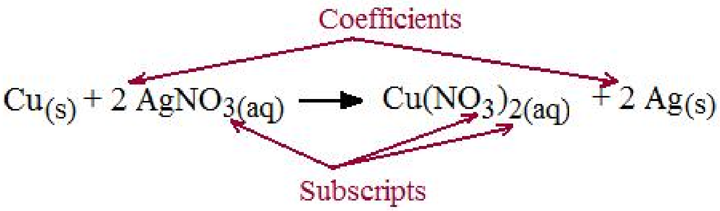
- Demonstrate the Law of Conservation of Matter in a chemical reaction.
- Explain the roles of coefficients and subscripts in a chemical reaction.
- Balance equations using the simplest whole number coefficients.

Introduction

Even though chemical compounds are broken up and new compounds are formed during a chemical reaction, atoms in the reactants do not disappear nor do new atoms appear to form the products. In chemical reactions, atoms are never created or destroyed. The same atoms that were present in the reactants are present in the products - they are merely re-organized into different arrangements. In a complete chemical equation, the two sides of the equation must be **balanced**. That is, in a complete chemical equation, **the same number of each atom must be present on the reactants and the products sides of the equation**.

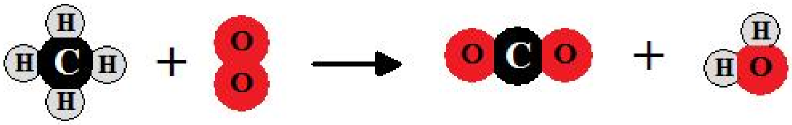
Subscripts and Coefficients

There are two types of numbers that appear in chemical equations. There are **subscripts** which are part of the chemical formulas of the reactants and products and there are **coefficients** that are placed in front of the formulas to indicate how many molecules of that substance is used or produced.



The subscripts are part of the formulas and once the formulas for the reactants and products are determined, the subscripts may not be changed. The coefficients indicate how many molecules of each substance is involved in the reaction and may be changed in order to balance the equation. The equation above indicates that **one** atom of solid copper is reacting with **two** molecules of aqueous silver nitrate to produce **one** molecule of aqueous copper (II) nitrate and **two** atoms of solid silver. When you learned how to write formulas, it was made clear that when only one atom of an element is present, the subscript of "1" is not written - so that when no subscript appears for an atom in a formula, you read that as one atom. The same is true in writing balanced chemical equations. If only one atom or molecule is present, the coefficient of "1" is omitted.

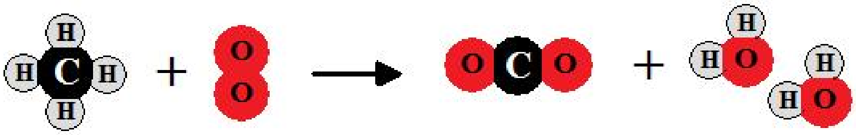
Coefficients are inserted into the chemical equation in order to **balance** it; that is, to make equal the total number of each atom on the two sides of the equation. Consider the equation representing the reaction that occurs when gaseous methane, CH_4, is burned in air (reacted with oxygen gas), and produces gaseous carbon dioxide and liquid water.



The unbalanced symbolic equation for this reaction is given below.

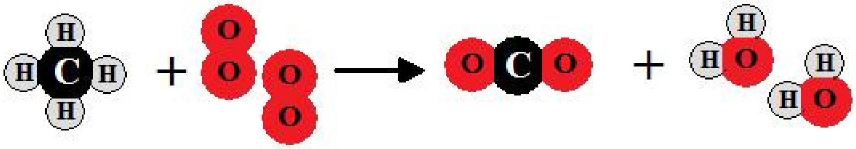
$CH_{4(g)} + O_{2(g)} \longrightarrow CO_{2(g)} + H_2O_{(L)}$ Equation 1

It is quickly apparent that equation 1 is not balanced. There are 4 hydrogen atoms in the reactants and only 2 hydrogen atoms in the products. The oxygen atoms in the equation are also not balanced. In order to balance this equation, it is necessary to insert coefficients in front of some of the substances to make the numbers of atoms of each element the same on the two sides of the equation. We can begin this process by placing a coefficient of 2 in front of the water molecule.



$CH_{4(g)} + O_{2(g)} \longrightarrow CO_{2(g)} + 2\ H_2O_{(L)}$ Equation 2

The insertion of this coefficient balanced the hydrogen atoms (there are now 4 on each side) but the equation is still not completely balanced. The oxygen atoms are not balanced. There are 4 oxygen atoms in the products but only two in the reactants. We can now insert a coefficient of 2 in front of the oxygen molecule in the reactants.



$CH_{4(g)} + 2\ O_{2(g)} \longrightarrow CO_{2(g)} + 2\ H_2O_{(L)}$ Equation 3

When we count up the number of each type of atom on the two sides of the equation now, we see that the equation is properly balanced. There is one carbon atom on each side, four hydrogen atoms on each side, and four oxygen atoms on each side. Equation balancing is accomplished by changing coefficients, **never** by changing subscripts.

The Process of Balancing an Equation

The process of writing a balanced chemical equation involves three steps. As a beginning chemistry student, you will not know whether or not two given reactants will react or not and even if you saw them react, you would not be sure what the products are without running tests to identify them. Therefore, for the time being, you will be told both the reactants and products in any equation you are asked to balance.

Step 1: Know what the reactants and products are, and write a word equation for the reaction.

Step 2: Write the formulas for all the reactants and products.

Step 3: Adjust the coefficients to balance the equation.

You must keep in mind that there are a number elements commonly appearing in equations that, under normal conditions, exist as diatomic molecules.

Elements that exist as diatomic molecules under normal conditions.

Element	Formula for Diatomic Molecule	Phase Under Normal Conditions
Hydrogen	H_2	Gaseous

Oxygen	O_2	Gaseous
Nitrogen	N_2	Gaseous
Chlorine	Cl_2	Gaseous
Fluorine	F_2	Gaseous
Bromine	Br_2	Liquid
Iodine	I_2	Solid

When the names of any of these elements appear in word equations, you must remember that the name refers to the diatomic molecule and insert the diatomic formula into the symbolic equation. If, under unusual circumstances, it was desired to refer to the individual atoms of these elements, the text would refer specifically to *atomic* hydrogen or *atomic* oxygen and so on.

Sample Problem 1

Write a balanced equation for the reaction that occurs between chlorine gas and aqueous sodium bromide to produce liquid bromine and aqueous sodium chloride.

Step 1: Write the word equation (keeping in mind that chlorine and bromine refer to the diatomic molecules).

Chlorine + sodium bromide → bromine + sodium chloride

Step 2: Substitute the correct formulas into the equation.

$Cl_2 + NaBr \rightarrow Br_2 + NaCl$

Step 3: Insert coefficients where necessary to balance the equation.

By placing a coefficient of 2 in front of the NaBr, we can balance the bromine atoms and by placing a coefficient of 2 in front of the NaCl, we can balance the chloride atoms.

$Cl_2 + 2\ NaBr \rightarrow Br_2 + 2\ NaCl$

A final check (always do this) shows that we have the same number of each atom on the two sides of the equation and we do not have a multiple set of coefficients so this equation is properly balanced.

Sample Problem 2

Write a balanced equation for the reaction between aluminum sulfate and calcium bromide to produce aluminum bromide and calcium sulfate. It might be worthwhile to note here that the reason you memorized the names and formulas for the polyatomic ions is that these ions usually remain as a unit throughout many chemical reactions.

Step 1: Write the word equation.

Aluminum sulfate + calcium bromide → aluminum bromide + calcium sulfate

Step 2: Replace the names of the substances in the word equation with formulas.

$Al_2(SO_4)_3 + CaBr_2 \rightarrow AlBr_3 + CaSO_4$ Equation 1

Step 3: Insert coefficients to balance the equation.

In order to balance the aluminum atoms, we must insert a coefficient of 2 in front of the aluminum compound in the products.

$Al_2(SO_4)_3 + CaBr_2 \rightarrow 2\ AlBr_3 + CaSO_4$ Equation 2

In order to balance the sulfate ions, we must insert a coefficient of 3 in front of the $CaSO_4$ in the products.

$Al_2(SO_4)_3 + CaBr_2 \rightarrow 2\ AlBr_3 + 3\ CaSO_4$ Equation 3

In order to balance the bromine atoms, we must insert a coefficient of 3 in front of the $CaBr_2$ in the reactants.

$Al_2(SO_4)_3 + 3\ CaBr_2 \rightarrow 2\ AlBr_3 + 3\ CaSO_4$ Equation 4

The insertion of the 3 in front of the $CaBr_2$ in the reactants also balances the calcium atoms in the $CaSO_4$ in the products. A final check shows 2 aluminum atoms on each side, 3 sulfur atoms on each side, 12 oxygen atoms on each side, 3 calcium atoms on each side, and 6 bromine atoms on each side. This equation is balanced.

Sample Problem 3

Balance the following skeletal equation. (The term "skeletal equation" refers to an equation that has the correct formulas but has not yet had the proper coefficients added.)

$Fe(NO_3)_3 + NaOH \rightarrow Fe(OH)_3 + NaNO_3$ (skeletal equation)

We can balance the hydroxide ion by inserting a coefficient of 3 in front of the NaOH on the reactant side.

$Fe(NO_3)_3 + 3\ NaOH \rightarrow Fe(OH)_3 + NaNO_3$ (intermediate equation)

Then we can balance the nitrate ions by inserting a coefficient of 3 in front of the sodium nitrate on the product side.

$Fe(NO_3)_3 + 3\ NaOH \rightarrow Fe(OH)_3 + 3\ NaNO_3$ (balanced equation)

Counting the number of each type of atom on the two sides of the equation will now show that this equation is balanced.

Simplest Whole Number Coefficients

Chemical equations should be balanced with the simplest whole number coefficients that balance the equation. Here is the properly balanced equation from the previous section.

$Al_2(SO_4)_3 + 3\ CaBr_2 \rightarrow 2\ AlBr_3 + 3\ CaSO_4$ Equation 4

You should note that the equation in the previous section would have the same number of atoms of each type on each side of the equation with the following set of coefficients.

$2\ Al_2(SO_4)_3 + 6\ CaBr_2 \rightarrow 4\ AlBr_3 + 6\ CaSO_4$ Equation 5

You should count the number of each type of atom on each side of the equation to confirm that this equation is "balanced". While this set of coefficients do "balance" the equation, they are not the **lowest** set of coefficients possible that balance the equation. We could divide each of the coefficients in this equation by 2 and get a another set of coefficients that are whole numbers and also balance the equation. Since it is required that an equation be balanced with the lowest whole number coefficients, equation 5 is NOT properly balanced. The properly balanced equation for this reaction is equation 4. When you have finished balancing an equation, you should not only check to make sure it is balanced, you should also check to make sure that it is balanced with the simplest set of whole number coefficients possible.

Let's consider another equation for balancing; the combustion of octane, C_8H_{18}.

$C_8H_{18} + O_2 \rightarrow CO_2 + H_2O$ Equation 1

To begin balancing this equation, we note that there are 8 carbon atoms on the reactant side and only 1 carbon on the product side. We can balance the carbon atoms by inserting a coefficient of 8 in front of the carbon dioxide on the product side.

$C_8H_{18} + O_2 \rightarrow 8\ CO_2 + H_2O$ Equation 2

Next, we note that there are 18 hydrogen atoms in the reactants and only 2 hydrogen atoms in the products. We can balance the hydrogen atoms by inserting a coefficient of 9 in front of the water molecule on the product side.

$C_8H_{18} + O_2 \rightarrow 8\ CO_2 + 9\ H_2O$ Equation 3

Now when we count up the number of oxygen atoms in the products, we find there are 25 oxygen atoms. What coefficient can you insert in front of the O_2 molecule in the reactants to have 25 oxygen atoms? Since the oxygen molecule has a subscript of 2, the only coefficient for this molecule that will produce 25 oxygen atoms is a coefficient of $\frac{25}{2}$. If we insert $\frac{25}{2}$ as the coefficient for the oxygen molecule, we get a balanced equation but we do not get an equation that is balanced with the simplest **whole** number coefficients.

$C_8H_{18} + \frac{25}{2}\ O_2 \rightarrow 8\ CO_2 + 9\ H_2O$ Equation 4

In order to have whole number coefficients for this equation, we must go through the equation and multiply all the coefficients by 2. That produces the coefficients shown in equation 5.

$2\ C_8H_{18} + 25\ O_2 \rightarrow 16\ CO_2 + 18\ H_2O$ Equation 5

Now the equation is balanced with the simplest whole number coefficients and is a properly balanced equation.

Sample Problem

Given the following skeletal (un-balanced) equations, balance them.

(a) $CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$

(b) $H_2SO_{4(aq)} + Al(OH)_{3(aq)} \rightarrow Al_2(SO_4)_{3(aq)} + H_2O_{(L)}$

(c) $Ba(NO_3)_{2(aq)} + Na_2CO_{3(aq)} \rightarrow BaCO_{3(aq)} + NaNO_{3(aq)}$

(d) $C_2H_{6(g)} + O_{2(g)} \rightarrow CO_{2(g)} + H_2O_{(L)}$

Solutions

(a) $CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$ (sometimes the equation balances with all coefficients of 1)

(b) $3\ H_2SO_{4(aq)} + 2\ Al(OH)_{3(aq)} \rightarrow Al_2(SO_4)_{3(aq)} + 6\ H_2O_{(L)}$

(c) $Ba(NO_3)_{2(aq)} + Na_2CO_{3(aq)} \rightarrow BaCO_{3(aq)} + 2\ NaNO_{3(aq)}$

(d) $2\ C_2H_{6(g)} + 7\ O_{2(g)} \rightarrow 4\ CO_{2(g)} + 6\ H_2O_{(L)}$

The Conservation of Mass in Chemical Reactions

Both the numbers of each type of atom and the mass are conserved during chemical reactions. An examination of a properly balanced equation will demonstrate that mass is conserved. Consider the following reaction.

$Fe(NO_3)_3 + 3\ NaOH \rightarrow Fe(OH)_3 + 3\ NaNO_3$

You should demonstrate that this equation is balanced by counting the number of each type of atom on each side of the equation.

We can also demonstrate that mass is conserved in this reaction by determining the total mass on the two sides of the equation.

$Fe(NO_3)_3 + 3\ NaOH \rightarrow Fe(OH)_3 + 3\ NaNO_3$

Reactant Side Mass

1 molecule of $Fe(NO_3)_3$ x molecular weight = (1)(241.9 daltons) = 241.9 daltons

3 molecules of NaOH x molecular weight = (3)(40.0 daltons) = 120. daltons

Total mass for reactants = 241.9 daltons + 120. daltons = **361.9 daltons**

Product Side Mass

1 molecule of $Fe(OH)_3$ x molecular weight = (1)(106.9 daltons) = 106.9 daltons

3 molecules of $NaNO_3$ x molecular weight = (3)(85.0 daltons) = 255 daltons

Total mass for products = 106.9 daltons + 255 daltons = **361.9 daltons**.

As you can see, both number of atom types and mass are conserved during chemical reactions. A group of 20 objects stacked in different ways will still have the same total mass no matter how you stack them.

Lesson Summary

- To be useful, chemical equations must always be balanced.
- Balanced chemical equations must have the same number and type of each atom on both sides of the equation.
- The coefficients in a balanced equation must be the simplest whole number ratio.
- Mass is always conserved in chemical reactions.

Review Questions

1. Explain in your own words why it is essential that subscripts remain constant but coefficients can change. **(Intermediate)**

2. Which set of coefficients will properly balance the following equation? **(Intermediate)**

$C_2H_6 + O_2 \rightarrow CO_2 + H_2O$

(a) 1, 1, 1, 1

(b) 1, 3, 2, 2

(c) 1, 3.5, 2, 3

(d) 2, 7, 4, 6

3.. When properly balanced, what is the sum of all the coefficients in the following chemical equation? **(Intermediate)**

$SF_4 + H_2O \rightarrow H_2SO_3 + HF$

(a) 4

(b) 7

(c) 9

(d) None of the above

4. When the following equation is balanced, what is the coefficient found in front of the O_2? **(Intermediate)**

$P_4 + O_2 + H_2O \rightarrow H_3PO_4$

(a) 1

(b) 3

(c) 5

(d) 7

5. Balance the following equations. **(Intermediate)**

(a) $XeF_{6(s)} + H_2O_{(L)} \rightarrow XeO_{3(s)} + HF_{(g)}$

(b) $Cu_{(s)} + AgNO_{3(aq)} \rightarrow Ag_{(s)} + Cu(NO_3)_{2(aq)}$

(c) $Fe_{(s)} + O_{2(g)} \rightarrow Fe_2O_{3(s)}$

(d) $Al(OH)_3 + Mg_3(PO_4)_2 \rightarrow AlPO_4 + Mg(OH)_2$

Further Reading / Supplemental Links

Website with lessons, worksheets, and quizzes on various high school chemistry topics.

- Lesson 8-1 is on Balancing Equations.

http://www.fordhamprep.org/gcurran/sho/sho/lessons/lesson81.htm

Vocabulary

law of conservation of matter	Matter is neither created nor destroyed in chemical reactions.
skeletal equation	a chemical equation before it has been balanced

balanced chemical equation	a chemical equation in which the number of each type of atom is equal on the two sides of the equation

Review Answers

1. The subscripts are part of the chemical formula. If you change a subscript, you have changed the compound involved in the reaction. Coefficients, on the other hand, indicate the number of molecules of each substance in the reaction. The coefficients can be changed in order to balance the equation.

2. (d)

3. (c)

4. (c)

5. Balance the following equations.

(a) $XeF_{6(s)} + 3\ H_2O_{(L)} \rightarrow XeO_{3(s)} + 6\ HF_{(g)}$

(b) $Cu_{(s)} + 2\ AgNO_{3(aq)} \rightarrow 2\ Ag_{(s)} + Cu(NO_3)_{2(aq)}$

(c) $4\ Fe_{(s)} + 3\ O_{2(g)} \rightarrow 2\ Fe_2O_{3(s)}$

(d) $2\ Al(OH)_3 + Mg_3(PO_4)_2 \rightarrow 2\ AlPO_4 + 3\ Mg(OH)_2$

Types of Reactions

Lesson Objectives

- Identify the types of reactions.
- Predict the products in different types of reactions.
- Distinguish between the different types of reactions.
- Write balanced chemical equations and identify the reaction type given only the reactants.

Introduction

Chemical reactions are classified into groups to help us analyze them and also to help us predict what the products of the reaction will be. The four major types of chemical reactions are synthesis, decomposition, single replacement, and double displacement. Sometimes other names are used for these basic types of reactions but the same four are always listed. There are also some sub-groups under these four but we will concentrate on the basic four groups.

Synthesis: A + B YIELDS C

A synthesis reaction is one in which two or more reactants combine to make **ONE** type of product.

General equation: $A + B \rightarrow AB$

Synthesis reactions occur as a result of two or more simpler elements or molecules combining to form a more complex molecule. Look at the example below. Here two elements (hydrogen and oxygen) are combining to form one product (water).

Example: $2\ H_{2(g)} + O_{2(g)} \longrightarrow 2\ H_2O_{(L)}$ + energy

(notice that energy is a product and therefore this synthesis reaction is exothermic)

We can always identify a synthesis reaction because there is only one product or one substance present after the arrow (on the right hand side) of the reaction.

We can write the synthesis reaction for sodium chloride just by knowing the elements that are present in the product.

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

You will recognize synthesis reactions by the fact that there is only one product. You should be able to write a formation synthesis reaction if you are given a product by picking out its elements and writing the reaction (just like we did with NaCl). Also, if you are given elemental reactants and told that the reaction is a synthesis reactant, you should be able to predict the products.

Sample Question:

(a) Write a synthesis reaction to produce silver bromide, AgBr.

(b) Predict the products for the following reaction: $CO_{2(g)} + H_2O_{(L)} \longrightarrow$

(c) Predict the products for the following reaction: $Li_2O_{(s)} + CO_{2(g)} \longrightarrow$

Solution:

(a) $2\ Ag_{(s)} + Br_{2(L)} \longrightarrow 2\ AgBr_{(s)}$
(b) $CO_{2(g)} + H_2O_{(L)} \longrightarrow H_2CO_{3(aq)}$
(c) $Li_2O_{(s)} + CO_{2(g)} \longrightarrow Li_2CO_{3(s)}$

Decomposition: C YIELDS A + B

The best way to remember a decomposition reaction is that for all reactions of this type, there is only one reactant. When **ONE** type of reactant breaks down to form two or more products, we have a decomposition reaction.

General Equation: $AB \longrightarrow A + B$

Look at the example below for the decomposition of ammonium nitrate to dinitrogen oxide and water.

Example: energy + $NH_4NO_{3(s)} \longrightarrow N_2O_{(g)} + 2\ H_2O_{(g)}$

(Notice the energy is a reactant and therefore this decomposition reaction is endothermic)

Notice the one reactant, $NH_4NO_{3(s)}$, is on the left of the arrow and there is more than one on the right side of the arrow. This is the exact opposite of the synthesis reaction type.

When studying decomposition reactions, we can predict reactants in a similar manner as we did for synthesis reactions. Look at the formula for magnesium nitride, Mg_3N_2. What elements do you see in this formula? You see magnesium, Mg, and nitrogen, N_2. Now we can write a decomposition reaction for magnesium nitride.

$$Mg_3N_{2(s)} \rightarrow 3\ Mg_{(s)} + N_{2(g)}$$

Notice there is only one reactant.

Sample Question:

(a) Write a decomposition reaction for aluminum oxide, Al_2O_3.

(b) Predict the products for the following reaction: $Ag_2S \rightarrow$

(c) Predict the products for the following reaction: $MgO \rightarrow$

Solution:

(a) $2\ Al_2O_3 \rightarrow 4\ Al + 3\ O_2$
(b) $Ag_2S \rightarrow 2\ Ag + S$
(c) $2\ MgO \rightarrow 2\ Mg + O_2$

Single Replacement (metal): A + BC YIELDS AC + B

A third type of reaction is the single replacement reaction. In single replacement reactions **one element** reacts with **one compound** to form products. The single element is said to replace an element in the compound when products form, hence the name single replacement.

There are actually three different types of single replacement reactions; 1) the single element is a metal and replaces the metal of the compound in the second reactant, 2) the single element is a metal and replaces the hydrogen of the compound in the second reactant which is always an acid, and 3) the single element is a non-metal and replaces the non-metal in the compound. The single replacement reaction in which hydrogen is replaced in an acid will be covered in detail in a later section. In this section, let us focus on single replacement reactions where the element reactant replaces the metal in the compound reactant. Look at the general reaction below.

General equation: $A + BC \rightarrow B + AC$

(element replaces cation of compound)

Example: $Zn_{(s)} + Cu(NO_3)_{2(aq)} \rightarrow Zn(NO_3)_{2(aq)} + Cu_{(s)}$

Notice there is only one reactant that is an element and one reactant that is a compound.

When studying single replacement reactions, we can predict reactants in a similar manner as we did for synthesis and decomposition reactions. Remember the oxidation numbers learned previously. This prior knowledge will become especially important here when predicting products for the rest of this chapter. Let's try an example where we will predict a series of products for an element reacting with a compound where the element will replace the metal ion.

Suppose that we know a single replacement reaction will occur between solid aluminum and solid iron (III) oxide.

$Al_{(s)} + Fe_2O_{3(s)} \longrightarrow$

In order to predict the products we need to know that aluminum will replace iron and form aluminum oxide. Aluminum has a charge of +3 (it is in group 3A) and oxygen has a charge of -2 (it is in group 6A). The compound formed between aluminum and oxygen, therefore, will be $Al_2O_{3(s)}$. Since iron is replaced in the compound by aluminum, the iron will now be the single element in the products. The unbalanced equation will be:

$Al_{(s)} + Fe_2O_{3(s)} \longrightarrow Al_2O_{3(s)} + Fe_{(s)}$

and the balanced equation will be:

$2\ Al_{(s)} + Fe_2O_{3(s)} \longrightarrow Al_2O_{3(s)} + 2\ Fe_{(s)}$

Sample Question:

(a) Write a single replacement reaction for the reaction between zinc solid and lead(II) nitrate solution to produce zinc nitrate solution and solid lead.

(b) Predict the products for the following reaction: $Fe + CuSO_4 \longrightarrow$

(b) Predict the products for the following reaction: $Al + CuCl_2 \longrightarrow$

Solution:

(a) $Zn_{(s)} + Pb(NO_3)_{2(aq)} \longrightarrow Pb_{(s)} + Zn(NO_3)_{2(aq)}$
(b) $Fe_{(s)} + CuSO_{4(aq)} \longrightarrow FeSO_{4(aq)} + Cu_{(s)}$
(c) $2\ Al + 3\ CuCl_2 \longrightarrow 3\ Cu + 2\ AlCl_3$

Single Replacement (many metals with acid): A + 2HC YIELDS $AC_2 + H_2$

These reactions are the same as those studied in the last section except the compound in the reactant side of the equation is always an **acid**. Since you may not have studied acids yet, you should consider an acid to be a compound in which hydrogen is combined with a anion. Therefore, in this section, the single replacement reactions will be where the element reactant replaces the hydrogen in the compound reactant. Look at the general reaction below.

General equation: $A + 2\ HC \longrightarrow AC_2 + H_2$ (element replaces hydrogen of compound)

Example: $Zn_{(s)} + 2HBr_{(aq)} \longrightarrow ZnCl_{2(aq)} + H_{2(g)}$

When studying these single replacement reactions, we can predict reactants in a similar manner as we did for the other types of single replacement reactions. Look at the reaction below. Since HCl is a compound that has hydrogen combined with an anion, it is an acid.

$Mg_{(s)} + 2\ HCl_{(aq)} \longrightarrow$

In order to predict the products, we need to know that magnesium will replace hydrogen and form magnesium chloride. Magnesium has a charge of +2 (it is in group 2) and chlorine has a charge of -1 (it is in group 7A). Therefore, the compound formed will be $MgCl_2$. When hydrogen is replaced from the compound, it will appear in the products as elemental hydrogen, H_2. All we need to do after the products are determined is to balance the equation.

$Mg(s) + 2\ HCl(aq) \rightarrow MgCl_2(s) + H_2(g)$

Notice there is one reactant that is an element (Mg) and one reactant that is an acid compound. The Mg has replaced the hydrogen in the HCl in the same manner as the Zn replaced the hydrogen in the HBr in the example above.

Sample Question:

(a) Write a single replacement reaction for the reaction between iron solid and hydrochloric acid solution to produce iron(II) chloride solution and hydrogen gas.

(b) Predict the products for the following reaction: $Zn_{(s)} + H_2SO_{4(aq)} \rightarrow$

(c) Predict the products for the following reaction: $Al_{(s)} + HNO_{3(aq)} \rightarrow$

Solution:

(a) $Fe_{(s)} + 2\ HCl_{(aq)} \rightarrow FeCl_{2(aq)} + H_{2(g)}$

(b) $Zn_{(s)} + H_2SO_{4(aq)} \rightarrow ZnSO_{4(aq)} + H_{2(g)}$

(c) $2\ Al_{(s)} + 6\ HNO_{3(aq)} \rightarrow 2\ Al(NO_3)_{3(aq)} + 3\ H_{2(g)}$

Single Replacement (non-metal): XY + Z YIELDS XZ + Y

In this section, we will focus on the final type of single replacement reactions where the element reactant replaces the **non-metal** (or the anion) in the compound reactant. Look at the general reaction below.

General equation: $A + BC \rightarrow C + BA$ (element replaces anion of compound)

Example: $Cl_{2(g)} + 2KI_{(aq)} \rightarrow 2KCl_{(aq)} + I_{2(s)}$

Notice, in the example, the chlorine replaced the iodine to produce solid iodine as a product. We can predict the products for these single replacement reactions in a similar manner as for all other single replacement reactions. The only difference here is that we have to remember that we are replacing the anion of the compound rather than the cation. Look at the reaction below between chlorine gas and sodium bromide. This is an actual extraction method for extracting bromine from the ocean water found to contain sodium bromide. Can you complete the reaction?

$Cl_{2(g)} + NaBr_{(aq)} \rightarrow$

In order to predict the products of this reaction we need to know that chlorine will replace bromine and form sodium chloride. Sodium has a charge of +1 (it is in group 1) and chlorine has a charge of -1 (it is in group 17). The compound formed will be NaCl.

$Cl_{2(g)} + 2\ NaBr_{(aq)} \rightarrow 2\ NaCl_{(aq)} + Br_{2(L)}$

Notice as with all of the other single replacement reactions, the reactants include one element and one compound and the products contain one element and one compound. This is the determining factor for identifying whether you have a single replacement reaction.

Sample Question:

(a) Write a single replacement reaction for the reaction between sodium iodide solution and bromine solution to produce sodium bromide solution and solid iodide.

(b) Predict the products for the following reaction: $Br_{2(aq)} + KI_{(aq)} \rightarrow$

(b) Predict the products for the following reaction: $MgI_{2(aq)} + Cl_{2(g)} \rightarrow$

Solution:

(a) $2\ NaI_{(aq)} + Br_{2(L)} \rightarrow 2\ NaBr_{(aq)} + I_{2(s)}$

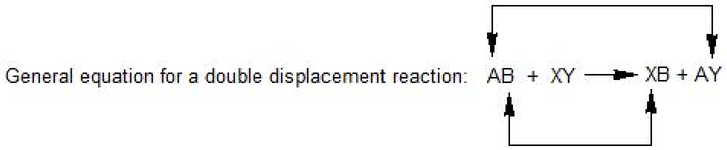
(b) $Br_{2(aq)} + 2\ KI_{(aq)} \rightarrow 2\ KBr_{(aq)} + I_{2(s)}$

(c) $MgI_{2(aq)} + Cl_{2(g)} \rightarrow MgCl_{2(aq)} + I_{2(s)}$

Double Replacement: AB + XY YIELDS AY + XB

For double replacement reactions two reactants will react by having the cations exchange places with the anions. The key to this type of reaction, as far as identifying it over the other types, is that it has two compounds as reactants (or before the arrow).

This type of reaction is more common than any of the others and there are many different types of double replacement reactions. Some double replacement reactions are more common than others. For example, precipitation and neutralization reactions are two of the most common double replacement reactions. Precipitation reactions are ones where two aqueous compound reactants combine to form products where one of the products is an insoluble solid. A neutralization reaction is one where the two reactant compounds are an acid and a base and the two products are a salt and water (i.e. acid + base → salt + water).



General equation for a double displacement reaction: AB + XY → XB + AY

In this reaction, the reactant compounds exchanged partners. A broke up with B and joined Y and X broke up with Y and joined B.

Example: $AgNO_{3(aq)} + NaCl_{(aq)} \rightarrow AgCl_{(s)} + NaNO_{3(aq)}$

(this is a precipitation reaction because $AgCl_{(s)}$ is formed)

$2\ NaOH_{(aq)} + H_2SO_{4(aq)} \rightarrow Na_2SO_{4(aq)} + 2H_2O_{(L)}$

(this is a neutralization reaction because the acid, H_2SO_4, is neutralized by the base, NaOH)

In order to write the products for a double displacement reaction, you must be able to determine the correct formulas for the new compounds. Let's practice with an example or two.

A common laboratory experiment involves the reaction between lead(II) nitrate and sodium iodide, both clear solutions. Here is the start of the reaction.

$Pb(NO_3)_{2(aq)} + NaI_{(aq)} \rightarrow$

Now, predict the products from your knowledge of oxidation numbers (or charges).

We know that the cations exchange anions. We now have to look at the charges of each of the cations and anions to see what the products will be.

We should presume the oxidation number of the lead will remain 2+ and since iodine forms ions with an oxidation number of 1-, one product will be PbI_2. The other product will form between sodium ions whose oxidation number is 1+ and nitrate ions whose oxidation number is 1-. Therefore, the second product will be $NaNO_3$. Once the products are written in, the equation can be balanced.

$$Pb(NO_3)_{2(aq)} + 2NaI_{(aq)} \rightarrow PbI_{2(s)} + 2\ NaNO_{3(aq)}.$$

The experiment produces a brilliant yellow precipitate. If you have use of a solubility table, it is easy to determine that the precipitate will be the lead (II) iodide. Lead compounds tend to precipitate and sodium compounds are always soluble so we would know that the PbI_2 is the brilliant yellow precipitate.

Look at the reaction between acetic acid and barium hydroxide below.

$$HC_2H_3O_{2(aq)} + Ba(OH)_{2(aq)} \rightarrow\ ?$$

Predict the products in the same manner as you did in the previous reaction by having the cations exchange places and writing the correct formulas for the products formed.

$$HC_2H_3O_{2(aq)} + Ba(OH)_{2(aq)} \rightarrow Ba(C_2H_3O_2)_{2(aq)} + H_2O_{(L)} \quad \text{(not balanced)}$$

Therefore the final reaction will be: $2\ HC_2H_3O_{2(aq)} + Ba(OH)_{2(aq)} \rightarrow Ba(C_2H_3O_2)_{2(aq)} + 2\ H_2O_{(L)}$ (balanced)

This is an acid-base reaction yielding the salt, barium acetate, and water. Notice that HOH and H_2O are the same.

Sample Question:

(a) Write a double replacement reaction for the reaction between calcium chloride solution and potassium hydroxide solution to produce potassium chloride solution and a precipitate of calcium hydroxide.

(b) Predict the products for the following reaction: $AgNO_{3(aq)} + NaCl_{(aq)} \rightarrow$

(c) Predict the products for the following reaction: $FeCl_3(aq) + KOH(aq) \rightarrow$

Solution:

(a) $CaCl_{2(aq)} + 2\ KOH_{(aq)} \rightarrow Ca(OH)_{2(s)} + 2\ KCl_{(aq)}$

(b) $AgNO_{3(aq)} + NaCl_{(aq)} \rightarrow AgCl_{(s)} + NaNO_{3(aq)}$

(c) $FeCl_3(aq) + 3\ KOH(aq) \rightarrow Fe(OH)_{3(s)} + 3\ KCl_{(aq)}$

Combustion: Fuel + O_2 YIELDS CO_2 + H_2O

A special type of single displacement reaction deserves some attention. These reactions are ***combustion*** reactions, specifically ones that involve fuels such as hydrocarbon compounds. In a particular branch of chemistry, known as organic chemistry, we study compounds known as hydrocarbons. You might remember this from previous science classes. In any event, hydrocarbons (hydrogen + carbon) represent the major components of all organic material including fuels. Combustion reactions usually have the same products, CO_2 and H_2O, and one of its reactants is always oxygen. In other words, the only part that changes from one combustion reaction to the next is the actual hydrocarbon that combusts. The general equation is given below. Notice the oxygen, carbon dioxide, and water parts of the reaction are listed for you to show you how these reactants and products remain the same from combustion reaction to combustion reaction.

General equation: Hydrocarbon + $O_{2(g)} \rightarrow CO_{2(g)} + H_2O_{(L)}$

Also, combustion reactions are all exothermic. Small hydrocarbons (hydrocarbons having 1 to 4 carbon atoms in them) are gases at room temperature; all of the rest are liquids. Look at the reaction for the combustion of octane, C_8H_{18}, below. Octane has 8 carbon atoms hence the prefix "oct".

Example: $2\ C_8H_{18(L)} + 25\ O_{2(g)} \rightarrow 16\ CO_{2(g)} + 18H_2O_{(L)}$

Now you try one. Write the combustion reaction for the combustion of hexane, $C_6H_{14\ (L)}$.

Step 1: We know the general equation: Hydrocarbon + $O_{2(g)} \rightarrow CO_{2(g)} + H_2O_{(L)}$, now put in our hydrocarbon, hexane, into the general equation.

$C_6H_{14(L)} + O_{2(g)} \rightarrow CO_{2(g)} + H_2O_{(L)}$

Step 2: We now have to balance the reaction. Remember we have to start with the carbon atoms, then the hydrogen and finally oxygen. Do you know why? Carbon is first because it is considered a main element - so we put a coefficient of 6 in front of the carbon dioxide in the products. Then if we look at hydrogen and oxygen, hydrogen is in 2 compounds (species: C_6H_{14} and H_2O) and oxygen is in 3 elements/compounds (species: O_2, CO_2, and H_2O). Since hydrogen appears fewer times, we do hydrogen before oxygen. Therefore, we would put a coefficient of 7 in front of the water in the products.

$C_6H_{14(L)} + O_{2(g)} \rightarrow 6\ CO_{2(g)} + 7\ H_2O_{(L)}$

In order to balance the oxygen, we have to insert a coefficient of $\frac{19}{2}$ in front of the oxygen gas in the reactants.

$C_6H_{14(L)} + \frac{19}{2}\ O_{2(g)} \rightarrow 6\ CO_{2(g)} + 7\ H_2O_{(L)}$

Step 3: Remove the fraction. (Multiply the entire reaction by 2)

$2\ C_6H_{14(L)} + 19\ O_{2(g)} \rightarrow 12\ CO_{2(g)} + 14\ H_2O_{(L)}$

Sample Question: Write the combustion reaction for the combustion of butane, C_4H_{10}.

Solution:

$2\ C_4H_{10(g)} + 13\ O_{2(g)} \rightarrow 8\ CO_{2(g)} + 10\ H_2O_{(L)}$

The reactions we have done so far are what are referred to as complete combustion. Complete combustion reactions occur when there is enough oxygen to burn the entire hydrocarbon. This is why there are only carbon dioxide and water as products. Have you ever, though, been in a lab, heating a beaker and seen the black soot appear on the bottom of the beaker. Or seen the black puffs of smoke come out from the exhaust pipe of a car? If there is not enough oxygen the result is an incomplete combustion reaction with

$CO_{(g)}$ and C_{soot} also formed as products. Incomplete combustion reactions are actually quite dangerous because one of the products in the reaction is not carbon dioxide but carbon monoxide. Carbon monoxide is the gas that causes people to become sleepy when they breathe it and then eventually, when the concentration in the blood becomes too high, the person dies.

Sample Question: Identify whether each of the following reactions are complete or incomplete combustions and then balance each reaction.

(a) $C_7H_{16(L)} + O_{2(g)} \rightarrow CO_{2(g)} + H_2O_{(L)}$

(b) $C_3H_{8(g)} + O_{2(g)} \rightarrow CO_{2(g)} + H_2O_{(L)}$

(c) $CH_{4(g)} + O_{2(g)} \rightarrow CO_{(g)}(g) + H_2O_{(L)}$

(d) $C_5H_{12(L)} + O_{2(g)} \rightarrow CO_{2(g)} + H_2O_{(L)}$

(e) $C_2H_{6(g)} + O_{2(g)} \rightarrow CO_{(g)} + H_2O_{(L)}$

Solution:

(a) Complete; $C_7H_{16(L)} + 11\ O_{2(g)} \rightarrow 7\ CO_{2(g)} + 8\ H_2O_{(L)}$

(b) Complete; $C_3H_{8(g)} + 5\ O_{2(g)} \rightarrow 3\ CO_{2(g)} + 4\ H_2O_{(L)}$

(c) Incomplete; $2\ CH_{4(g)} + 3\ O_{2(g)} \rightarrow 2\ CO_{(g)}(g) + 4\ H_2O_{(L)}$

(d) Complete; $C_5H_{12(L)} + 8\ O_{2(g)} \rightarrow 5\ CO_{2(g)} + 6\ H_2O_{(L)}$

(e) Incomplete; $2\ C_2H_{6(g)} + 5\ O_{2(g)} \rightarrow 4\ CO_{(g)} + 6\ H_2O_{(L)}$

Lesson Summary

- There are five types of chemical reactions:

Reaction Name	**Reaction Description**
Synthesis:	two or more reactants make one product.
Decomposition:	one type of reactant makes two or more products.
Single replacement:	one element species reacts with one compound species to form products.
Double replacement:	two compounds act as reactants.
Combustion:	a fuel reactant reacts with oxygen gas.

Review Questions

1. When balancing combustion reactions, did you notice a consistency relating to whether the number of carbons in the hydrocarbon was odd or even? **(Intermediate)**

2. Distinguish between synthesis and decomposition reactions. **(Intermediate)**

3. When dodecane, $C_{10}H_{22}$, burns in excess oxygen, the products would be **(Intermediate)**

a. $CO_2 + 2H_2$

b. $CO + H_2O$

c. $CO_2 + H_2O$

d. CH_4O_2

4. In the decomposition of antimony trichloride, which of the following products and quantities will be found? **(Intermediate)**

a. $An + Cl_2$

b. $2An + 3Cl_2$

c. $Sb + Cl_2$

d. $2Sb + 3Cl_2$

5. Acetylsalicylic acid (Aspirin^{TM}), $C_9H_8O_4(s)$, is produced by reacting acetic anhydride, $C_4H_6O_3(l)$, with salicylic acid, $C_7H_6O_3(s)$. The other product in the reaction is water. Write the balanced chemical equation. **(Intermediate)**

6. When iron rods are placed in liquid water, a reaction occurs. Hydrogen gas evolves from the container and iron(III) oxide forms onto the iron rod. **(Intermediate)**

a. Write a balanced chemical equation for the reaction.

b. What type of reaction is this?

7. A specific fertilizer is being made at an industrial plant nearby. The fertilizer is called a triple superphosphate and has a formula $Ca(H_2PO_4)_2$. It is made by sand and clay that contains phosphate and then treating it with a calcium phosphate solution and phosphoric acid. The simplified reaction is calcium phosphate reacting with the phosphoric acid to yield the superphosphate. Write the balanced chemical reaction and name the type. **(Intermediate)**

Further Reading / Supplemental Links

Website with lessons, worksheets, and quizzes on various high school chemistry topics.

- Lesson 8-2 is on the Classification of Chemical Reactions.

http://www.fordhamprep.org/gcurran/sho/sho/lessons/lesson82.htm

http://library.thinkquest.org/2923/react.html

http://en.wikipedia.org

Vocabulary

synthesis	A synthesis reaction is one in which two or more reactants combine to make ONE type of product. ($A + B \longrightarrow C$).
decomposition	A decomposition reaction is one in which ONE type of reactant breaks down to form two or more products. ($C \longrightarrow A + B$).
single replacement (metal)	In a single replacement (metal) reaction, one element replaces the metal cation of the compound reactant to form products. ($A + BC \longrightarrow AC + B$).

single replacement (many metals with acid)	In a single replacement (many metals with acid) reaction, one element replaces the hydrogen cation of the compound (which is an acid) reactant to form products. Example: $A + 2HC \longrightarrow AC_2 + H_2$.
single replacement (non-metal)	In a single replacement (non-metal) reaction, one element replaces the non-metal (anion) of the compound reactant to form products. ($XY + Z \longrightarrow XZ + Y$).
double replacement	For double replacement reactions two reactants will react by having the cations replace the anions. ($AB + XY \longrightarrow AY + XB$).
combustion (complete)	Combustion is the burning in oxygen, usually a hydrocarbon. (fuel + $O_2 \longrightarrow CO_2 + H_2O$).
combustion (incomplete)	Incomplete combustion is the inefficient burning in oxygen, usually a hydrocarbon. Inefficient burning means there in not enough oxygen to burn all of the hydrocarbon present, sometimes carbon (soot) is also a side product of these reactions. (fuel + $O_2 \longrightarrow CO_2 + H_2O$).
hydrocarbons	Compounds containing hydrogen and carbon.

Review Answers

1. For complete combustion, when the number of carbon atoms is even, you always have to multiply the hydrocarbon by the coefficient 2 when balancing.

$2C_6H_{14}(l) + 19O_2(g) \longrightarrow 12CO_2(g) + 14H_2O(l)$

This is due to the fact that if the carbon atom subscript is even, the hydrogen number will cause the number of oxygen atoms to be odd unless the coefficient 2 is used.

$C_3H_8(l) + 5\ O_2(g) \longrightarrow 3\ CO_2(g) + 4\ H_2O(l)$

$2\ C_6H_{14}(l) + 19\ O_2(g) \longrightarrow 12\ CO_2(g) + 14\ H_2O(l)$.

2. Synthesis reactions have only one product so only have one substance after the arrow.

$2Na^+ + S^{2-} \longrightarrow Na_2S$

Decomposition reactions are the opposite with one substance before the arrow

$2BiCl_3 \longrightarrow 2Bi + 3Cl_2$

3. c. $CO_2 + H_2O$

4. d. $2Sb + 3Cl_2$

5. $C_4H_6O_3(l) + 2C_7H_6O_3(s) \longrightarrow 2C_9H_8O_4(s) + H_2O(l)$

6. (a) $2Fe(s) + 3H_2O(l) \longrightarrow Fe_2O_3(s) + 3H_2(g)$

(b) Single replacement

7. $Ca_3(PO_4)_2 + 4H_3PO_4 \longrightarrow 3Ca(H_2PO_4)_2$; synthesis

17. Mathematics and Chemical Equations

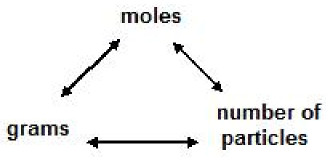
The Mole Concept and Equations

Lesson Objectives

- Express chemical equations in terms of molecules, formula units, and moles.
- Determine mole ratios in chemical equations.
- Explain the importance of balancing equations before determining mole ratios.
- Use mole ratios in balanced chemical equations.

Introduction

In previous chapters, you spent time working with molar mass, and mass to mole conversions. You worked with the astounding figure known as Avogadro's number. If Avogadro's number of particles were translated into seconds, the number of seconds the earth has been in existence since the Big Bang does not exceed Avogadro's number, 6.02×10^{23}. You may think that a second is a short time span, and it is, but this means that we have not had 6.02×10^{23} seconds of time pass since the beginning of the universe. Wow. Now that is a huge number don't you think? You also probably worked with all of these conversions using something similar to the mole hill shown below.



Notice that all of the conversions that you have learned to date are represented in this mole triangle. If you know one of the three (moles, grams, or number of particles) you can calculate how much you have of the other two.

This chapter will begin your journey into the connection between the mole and the mole-mass conversions with the balanced chemical equations of the previous chapter. In chemistry we "talk" to each other using chemical equations, the same way mathematicians talk to each other using mathematical equations. But in chemistry, we also want to talk about quantities. So herein lays the need to connect the two concepts of the mole and the mass with the chemical equation. Let's now begin the journey!

Coefficients Represent Number of Molecules, Formula Units, or Moles

Before getting too far into this lesson, we should review what we mean by the terms molecules or formula units. A ***formula unit*** is used specifically with ionic compounds and refers to the smallest unit in the ionic compound. For example, look at the formula for potassium chloride, KCl. Potassium chloride is considered ionic for many reasons, mainly because there is a transfer of an electron from the potassium atom to the chlorine atom. One formula unit of potassium chloride contains one ion of potassium and one ion of chlorine.

$$KCl \rightarrow K^+ + Cl^-$$

However, when we write KCl we are only writing the ratio of the number of K^+ to the number of Cl^{1-} involved in a crystal of potassium chloride, not an actual unit that exists by itself.

Another example of an ionic compound is copper (II) chloride, $CuCl_2$. It too would contain ions; one ion of copper and two chloride ions. And again, there is no one unit of $CuCl_2$ but a crystalline structure that has a ratio of one copper ion to two chloride ions.

$$CuCl_2 \rightarrow Cu^{2+} + 2\ Cl^-$$

In other words, there are no molecules in ionic compounds therefore we need to use a different term to represent this kind of compound and it is **formula unit.**

Discrete **molecules** are present in compounds where the atoms join together by the sharing of electrons. In this case we are working with covalent compounds. To look at the formula for carbon tetrachloride, for example, one molecule contains one carbon atom and four chlorine atoms joined together by the sharing of electrons; they are not ions.

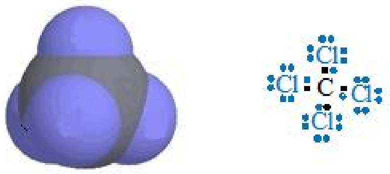
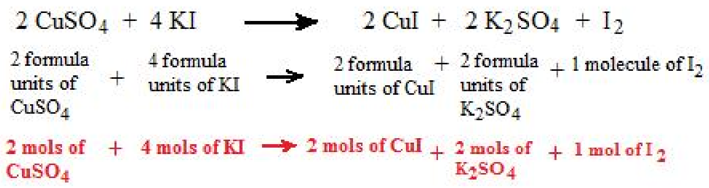


Figure 1: A space-filling model and the Lewis structure for CCl_4.

(*Created by:* Richard Parsons, *License:* CC-BY-SA)

We can call this a molecule since there is an actual singular unit that consists of one carbon atom and four chlorine atoms sharing electrons acting together as one unit or molecule. Water, H_2O, is of course another example of a covalently bonded compound that exists as discrete molecules. Therefore we can use the term **molecule** to accurately describe these kinds of compounds.

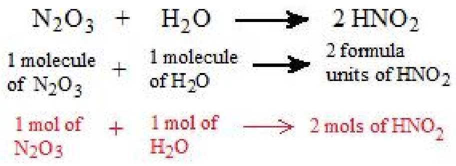
The **mole**, as you remember, is a quantitative measure that is equivalent to Avogadro's number of molecules. So how do these all relate to the chemical equation? Look at the chemical equation below. Indicate the number of formula units, molecular units, and moles of each in the equation.



$2\ CuSO_4$	+	4 KI	$\longrightarrow$	2 CuI	+	$2\ K_2SO_4$	+	I_2
2 formula units of $CuSO_4$	+	4 formula units of KI	$\rightarrow$	2 formula units of CuI	+	2 formula units of K_2SO_4	+	1 molecule of I_2
2 mols of $CuSO_4$	+	4 mols of KI	$\rightarrow$	2 mols of CuI	+	2 mols of K_2SO_4	+	1 mol of I_2

The coefficients used, as we have learned, tell us the relative amounts of each substance in the equation. So for every 2 units of copper (II) sulfate ($CuSO_4$) we have, we need to have 4 units of potassium iodide (KI). Notice that when mole is used rather than formula or molecular units, all of the ionic and molecular compounds use the same unit. The mole is a term that is equivalent to Avogadro's number of particles, molecules or formulas units. Therefore, it does not make a difference whether we have ionic or molecular formulas, the mole can be used as a unit for both. The molecule and formula units distinguish the ionic compounds from the covalent compounds. In the previous example with the ionic compound copper (II) sulfate, formula units were used as the unit. In the following example with the covalent compound dinitrogen trioxide molecules are used.

Look at the chemical equation below. Indicate the number of formula units, molecular units, and moles of each in the equation.



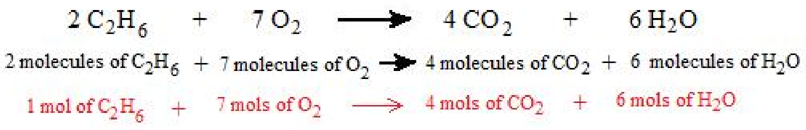
N_2O_3	+	H_2O	$\longrightarrow$	2 HNO_2
1 molecule of N_2O_3	+	1 molecule of H_2O	$\longrightarrow$	2 formula units of HNO_2
1 mol of N_2O_3	+	1 mol of H_2O	$\longrightarrow$	2 mols of HNO_2

Sample Question: For each of the following equations, indicate the number of formula units or molecules, and the number of moles present in the balanced chemical equation.

(a) $2\ C_2H_6 + 7\ O_2 \longrightarrow 4\ CO_2 + 6\ H_2O$

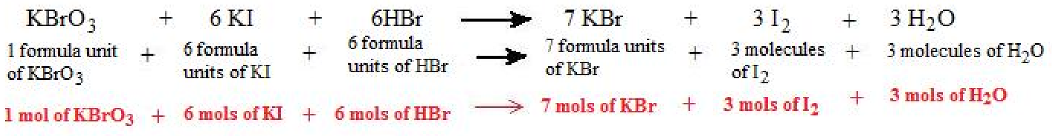
(b) $KBrO_3 + 6\ KI + 6\ HBr \longrightarrow 7\ KBr + 3\ I_2 + 3\ H_2O$

Solution: (a)



2 C_2H_6	+	7 O_2	$\longrightarrow$	4 CO_2	+	6 H_2O
2 molecules of C_2H_6	+	7 molecules of O_2	$\longrightarrow$	4 molecules of CO_2	+	6 molecules of H_2O
1 mol of C_2H_6	+	7 mols of O_2	$\longrightarrow$	4 mols of CO_2	+	6 mols of H_2O

(b)



$KBrO_3$	+	6 KI	+	6HBr	$\longrightarrow$	7 KBr	+	3 I_2	+	3 H_2O
1 formula unit of $KBrO_3$	+	6 formula units of KI	+	6 formula units of HBr	$\longrightarrow$	7 formula units of KBr	+	3 molecules of I_2	+	3 molecules of H_2O
1 mol of $KBrO_3$	+	**6 mols of KI**	+	**6 mols of HBr**	$\longrightarrow$	**7 mols of KBr**	+	**3 mols of I_2**	+	**3 mols of H_2O**

Ratio of Coefficients is the Mole/Mole Ratio

Now that we have learned a little about how the formula unit, molecules, and the mole fit individually into the balanced chemical equation, we can move on to reading the chemical equation as we do a written sentence. When we do this, we can see that the molecular and ionic compounds present in the equation work together to represent the whole reaction. They are interacting, more specifically, reacting and producing; each reactant being dependant on the other to be active, engaged, and be present in the correct amount to give products. You can tell by looking at a chemical equation that the species are dependent on one another. Let's look at a chemical equation and read it as if it were a sentence in a novel in English class. Look at the balanced chemical equation below.

$Fe_{(s)} + 2\ HCl_{(aq)} \longrightarrow FeCl_{2(s)} + H_{2(g)}$

When you "read this sentence" you might say that one mole of solid iron reacts with two moles of aqueous hydrochloric acid to produce one mole of solid iron(II) chloride and one mole of hydrogen gas. Remember the subscripts are used to represent the atoms that are chemically combined in the compound. If you were to read the previous sentence, could you write the balanced chemical equation?

Once you read the sentence, you can start to look at it and see how the reactants are working together. This means that we can start looking at the mole ratios. A ***mole ratio*** is the relationship of the number of moles in the substances in a reaction. For instance, in the following reaction we read the coefficients as molecules (or formula units) and moles:

$2\ H_{2(g)} + O_{2(g)} \longrightarrow 2\ H_2O_{(L)}$

2 moles of $H_{2(g)}$ react with 1 mole of $O_{2(g)}$ to produce 2 moles of water (L)

Or, an alternate method to represent this information is with mole ratios. The mole ratio for $H_{2(g)}$ to $O_{2(g)}$ can be written as:

$\frac{1\ \text{mols}\ H_2}{1\ \text{mol}\ O_2}$ or $\frac{1\ \text{mol}\ O_2}{2\ \text{mols}\ H_2}$

What is the ratio of the number of hydrogen molecules to the number of water molecules? To answer this question, we again need to look at the coefficients. The coefficient in front of the hydrogen (H_2) is 2, in front of the water (H_2O) is 2. Therefore the mole ratio can be written as:

$\frac{2\ \text{mols}\ H_2}{2\ \text{mol}\ H_2O}$ or $\frac{2\ \text{mols}\ H_2O}{2\ \text{mols}\ H_2}$

What is the ratio of the number of oxygen molecules to the number of water molecules? To answer this question, we again need to look at the coefficients. The coefficient in front of the oxygen (O_2) is 1, in front of the water (H_2O) is 2. Therefore the mole ratio can be written as:

$\frac{1\ \text{mol}\ O_2}{2\ \text{mols}\ H_2O}$ or $\frac{2\ \text{mols}\ H_2O}{1\ \text{mols}\ O_2}$

Now, let's try writing a balanced chemical equation from a "chemical sentence" and then finding the mole ratios. Four moles of solid aluminum are mixed with three moles of gaseous oxygen to produce two moles of solid aluminum oxide. What is the mol ratio of (a) aluminum to oxygen, (b) aluminum to aluminum oxide, and (c) oxygen to aluminum oxide?

Balanced Chemical Equation: $4\ Al_{(s)} + 3\ O_{2(g)} \longrightarrow 2\ Al_2O_{3(s)}$

(a) mol ratio of aluminum to oxygen

$\frac{4\ \text{mols}\ Al}{3\ \text{mols}\ O_2}$ or $\frac{3\ \text{mols}\ O_2}{4\ \text{mols}\ Al}$

(b) mol ratio of aluminum to aluminum oxide

$\frac{4\ \text{mols}\ Al}{2\ \text{mols}\ Al_2O_3}$ or $\frac{2\ \text{mols}\ Al_2O_3}{4\ \text{mols}\ Al}$

(c) mol ratio of oxygen to aluminum oxide

$\frac{3\ \text{mols}\ O_2}{2\ \text{mols}\ Al_2O_3}$ or $\frac{2\ \text{mols}\ Al_2O_3}{3\ \text{mols}\ O_2}$

Sample question: Write the balanced chemical equation for the reaction of calcium carbide (CaC_2) solid with water to form aqueous calcium hydroxide and acetylene (C_2H_2) gas. When written, find the mol ratios for (a) calcium carbide to water and (b) calcium carbide to calcium hydroxide.

Solution:

Balanced Chemical Equation: $CaC_{2(s)} + 2H_2O_{(L)} \longrightarrow Ca(OH)_{2(aq)} + C_2H_{2(g)}$

(a) mol ratio of calcium carbide to water

$\frac{1\text{ mol }CaC_2}{2\text{ mols }H_2O}$ or $\frac{2\text{ mols }H_2O}{1\text{ mol }CaC_2}$

(b) mol ratio of calcium carbide to calcium hydroxide

$\frac{1\text{ mol }CaC_2}{1\text{ mol }Ca(OH)_2}$

Mole/Mole Ratios Are Based on Correctly Balanced Equations

The correct mole ratios of the reactants and products in a chemical equation are determined by the balanced equation. Therefore, the chemical equation must always be balanced before the mole ratios are used for calculations. Looking at the unbalanced equation for the reaction of phosphorus trihydride with oxygen, it is virtually impossible to guess the correct mole ratio of phosphorus trihydride to oxygen gas.

$$PH_{3(g)} + O_{2(g)} \rightarrow P_4O_{10(s)} + H_2O_{(g)}$$

Once the equation is balanced, however, the mole ratio of phophorus trihydride to oxygen gas is apparent.

$$4\ PH_{3(g)} + 8\ O_{2(g)} \rightarrow P_4O_{10(s)} + 6\ H_2O_{(g)}$$

$\frac{4\text{ mols }PH_3}{8\text{ mols }O_2}$

Keep in mind that before any mathematical calculations are made relating to a chemical equation, the equation MUST be balanced.

Using the Mole Ratios in Balanced Equations

Now to go one step further with mole ratios before we move into the next section. The fact of the matter is that we rarely, in the chemistry lab, work with whole number units of moles. For example, using the reaction below, we may want to have only have 0.50 mol of SO_3 reacting with 0.50 mol of water rather than the 1:1 ratio indicated in the balanced chemical equation. In industry, they use multiples of the number found in the balanced chemical equation. In the United States alone, over 40 million tons of sulfuric acid are produced per year. For example, if a company wanted to make sulfuric acid using the equation below…

$$SO_{3(g)} + H_2O_{(L)} \rightarrow H_2SO_{4(aq)}$$

it would probably make more than one mole at a time. That would be time consuming. They would use the molar ratios and calculate multiples of the moles required.

Look at the following equation. If only 0.50 mole of magnesium hydroxide, $Mg(OH)_2$, is present, how many moles of phosphoric acid, H_3PO_4, would be required for the reaction?

$$2H_3PO_4 + 3Mg(OH)_2 \rightarrow Mg_3(PO_4)_2 + 6H_2O$$

Step 1: We have to determine the conversion factor. We want to convert from moles of $Mg(OH)_2$ to moles of H_3PO_4. Therefore our conversion factor is:

$$\text{mole ratio} = \frac{2\text{ mols }H_3PO_4}{3\text{ mols }Mg(OH)_2}$$

Notice that what we are finding is in the numerator; what we know is in the denominator

Step 2: Use the conversion factor to determine the moles for the question.

$$\text{mols } H_3PO_4 = \left(0.50 \text{ mol } Mg(OH)_2\right)\left(\frac{2 \text{ mols } H_3PO_4}{3 \text{ mols } Mg(OH)_2}\right) = 0.33 \text{ mol } H_3PO_4$$

Therefore, if we have 0.50 mol of $Mg(OH)_2$, we would need 0.33 mol of H_3PO_4 to react all of the magnesium hydroxide. Notice if the equation was not balanced, the amount of H_3PO_4 would have been different. The ratio would have been 1:1 and we would then say we require 0.5 mol of H_3PO_4.

Sample Problem #1: How many moles of sodium oxide (Na_2O) can be formed from 2.36 mol of sodium nitrate ($NaNO_3$) using the balanced chemical equation below?

$$10\ Na + 2\ NaNO_3 \rightarrow 6\ Na_2O + N_2O$$

Solution:

$$\text{mols } Na_2O = (2.36 \text{ mols } NaNO_3)\left(\frac{6 \text{ mols } Na_2O}{2 \text{ mols } NaNO_3}\right) = 7.08 \text{ mols } Na_2$$

Sample Problem #2: How many moles of sulfur are required to produce 5.42 mol of carbon disulfide, CS_2, using the balanced chemical equation below?

$$C + 2\ S \rightarrow CS_2$$

Solution:

$$\text{mols } S = (5.42 \text{ mols } CS_2)\left(\frac{2 \text{ mols } S}{1 \text{ mol } CS_2}\right) = 10.84 \text{ mols } S$$

As you can see, the mole ratios are useful for converting between the number of moles of one substance and another

Lesson Summary

- Coefficients in equations represent molecules, formulas units and/or moles.
- In order to work with the mathematics of reactions, equations must be balanced correctly.
- The coefficients in a balanced chemical equation represent the reacting rations of the substances in the reaction.
- When the moles of one substance in a reaction is known, the coefficients of the balanced equation can be used to determine the moles of all the substances in a reaction.

Review Questions

1. Distinguish between formula unit, molecular unit, and mole. Use an example in your answer. **(Intermediate)**

2. Why is balancing the equation so important before the mol ratios are to be determined? **(Intermediate)**

3. Is it ever possible to use mol ratios when the chemical equation has not been balanced? **(Intermediate)**

4. Given the reaction between ammonia and oxygen to produce nitrogen monoxide, how many moles of water vapor can be produced from 2 mols of ammonia? **(Intermediate)**

$$4\ NH_{3(g)} + 5\ O_{2(g)} \rightarrow 4\ NO_{(g)} + 6\ H_2O_{(g)}$$

(a) 3 mol

(b) 6 mol

(c) 12 mol

(d) 24 mol

5. When properly balanced, how many moles of bismuth(III) oxide can be produced from 0.625 mol of bismuth? **(Intermediate)**

$Bi_{(s)} + O_{2(g)} \longrightarrow Bi_2O_{3(s)}$

(a) 0.313 mol

(b) 0.625 mol

(c) 1 mol

(d) 1.25 mol

(e) 2 mol

6. For the following reaction, balance the equation and then determine the mole ratio of moles of $B(OH)_3$ to moles of water? **(Intermediate)**

$B_2O_{3(s)} + H_2O_{(L)} \longrightarrow B(OH)_{3(s)}$

(a) 1:1

(b) 2:3

(c) 3:2

(d) None of the above

7. Write the balanced chemical equation for the reactions below. When written, find the mol ratios indicated following each reaction. **(Intermediate)**

a. Gaseous propane (C_3H_8) combusts to form gaseous carbon dioxide and water; find ratio of mol O_2 to mol CO_2.

b. Solid lithium reacts with an aqueous solution of aluminum chloride to produce aqueous lithium chloride and solid aluminum; find ratio of mol $AlCl_3$(aq) to mol LiCl(aq).

c. Gaseous ethane (C_2H_6) combusts to form gaseous carbon dioxide and water; find ratio of mol CO_2(g) to mol O_2(g).

d. An aqueous solution of ammonium hydroxide reacts with an aqueous solution of phosphoric acid to produce aqueous ammonium phosphate and water; find ratio of mol H_3PO_4(aq) to mol H_2O(l).

e. Solid rubidium reacts with solid phosphorous to produce solid rubidium phosphide; find ratio of mol Rb(s) to mol P(s).

8. For the given reaction (unbalanced), **(Intermediate)**

$Ca_3(PO_4)_2 + SiO_2 + C \longrightarrow CaSiO_3 + CO + P$

a. how many moles of silicon dioxide are required to react with 0.35 mol of carbon?

b. how many moles of calcium phosphate are required to produce 0.45 mol of calcium silicate?

9. For the given reaction (unbalanced), **(Intermediate)**

$FeS + O_2 \longrightarrow Fe_2O_3 + SO_2$

a. how many moles of iron(III) oxide are produced from 1.27 mol of oxygen?

b. how many moles of iron(II) sulfide are required to produce 3.18 mol of sulfur dioxide?

10. Write the following balanced chemical equation. Ammonia and oxygen are allowed to react in a closed container to form nitrogen and water. All species present in the reaction vessel are in the gas state. **(Intermediate)**

a. how many moles of ammonia are required to react with 4.12 mol of oxygen?

b. how many moles of nitrogen are produced when 0.98 mol of oxygen are reacted with excess ammonia?

Further Reading / Supplemental Links

http://en.wikipedia.org

Vocabulary

chemical coefficient	The number in front of a molecule's symbol in a chemical equation indicates the number molecules participating in the reaction. If no coefficient appears, we interpret it as meaning one.
formula unit	The empirical formula of an ionic or covalent compound.
stoichiometry	The calculation of quantitative relationships of the reactants and products in a balanced chemical reaction. Sometimes it is called reaction stoichiometry to distinguish it from composition stoichiometry.

Review Answers

1. Answers will vary but students should indicate that formula units deal specifically with ionic compounds, molecular units with covalent compounds, and the mole deals with both. The equations they choose for their example should have both molecular and ionic compounds in them to show they understand the difference.

2. The mole ratio is a conversion factor used to convert moles of one substance to moles of another substance. When the chemical equation is not balanced, the mole ratio is not a correct ratio.

3. No. Even if all of the coefficients in the balanced chemical equation end up being one (1), you must verify that the equation is balanced before you can use it in calculations.

4. (a) 3 mol

5. (a) 0.313 mol

6. (b) 2:3

7.

(a) $C_3H_{8(g)} + 5\ O_{2(g)} \longrightarrow 3\ CO_{2(g)} + 4\ H_2O_{(L)}$; mol ratio = 5 mol of O_2: 3 mol of CO_2

(b) $3\ Li_{(s)} + AlCl_{3(aq)} \longrightarrow 3\ LiCl_{(aq)} + Al_{(s)}$; mol ratio = 1 mol of $AlCl_3$: 3 mol of LiCl

(c) $2\ C_2H_{6(g)} + 7\ O_{2(g)} \longrightarrow 4\ CO_{2(g)} + 6\ H_2O_{(L)}$; mol ratio = 4 mol of CO_2: 7 mol of O_2

(d) $3\ NH_4OH_{(aq)} + H_3PO_{4(aq)} \longrightarrow (NH_4)_3PO_{4(aq)} + 3\ H_2O_{(L)}$; mol ratio = 1 mol of H_3PO_4: 3 mol of H_2O

(e) $3\ Rb_{(s)} + P_{(s)} \longrightarrow Rb_3P_{(s)}$; mol ratio = 3 mol of Rb: 1 mol of P

8.

$Ca_3(PO_4)_2 + 3\ SiO_2 + 5\ C \longrightarrow 3\ CaSiO_3 + 5\ CO + 2\ P$

(a) mols SiO_2 = (0.35 mols C) $\left(\frac{3\ mols\ SiO_2}{5\ mols\ C}\right)$ = 0.21 mols SiO_2

(b) mols $Ca_3(PO_4)_2$ = (0.45 mol $CaSiO_3$) $\left(\frac{1\ mol\ Ca_3(PO_4)_2}{3\ mols\ CaSiO_3}\right)$ = 0.15 mols $Ca_3(PO_4)_2$

9. $4\ FeS + 7\ O_2 \longrightarrow 2\ Fe_2O_3 + 4\ SO_2$

(a) mols Fe_2O_3 = (1.27 mols O_2) $\left(\frac{2\ mols\ Fe_2O_3}{7\ mols\ O_2}\right)$ = 0.36 mols Fe_2O_3

(b) mols FeS = (3.18 mols SO_2) $\left(\frac{4\ mols\ FeS}{4\ mols\ SO_2}\right)$ = 3.18 mols FeS

10. $4\ NH_{3(g)} + 3\ O_{2(g)} \longrightarrow 2\ N_{2(g)} + 6\ H_2O_{(g)}$

(a) mols NH_3 =(4.12 mols O_2) $\left(\frac{4\ mols\ NH_3}{3\ mols\ O_2}\right)$ = 5.49 mols NH_3

(b) mols N_2 = (0.98 mols O_2) $\left(\frac{2\ mols\ N_2}{3\ mols\ O_2}\right)$ = 0.65 mols N_2

Mass-mass Calculations

Lesson Objectives

- Define stoichiometry.
- Convert from mass of reactant to mass of product.
- Convert from mass of product to mass of reactant.
- Use factor label method in mass-mass calculations.

Introduction

In the previous section we found that the mole is a useful unit to use in the balanced chemical equation. We can use the mole as a conversion factor to calculate moles of product from a given number of moles of reactant or moles of reactant from a given number of moles of product. Masses of substances are measured in grams but calculations on chemical equations are carried out in moles. Therefore, chemists must constantly convert quantities given in grams to moles and must also convert quantities calculated in moles to grams.

Calculations to Determine Mass of Unknown from Given Mass

Stoichiometry, by definition, is the calculation of the quantities of reactants or products in the chemical equation using the relationships found in the balanced chemical equation. The word stoichiometry is actually Greek coming from two words *stoikheion*, which means *element* and *metron,* which means *measure.* Being able to do mass-mass calculations allows you to determine the mass of reactant you require to produce a given amount of product; or to calculate the mass of product you can obtain from a given mass of reactant. Just as when working with mole ratios, it is important to make sure you have a balanced chemical equation before you begin.

A note about the $\frac{\textit{unknown}}{\textit{known}}$ ratio must be made before we go on. In the balanced chemical equation, the balancing coefficient for the species that is given in the equation will be the "known." Therefore given = known. The balancing coefficient for the species that is required in the equation will be the "unknown." Therefore required = unknown.

Using Proportion to Solve Stoichiometry Problems

All methods for solving stoichiometry problems contain the same four steps.

Step 1: Write and balance the chemical equation.

Step 2: Convert the given quantity to moles.

Step 3: Convert the moles of known to moles of unknown.

Step 4: Convert the moles of unknown to the requested units.

Step 1 never changes. You will always be required to **write and balance the chemical equation**. In this section, you are being asked to solve mass-mass stoichiometry problems. This means that the given quantity will be given to you as mass (grams). To convert mass into moles (Step 2), you **divide grams by molar mass**. In the future, the given quantity will be given to you in some form other than mass and you will use other methods to convert it to moles. The same is true of Step 4. In this section you are solving mass-mass problems so you are requested to report the mass of the unknown quantity. To convert the moles of unknown (that you found in Step 3) to mass, you **multiply the moles of unknown by the molar mass** of the substance. In the future, you may be requested to report the amount of unknown in some other form and so some other method will be used to convert the unknown moles into the requested units.

The only step that may appear to vary is **Step 3**, converting moles of known to moles of unknown. This section will show you how to carry out this step using a proportion. In different chemistry texts, you may see different methods of solving stoichiometry problems but these different methods are different mechanical methods but involve exactly the same mathematical process.

The balanced equation shows you the reacting ratio of all substances involved in the reaction in terms of moles. The coefficients in the balanced equation are true for moles or molecules but **not** for grams. Consider the equation for the reaction between hydrogen gas and oxygen gas to produce water.

$$2\ H_{2(g)} + O_{2(g)} \rightarrow 2\ H_2O_{(L)}$$

The molar reacting ratio in this equation is two moles of hydrogen react with one mole of oxygen to produce two moles of water. If you were told that you were going to use 2.00 moles of hydrogen in this reaction and were asked for the moles of oxygen that would be required and the moles of water that would be produced, the answers are present in the balanced equation. The same question becomes only slightly more difficult if you were told that you will be using one mole of hydrogen in the reaction. Since you are using half as much hydrogen, you would need half as much oxygen and would produce half as much water. This is because the reacting ratios keep the same **proportion**.

To set up a proportion to find the moles of unknown when you have the moles of known, you create a ratio using X for the moles of unknown over the given quantity of moles for the known and set this ratio equal to the ratio of the coefficients of unknown over known from the balanced equation. For the equation of hydrogen and oxygen producing water, suppose you wanted to find the moles of oxygen that are needed to react with 0.50 moles of hydrogen. The proportion would look like this.

$$\frac{x \text{ mols } O_2}{0.50 \text{ mols } H_2} = \frac{1 \text{ mols } O_2}{2 \text{ mols } H_2}$$

The left side of the proportion consists of the unknown moles of oxygen you are finding in the numerator and the given moles of hydrogen (from step 2) in the denominator. The members of the right side of the proportion are the coefficients from the balanced equation with the unknown again in the numerator and the known in the denominator. When you solve this proportion by multiplying the denominator from the left side times the ratio on the right side, you will have exactly the same mathematical expression that is found in all the other methods for doing mass-mass problems. In this case, you will find that x = 0.25 moles of O_2.

Sample Problem 1

Pentane, C_5H_{12}, reacts with oxygen gas to produce carbon dioxide and water. How many grams of carbon dioxide will be produced by the reaction of 108.0 grams of pentane?

Step 1: Write and balance the equation.

$$C_5H_{12} + 8\ O_2 \rightarrow 5\ CO_2 + 6\ H_2O$$

Step 2: Convert the given quantity to moles.

$$\text{mols } C_5H_{12} = \frac{108.0 \text{ g}}{72.0 \text{ g/mol}} = 1.50 \text{ mols } C_5H_{12}$$

Step 3: Set up and solve the proportion to find moles of unknown.

$$\frac{x \text{ mols } CO_2}{1.50 \text{ mols } C_5H_{12}} = \frac{5 \text{ mols } CO_2}{1 \text{ mol } C_5H_{12}}$$

Therefore, mols CO_2 = 7.50 mols

Step 4: Convert the unknown moles to requested units (grams).

grams CO_2 = (mols)(molar mass) = (7.50 mols)(44.0 g/mol) = 330. grams

Sample Problem 2

Aluminum hydroxide reacts with sulfuric acid to produce aluminum sulfate and water. How many grams of aluminum hydroxide are necessary to produce 108 grams of water?

Step 1: Write and balance the equation.

$$2\ Al(OH)_3 + 3\ H_2SO_4 \rightarrow Al_2(SO_4)_3 + 6\ H_2O$$

Step 2: Convert the given quantity to moles.

$$\text{mols } H_2O = \frac{108.0 \text{ g}}{18.0 \text{ g/mol}} = 6.00 \text{ mols } H_2O$$

Step 3: Set up and solve the proportion to find moles of unknown.

$$\frac{x \text{ mols Al(OH)}_3}{6.00 \text{ mols H}_2\text{O}} = \frac{2 \text{ mols Al(OH)}_3}{6 \text{ mols H}_2\text{O}}$$

Therefore, mols $Al(OH)_3$ = 2.00 mols

Step 4: Convert the moles of unknown to grams.

grams $Al(OH)_3$ = (2.00 mols)(78.0 g/mol) = 156 grams

Sample Problem 3

15.0 grams of chlorine gas is bubbled over liquid sulfur to produce liquid disulfur dichloride. How much product is produced, in grams?

Step 1: Write and balance the chemical equation.

$Cl_{2(g)} + 2\ S_{(L)} \rightarrow S_2Cl_{2(L)}$

Step 2: Convert the given quantity to moles.

moles $Cl_2 = \frac{15.0 \text{ g}}{70.9 \text{ g/mol}}$ = 0.212 mols

Step 3: Set up and solve the proportion to find moles of unknown.

$$\frac{x \text{ mol S}_2\text{Cl}_2}{0.212 \text{ mol Cl}_2} = \frac{1 \text{ mol S}_2\text{Cl}_2}{1 \text{ mol Cl}_2}$$

Therefore, mols S_2Cl_2 = 0.212 mols

Step 4: Convert the moles of unknown to grams.

grams S_2Cl_2 = (0.212 mols)(135 g/mol) = 28.6 grams

Sample Problem 4

The thermite reaction occurs between elemental aluminum and iron (III) oxide and releases enough heat to melt the iron that is produced in the reaction. If 500. g of iron is produced in the reaction, how much iron (III) oxide was used as reactant?

Step 1: Write and balance the chemical equation.

$Fe_2O_{3(s)} + 2\ Al_{(s)} \rightarrow 2\ Fe_{(L)} + Al_2O_{3(s)}$

Step 2: Convert the given quantity to moles.

moles Fe = $\frac{500. \text{ g}}{55.9 \text{ g/mol}}$ = 8.95 mols

Step 3: Set up and solve the proportion to find moles of unknown.

$$\frac{x \text{ mol Fe}_2\text{O}_3}{8.95 \text{ mol Fe}} = \frac{1 \text{ mol Fe}_2\text{O}_3}{2 \text{ mol Fe}}$$

Therefore, mols Fe_2O_3 = 4.48 mols

Step 4: Convert the moles of unknown to grams.

grams Fe_2O_3 = (4.48 mols)(160. g/mol) = 717 grams

Sample Problem 5

Ibuprofen is a common painkiller used by many people around the globe. It has the formula $C_{13}H_{18}O_2$. If a 200. g tablet of ibuprofen is combusted, how much carbon dioxide is produced?

Step 1: Write and balance the chemical equation.

$2\ C_{13}H_{18}O_{2(s)} + 33\ O_{2(s)} \rightarrow 26\ CO_{2(g)} + 18\ H_2O_{(L)}$

Step 2: Convert the given quantity to moles.

moles $C_{13}H_{18}O_2 = \frac{200.\ \text{g}}{206\ \text{g/mol}}$ = 0.967 mols

Step 3: Set up and solve the proportion to find moles of unknown.

$$\frac{x\ \text{mol}\ CO_2}{0.967\ \text{mol}\ C_{13}H_{18}O_2} = \frac{26\ \text{mol}\ CO_2}{2\ \text{mol}\ C_{13}H_{18}O_2}$$

Therefore, CO_2 mols = 12.6 mols

Step 4: Convert the moles of unknown to grams.

grams CO_2 = (12.6 mols)(44.0 g/mol) = 554 grams

Sample Problem 6

If sulfuric acid is mixed with sodium cyanide, the deadly gas hydrogen cyanide is produced. How much sulfuric acid would have been reacted to produce 12.5 grams of hydrogen cyanide?

Step 1: Write and balance the chemical equation.

$2\ NaCN_{(s)} + H_2SO_{4(aq)} \rightarrow Na_2SO_{4(aq)} + 2\ HCN_{(g)}$

Step 2: Convert the given quantity to moles.

moles HCN = $\frac{12.5\ \text{g}}{27.0\ \text{g/mol}}$ = 0.463 mols

Step 3: Set up and solve the proportion to find moles of unknown.

$$\frac{x\ \text{mol}\ H_2SO_4}{0.463\ \text{mol HCN}} = \frac{1\ \text{mol}\ H_2SO_4}{2\ \text{mol HCN}}$$

Therefore, H_2SO_4 mols = 0.232 mols

Step 4: Convert the moles of unknown to grams.

grams H_2SO_4 = (0.232 mols)(98.1 g/mol) = 22.7 grams

Using Dimensional Analysis in Stoichiometry

Many chemists (and chemistry teachers) prefer to solve the above stoichiometry problems with a single line of math rather than writing out the multiple steps as was done in the last section. This can be done using dimensional analysis or what is also called the factor-label method. This is simply a strategy of using conversion factors to convert from one unit to another. In this method, we can follow the cancellation of units to the correct answer.

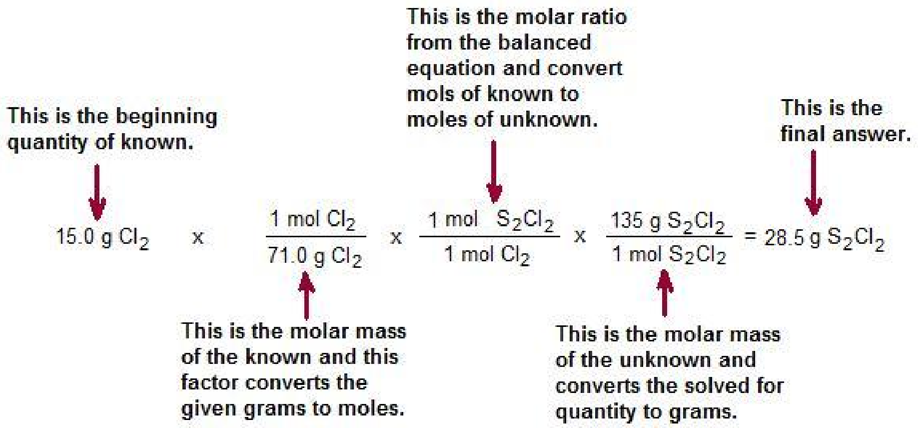
Let's return to the problems from the previous section and use dimensional analysis to solve them. For instance: 15.0 g of chlorine gas is bubbled over liquid sulfur to produce disulfur dichloride. How much product is produced, in grams?

(1) *Always,* the first step is to correctly write and balance the equation:

$Cl_{2(g)} + 2\ S_{(L)} \longrightarrow S_2Cl_{2(L)}$

(2) Identify what is being given (for this question that is 15.0 g of Cl_2) and what is needed to be calculated (grams of S_2Cl_2)

(3) Next, use the correct factors that allow you to cancel the units you don't want and get to the unit you are calculating for:



$$15.0\text{ g }Cl_2 \times \frac{1\text{ mol }Cl_2}{71.0\text{ g }Cl_2} \times \frac{1\text{ mol }S_2Cl_2}{1\text{ mol }Cl_2} \times \frac{135\text{ g }S_2Cl_2}{1\text{ mol }S_2Cl_2} = 28.5\text{ g }S_2Cl_2$$

This is the beginning quantity of known.

This is the molar ratio from the balanced equation and convert mols of known to moles of unknown.

This is the final answer.

This is the molar mass of the known and this factor converts the given grams to moles.

This is the molar mass of the unknown and converts the solved for quantity to grams.

The second example was the thermite reaction. This reaction occurs between elemental aluminum and iron(III) oxide and releases enough heat to melt the iron that is produced in the reaction. If 500.0 g of iron is produced in the reaction, how much iron(III) oxide was placed in the original container?

(1) Write and balance the equation:

$Fe_2O_{3(s)} + 2Al_{(s)} \longrightarrow 2Fe_{(L)} + Al_2O_{3(s)}$

(2) Determine what is given and what needs to be calculated:

given: 715 grams of Fe_2O_3 calculate: grams of Fe

(3) Set-up dimensional analysis system:

$$715\text{ g }Fe_2O_3 \times \frac{1\text{ mol }Fe_2O_3}{159.7\text{ g }Fe_2O_3} \times \frac{2\text{ mols }Fe}{1\text{ mol }Fe_2O_3} \times \frac{55.85\text{ g }Fe}{1\text{ mol }Fe} = 500.\text{ g Fe}$$

Sample Question #1: Ibuprofen is a common painkiller used by many people around the globe. It has the formula $C_{13}H_{18}O_2$. If a 200. g tablet of Ibuprofen is combusted how much carbon dioxide is produced?

(1) $C_{13}H_{18}O_{2(s)} + \frac{33}{2}\ O_{2(g)} \longrightarrow 13\ CO_{2(g)} + 9\ H_2O_{(L)}$

(2) Given: 200. g ibuprofen Calculate: grams of CO_2

(3) Using dimensional analysis:

$$200.\text{ g } C_{13}H_{18}O_2 \times \frac{1\text{ mol } C_{13}H_{18}O_2}{206.3\text{ g } C_{13}H_{18}O_2} \times \frac{13\text{ mols } CO_2}{1\text{ mol } C_{13}H_{18}O_2} \times \frac{44.1\text{ g } CO_2}{1\text{ mol } CO_2} = 555\text{ g } CO_2$$

Sample Question #2: If sulfuric acid is mixed with sodium cyanide, the deadly gas hydrogen cyanide is produced. How much sulfuric acid would have been placed in the container to produce 12.5 g of hydrogen cyanide?

(1) $2\ NaCN_{(s)} + H_2SO_{4(aq)} \rightarrow Na_2SO_{4(s)} + 2\ HCN_{(g)}$

(2) given: 12.5 g HCN calculate: grams of H_2SO_2

(3) dimensional analysis set-up

$$12.5\text{ g HCN} \times \frac{1\text{ mol HCN}}{27.0\text{ g HCN}} \times \frac{1\text{ mol } H_2SO_4}{2\text{ mols HCN}} \times \frac{98.06\text{ g } H_2SO_4}{1\text{ mol } H_2SO_4} = 22.7\text{ g } H_2SO_4$$

Lesson Summary

- Stoichiometry is the mathematics of reactions. Mass-mass calculations can be done using a four-step proportion method or with dimensional analysis, that is, a factor label-method.

Review Questions

1. Why is it important to have a balanced chemical equation before you begin the calculations involving mass-mass conversions? **(Intermediate)**

2. The standard length of a football field is 360. feet. Use the factor label method to convert this length into centimeters. **(Intermediate)**

3. Given the reaction between copper (II) sulfide and nitric acid, how many grams of nitric acid will react with 2.00 g of copper(II) sulfide? **(Intermediate)**

$3\ CuS_{(s)} + 8\ HNO_{3(aq)} \rightarrow 3\ Cu(NO_3)_{2(aq)} + 2\ NO_{(g)} + 4\ H_2O_{(L)} + 3\ S_{(s)}$

(a) 0.49 g

(b) 1.31 g

(c) 3.52 g

(d) 16.0g

4. When properly balanced, what mass of iodine was needed to produce 2.5 g of sodium iodide in the equation below? **(Intermediate)**

$I_{2(aq)} + Na_2S_2O_{3(aq)} \rightarrow Na_2S_4O_{6(aq)} + NaI_{(aq)}$

(a) 1.0 g

(b) 2.1 g

(c) 2.5 g

(d) 8.5 g

5. Donna was studying the following reaction for a stoichiometry project.

$S_{(s)} + 3F_{2(g)} \longrightarrow SF_{6(s)}$

She wondered how much she could obtain if she used 3.5 g of fluorine. First she has to balance the equation. What mass of SF_6(s) would she obtain from the calculation using this amount of fluorine? **(Intermediate)**

(a) 3.5g

(b) 4.5 g

(c) 10.5g

(d) 13.4 g

6. Aqueous solutions of aluminum sulfate and sodium phosphate are placed in a reaction vessel and allowed to react. The products of the reaction are aqueous sodium sulfate and solid aluminum phosphate. **(Intermediate)**

a. Write a balanced chemical equation to represent the above reaction.

b. How many grams of sodium phosphate must be added to completely react all of 5.00 g of aluminum sulfate?

c. If 3.65 g of sodium phosphate was placed in the container, how many grams of sodium sulfate would be produce?

7. For the given reaction (unbalanced), **(Intermediate)**

$Ca(NO_3)_2 + Na_3PO_4 \longrightarrow Ca_3(PO_4)_2 + NaNO_3$

a. how many grams of sodium nitrate are produced from 0.35 grams of sodium phosphate?

b. how many grams of calcium nitrate are required to produce 5.5 grams of calcium phosphate?

8. For the given reaction (unbalanced), **(Intermediate)**

$Na_2S + Al(NO_3)_3 \longrightarrow NaNO_3 + Al_2S_3$

a. how many grams of aluminum sulfide are produced from 3.25 grams of aluminum nitrate?

b. how many grams of sodium sulfide are required to produce 18.25 grams of aluminum sulfide?

Further Reading / Supplemental Links

Website with lessons, worksheets, and quizzes on various high school chemistry topics.

- Lesson 9-3 is on Mass-Mass Problems.

http://www.fordhamprep.org/gcurran/sho/sho/lessons/lesson31.htm

Vocabulary

stoichiometry	The calculation of quantitative relationships of the reactants and products in a balanced chemical reaction. Sometimes it is called reaction stoichiometry to distinguish it form

composition stoichiometry.

Review Answers

1. When doing calculations involved in the mass-mass conversion, there are three steps:

Step 1: Convert given mass to moles.

Step 2: Use mole ratio to convert moles of known to moles of required.

Step 3: Convert moles of required to grams of required.

Notice in step 2, the mole ratio is used which we know from Lesson 17.1 requires a balanced chemical equation.

2. $360.\text{ feet} \times \frac{12\text{ inches}}{1\text{ foot}} \times \frac{2.54\text{ cm}}{1\text{ inch}} = 10{,}970\text{ cm}$

3. (c) 3.52 g

4. (b) 2.1 g

5. (b) 4.5 g

6.

(a) $Al_2(SO_4)_{3(aq)} + 2\ Na_3PO_{4(aq)} \longrightarrow 3\ Na_2SO_{4(aq)} + 2\ AlPO_{4(s)}$

(b) $5.00\text{ g } Al_2(SO_4)_3 \times \frac{1\text{ mol } Al_2(SO_4)_3}{342.1\text{ g } Al_2(SO_4)_3} \times \frac{3\text{ mol } Na_2SO_4}{1\text{ mol } Al_2(SO_4)_3} \times \frac{142\text{ g } Na_2SO_4}{1\text{ mol } Na_2SO_4} = 6.22\text{ g } Na_2SO_4$

(c) $3.65\text{ g } Na_3PO_4 \times \frac{1\text{ mol } Na_3PO_4}{164\text{ g } Na_3PO_4} \times \frac{3\text{ mol } Na_2SO_4}{2\text{ mol } Na_3PO_4} \times \frac{142\text{ g } Na_2SO_4}{1\text{ mol } Na_2SO_4} = 4.74\text{ g } Na_2SO_4$

7.

(a) $3\ Ca(NO_3)_3 + 2\ Na_3PO_4 \rightarrow Ca_3(PO_4)_2 + 6\ NaNO_3$

$0.35\text{ g } Na_3PO_4 \times \frac{1\text{ mol } Na_3PO_4}{164\text{ g } Na_3PO_4} \times \frac{6\text{ mols } NaNO_3}{2\text{ mols } Na_3PO_4} \times \frac{85.0\text{ g } NaNO_3}{1\text{ mol } NaNO_3} = 0.54\text{ g } NaNO_3$

(b) $3\ Ca(NO_3)_3 + 2\ Na_3PO_4 \rightarrow Ca_3(PO_4)_2 + 6\ NaNO_3$

$\text{mols } Ca_3(PO_4)_2 = \frac{5.50\text{ g}}{310.\text{ g/mol}} = 0.0177\text{ mol } Ca_3(PO_4)_2$

$\frac{x\text{ mols } Ca(NO_3)_2}{0.0177\text{ mol } Ca_3(PO_4)_2} = \frac{3\text{ mols } Ca(NO_3)_2}{1\text{ mol } Ca_3(PO_4)_2}$ $x = 0.0532\text{ mol } Ca(NO_3)_2$

grams $Ca(NO_3)_2$ = (mols)(molar mass) = (0.0532 mols)(164 g/mol) = 8.7 g

8.

(a) $3\ Na_2S + 2\ Al(NO_3)_3 \rightarrow 6\ NaNO_3 + Al_2S_3$

$$3.25\text{ g Al(NO}_3)_3 \times \frac{1\text{ mol Al(NO}_3)_3}{213\text{ g Al(NO}_3)_3} \times \frac{1\text{ mol Al}_2\text{S}_3}{2\text{ mol Al}_2(\text{NO}_3)_3} \times \frac{150.\text{ g Al}_2\text{S}_3}{1\text{ mol Al}_2\text{S}_3} = 1.14\text{ g Al}_2\text{S}_3$$

(b) $3\text{ Na}_2\text{S} + 2\text{ Al(NO}_3)_3 \rightarrow 6\text{ NaNO}_3 + \text{Al}_2\text{S}_3$

$$\text{mols Al}_2\text{S}_3 = \frac{18.25\text{ g}}{150.\text{ g/mol}} = 0.122\text{ mol Al}_2\text{S}_3$$

$$\frac{x\text{ mol Al(NO}_3)_3}{0.122\text{ mol Al}_2\text{S}_3} = \frac{2\text{ mol Al(NO}_3)_3}{1\text{ mol Al}_2\text{S}_3} \qquad x = 0.244\text{ mol Al(NO}_3)_3$$

$$\text{grams Al(NO}_3)_3 = (\text{mols})(\text{molar mass}) = (0.244\text{ mols})(213\text{ g/mol}) = 52.0\text{ g}$$

Limiting Reactant

Lesson Objectives

- Identify a limiting reactant in your everyday life.
- Identify limiting reactants in chemical reactions.
- Identify excess reactants in chemical reactions.
- Calculate the limiting reactant using the mole-mole ratios.
- Calculate the products using the limiting reactant and the mass-mass ratios.

Introduction

Suppose you were in the business of building tricycles from the components of frames, handlebars, seats, and wheels. After you completed constructing the tricycle, you boxed it up and shipped it. Suppose further that your component supplies consisted of 100 frames, 120 sets of handlebars, 80 seats, and 300 wheels. What is the maximum number of tricycles you could build and ship? With only a small amount of thinking, you probably came with 80 tricycles. When you run out of seats, you can no longer complete and ship tricycles. The number of tricycles you could build was **limited** by the number of seats you had available. The seats would be called the **limiting component** in your tricycle construction. The other components, the ones you have more than enough of, are said to be **in excess**. If you received a shipment of 100 more seats, could you build 100 more tricycles? Of course not, because one of the other components would become the limiting component.

In the chemical reactions that you have been working with, you were given the amount of one of the substances involved in the reaction and it was assumed that you had exactly the required amount of all the other reagents (reacting chemicals). In this next section, you will be given the amounts of all the reagents but not in the correct reacting amounts. Your task will be to determine which of the reactants is the **limiting reactant** and how much product can be produced from that limiting reactant.

Limiting reactants determine the maximum amount of product that can be formed. Limiting reactants are all around us. We are faced with them on a daily basis. When we work in the kitchen, baking, the limiting reagent may be the ingredients that we have in the cupboard.

Sample Question: You are preparing lunch for a family reunion. You have 25 people attending and are making sandwiches. You go to the store and buy 3 loaves of bread, 5 packages of chicken breast, and 2 bags of lettuce leaves. Each bread bag has 18 slices in it, each package of chicken breast has 10 slices in it, and each bag of lettuce has 30 leaves in it. In order to make one sandwich, you need two slices of bread, two slices of meat and two lettuce leaves. What is your limiting "reactant?"

Solution:

18 slices × 3 loaves → 54 slices of bread → 27 possible sandwiches

10 slices × 5 packages → 50 slices of chicken breast → 25 possible sandwiches

2 bags × 30 leaves → 60 lettuce leaves → 30 possible sandwiches

Therefore, the limiting "reactant" is chicken breast, and you can make 25 sandwiches with lettuce and bread left over. Hopefully everyone only takes one sandwich!

Limiting Reactant: The One That's Used Up in the Reaction

As we discussed in the last section, the ***limiting reactant*** is the one that is used up in the reaction. Often, when we run experiments we want them to run to completion so we add one reactant in excess and have the other as the limiting reactant. For example if we wanted to find out how much $CO_{2(g)}$ we would obtain if we combusted an aspirin tablet we would use excess oxygen to make sure that the entire aspirin tablet reacted.

$$C_9H_8O_{4(s)} + 9\ O_{2(g)} \rightarrow 9\ CO_{2(g)} + 4\ H_2O_{(L)}$$

The limiting reagent is the aspirin tablet because it is the one used up in the experiment. The other reagent, the oxygen, is in excess.

Let's look at another example. A common reaction is when you take a piece of aluminum foil and place it into a solution of copper (II) chloride. Rather quickly, there's lots of heat and gas given off. When the reaction to goes to completion, the blue color of the copper (II) chloride solution fades and a brownish solid is produced, that is, copper. What is the maximum number of grams of copper that can be produced when 53.96 grams of aluminum are reacted with 134.4 grams of copper (II) chloride?

The reaction is:

$2\ Al_{(s)}$	$+3\ CuCl_{2(aq)}$	$\rightarrow$	$3\ Cu_{(s)}$	$+2\ AlCl_{3(aq)}$
2 moles	3 moles		3 moles	2 moles
53.96 g	134.44 g			

Since 53.96 g of Al is 2 moles; and, 134.44 grams of $CuCl_2$ is 3 moles, we know that both reactants will be completely used up and 3 moles of Cu, or 187.3 grams, will be produced.

But, instead of having 53.96 grams of Al, suppose we only have 10.0 grams, what is the maximum number of grams of copper that can be produced? Assuming we still have the 134.44 grams of $CuCl_2$, then it must be obvious that the Al is the limiting reactant and only 35.5 grams of Cu will be produced. Not all reactions are this obvious.

Look at another example. Assume that we have 72.0 g of water reacting with 190. g of $TiCl_4$. The balanced equation is:

$$TiCl_{4(s)} + 2\ H_2O_{(L)} \rightarrow TiO_{2(s)} + 4\ HCl_{(aq)}$$

We can see from the balanced equation that one mole of $TiCl_4$ reacts with two moles of water. The 190. g of $TiCl_4$ is exactly one mole. Therefore, this $TiCl_4$ will react with two moles or 36.0 g of water. But in this reaction, we are given 72.0 g of water. Therefore, the water is in excess and 36.0 g of water will be left over when the reaction is complete.

Sample Question

You are given 34.0 g of NH_3 and 36.5 g of HCl which react according to the following balanced equation. Determine the limiting reactant and the reactant in excess.

$NH_{3(g)} + HCl_{(aq)} \longrightarrow NH_4Cl_{(s)}$

According to the balanced equation, one mole of NH_3 reacts with one mole of HCl. The 34.0 g of NH_3 is two moles and the 36.5 g of HCl is one mole. Since they react with a ratio of one-to-one, one mole of HCl will react with one mole of NH_3 and one mole of NH_3 will be left over. HCl is the limiting reactant and NH_3 is in excess.

Limiting Reactant Determined Using the Mole-Mole Ratio

We can use a stepwise strategy as we did in earlier mathematical calculations to determine the limiting reactant. Remember that with chemical equations, the key to the entire chemical equation is the mole. The balancing coefficients represent the number of moles in the chemical equation. Look at the equation below.

$Al_4C_3 + 12\ H_2O \longrightarrow 4\ Al(OH)_3 + 3\ CH_4$

We can say that one mole of aluminum carbide reacts with twelve moles of water to produce four moles of aluminum hydroxide and three moles of methane. Notice how the amounts of each substance relate to each other in terms of the number of moles. This is the reason we learned to balance equations. Once we have our balanced chemical equation, we can determine such key features as the limiting reagent(s), and the excess reagent(s) using a stepwise strategy.

Start with a balanced equation and then follow these steps for finding the limiting reagent.

Step 1: Determine the number of moles given of each reactant.

Step 2: Determine the moles of reactant A that are required to consume all of reactant B. This is done by multiplying the given moles of B by the molar ratio A/B.

Step 3: Compare the necessary moles of reactant A found in step 2 with actual amount given in step 1. If the amount of A in step 2 is greater than that in step 1, A is the limiting reactant. If the amount of A in step 1 is greater than in step 2, B is the limiting reactant.

Let's try an example:

Andrew was working in the lab on the reaction between hydrochloric acid and iron(II) sulfide. He mixed a solution containing 25.0 g of HCl and one containing 25.0 g of iron (II) sulfide. What is the limiting reagent and what reagent was in excess?

The balanced equation is: $FeS + 2\ HCl \longrightarrow H_2S + FeCl_2$

Step 1: Determine the number of moles of each reactant in the chemical equation.

mols FeS = $\frac{25.0\ \text{g}}{87.9\ \text{g/mol}}$ = 0.284 mol FeS   mols HCl = $\frac{25.0\ \text{g}}{36.5\ \text{g/mol}}$ = 0.686 mol HCl

Step 2: Determine the moles of FeS that are required to consume all of the HCl.

mols FeS required to react with all of the HCl = (0.686 mol HCl) $\left(\frac{1\ mol\ FeS}{2\ mol\ HCl}\right)$ = 0.343 mols FeS

Step 3: Compare moles of FeS found in step 2 with actual amount given in step 1. If the amount in step 2 is greater than in step 1, FeS is limiting reagent. If the amount in step 2 is less than in step 1, FeS is in excess.

We know that we have 0.284 mol of FeS (Step 1)

We know that we need 0.343 mol of FeS (Step 2) to use up all of the HCl.

Therefore step 2 > step1, and FeS is the limiting reagent. This means that HCl is the species in excess.

Let's try another one:

A student mixed 5.0 g of carbon with 23.0 g iron (III) oxide. What is the limiting reactant and what reactant was in excess? The reaction she used is below:

$2\ Fe_2O_3 + 3\ C \rightarrow 4\ Fe + 3\ CO_2$

Step 1: Determine the number of moles of each reactant in the given quantities.

mols C = $\frac{5.0\ g}{12.0\ g/mol}$ = 0.417 mol C   mols Fe_2O_3 = $\frac{23.0\ g}{159.7\ g/mol}$ = 0.144 mol Fe_2O_3

Step 2: Determine the moles of Fe_2O_3 that are required to consume all of the carbon.

mols of Fe_2O_3 required to react with all the carbon = (0.143 mol C) $\left(\frac{2\ mols\ Fe_2O_3}{3\ mols\ C}\right)$ = 0.277 mols Fe_2O_3

Step 3: Compare moles of Fe_2O_3 found in step 2 with actual amount given in step 1. If step 2 > step 1, Fe_2O_3 is limiting reagent. If step 2 < step 1, Fe_2O_3 is in excess.

We know that we have 0.144 mol of Fe_2O_3 (Step 1)

We know that we need 0.275 mol of Fe_2O_3 (Step 2) to use up the entire C.

Therefore Step 2 > Step1, and Fe_2O_3 is the limiting reagent. This means that C is the species in excess.

Sample Problem: While working in the lab, Brenda decided to add 5.0 g of aluminum chloride to 7.0 g of silver nitrate in order to work on her double replacement reactions. Her first goal was to determine the limiting reagent. Can you help her determine which reactant is limiting and which is in excess? Her reaction is listed below.

$AlCl_3 + 3\ AgNO_3 \rightarrow 3\ AgCl + Al(NO_3)_3$

Solution:

Step 1: Determine the number of moles of each reactant in the given quantities.

mols $AlCl_3$ = $\frac{5.0\ g}{133\ g/mol}$ = 0.037 mol $AlCl_3$ mols $AgNO_3$ = $\frac{7.0\ g}{170.\ g/mol}$ = 0.041 mol $AgNO_3$

Step 2: Determine the moles of $AlCl_3$ that are required to consume all of the $AgNO_3$.

mols $AlCl_3$ required to react with all the $AgNO_3$ = (0.041 mol $AgNO_3$) $\left(\frac{1\ mol\ AlCl_3}{3\ mol\ AgNO_3}\right)$ = 0.014 mol $AlCl_3$

Step 3: Compare moles of $AlCl_3$ found in step 2 with actual amount given in step 1. If step 2 > step 1, $AlCl_3$ is limiting reagent. If step 2 < step 1, $AlCl_3$ is in excess.

We know that we have 0.037 mol of $AlCl_3$ (Step 1)

We know that we need 0.014 mol of $AlCl_3$ (Step 2) to use up the entire $AgNO_3$.

Therefore Step 2 < Step1, and $AlCl_3$ is in excess. This means that $AgNO_3$ is the limiting reagent.

After Limiting Reactant Determined, It's a Mass-Mass Calculation

Once we have determined the limiting reactant, we still need to determine the amount of product the limiting reactant will produce. We might even want to know how much of the other reactant we are using and how much is left over. We want these answers in grams. Using one of the examples above, we now want to determine the mass of iron produced. We simply have to add two additional steps. Here is the equation and the moles of limiting reactant we determined.

$2\ Fe_2O_3 + 3\ C \longrightarrow 4\ Fe + 3\ CO_2$

Fe_2O_3 is the limiting reagent and 23.0 g was placed in the container which is equivalent to 0.144 mol.

Step 4: Convert moles of limiting reactant to moles of product (using molar ratios).

Step 5: Convert moles of product to mass (using mass = moles × molar mass).

Step 4:

$$\text{mols Fe} = (0.144\ \text{mol}\ Fe_2O_3\ \left(\frac{4\ mols\ Fe}{2\ mols\ Fe_2O_3}\right) = 0.28\ \text{mol Fe}$$

Step 5:

mass Fe = 0.28 mol Fe × 55.85 g/mol

mass Fe = 16 g Fe

Therefore the mass of Fe formed from this reaction would be 16 g.

Now, let's do one problem from the top:

Sample Problem #1

Magnesium chloride is used as a fireproofing agent but surprisingly it is also a coagulant in tofu – imagine that! Jack was working in the lab one day and mixed 4.56 g of magnesium chloride with 8.25 g of water. The reaction is given below. What mass of magnesium oxide was formed? (Hint: Remember to balance the equation first!)

$MgCl_2 + H_2O \longrightarrow MgO + HCl$

Solution:

$MgCl_2 + H_2O \longrightarrow MgO + 2\ HCl$

$\text{mols } MgCl_2 = \frac{4.56\ g}{95.2\ g/mol} = 0.0479\ \text{mol } MgCl_2$ $\qquad$ $\text{mols } H_2O = \frac{8.25\ g}{18.0\ g/mol} = 0.458\ \text{mol } H_2O$

Step 2: Determine the moles of $MgCl_2$ that are required to consume all of the H_2O.

mols $MgCl_2$ required to consume all the H_2O = (0.458 mol H_2O) $\left(\frac{1\ mol\ MgCl_2}{1\ mol\ H_2O}\right)$ = 0.458 mol $MgCl_2$

Step 3: Compare moles of $MgCl_2$ found in step 2 with actual amount given in step 1. If step 2 > step 1, $MgCl_2$ is limiting reagent. If step 2 < step 1, $MgCl_2$ is in excess.

We know that we have 0.0479 mol of $MgCl_2$ (Step 1)

We know that we need 0.458 mol of $MgCl_2$ (Step 2) to use up the entire H_2O.

Since step 2 > step 1, $MgCl_2$ is the limiting reactant. This means that H_2O is in excess.

Step 4:

mols MgO = (0.0479 mol $MgCl_2$) $\left(\frac{1\ mol\ MgO}{1\ mol\ MgCl_2}\right)$ = 0.0479 mol MgO

Step 5:

mass MgO = 0.0479 mol MgO × 40.31 g/mol = 1.93 g MgO

Therefore the mass of MgO formed from this reaction would be 1.93 g.

Sample Problem #2: In the following reaction, carried out in a laboratory, 12.8 g of ammonia and 14.5 g of oxygen were allowed to react. How many grams of nitrogen monoxide were formed?

$4\ NH_3 + 5\ O_2 \longrightarrow 4\ NO + 6\ H_2O$ (balanced)

Solution:

Step 1: Convert the given quantities to moles.

mols NH_3 = $\frac{12.8\ g}{17.0\ g/mol}$ = 0.752 mol NH_3 mols O_2 = $\frac{14.5\ g}{32.0\ g/mol}$ = 0.453 mol O_2

Step 2: Determine the moles of NH_3 that are required to consume all the O_2.

mols NH_3 required to consume all the O_2 = (0.453 mol O_2) $\left(\frac{4\ mol\ NH_3}{5\ mol\ O_2}\right)$ = 0.362 mol NH_3

Step 3: Compare moles of NH_3 found in step 2 with actual amount given in step 1. If step 2 > step 1, NH_3 is limiting reagent. If step 2 < step 1, NH_3 is in excess.

We know that we have 0.752 mol of NH_3 (Step 1)

We know that we need 0.362 mol of NH_3 (Step 2) to use up the entire O_2.

Since step 2 < step1, NH_3 is in excess. This means that O_2 is limiting reagent.

Step 4:

mols NO = (0.453 mol O_2 $\left(\frac{4\ mols\ NO}{5\ mols\ O_2}\right)$ = 0.362 mol NO

Step 5:

mass NO = 0.362 mol NO × 30.01 g/mol = 10.9 g NO

Therefore the mass of NO formed from this reaction would be 10.9 g.

Lesson Summary

- The limiting reagent is the one that will limit the amount of product that is formed. The reactant that is not the limiting reagent is considered to be "in excess." The calculations to determine the limiting reagent are determined using moles.

Review Questions

1. Consider the balanced reaction: $2\ Al + 6\ HBr \rightarrow 2\ AlBr_3 + 3\ H_2$.

A. When 3.22 moles of Al reacts with 4.96 moles of HBr, how many moles of H_2 are formed? **(Intermediate)**

B. What is the limiting reactant? **(Intermediate)**

C. For the reactant in excess, how many moles are left over at the end of the reaction? **(Challenging)**

2.

A. Write the balanced equation for this reaction: copper (II) chloride reacts with sodium nitrate to form copper (II) nitrate and sodium chloride. **(Intermediate)**

B. If 15.0 grams of copper (II) chloride react with 20.0 grams of sodium nitrate, how much sodium chloride can be formed? **(Intermediate)**

C. What is the limiting reactant for this reaction? **(Intermediate)**

D. How much of the non-limiting reactant will be left over in this reaction? **(Challenging)**

Supplemental Links

http://en.wikipedia.org

Review Answers

1. A. We can see in the equation that three times as many moles of HBr are required to react with Al and the 4.96 moles of HBr given do not appear to be three times 2.48 moles of Al. Therefore, we begin with the assumption (yet to be proven) that HBr is the limiting reactant.

$\frac{2\ \text{mol Al}}{6\ \text{mol HBr}} = \frac{x\ \text{mol Al}}{4.96\ \text{mol HBr}}$ x = 1.65 mol Al used

Since we were given 2.48 moles of Al and only 1.65 moles of Al were used, it is now proven that HBr is the limiting reactant. Along with the 1.65 moles of Al used, the entire 4.96 moles of HBr was used. We can use either the 1.65 moles of Al or the 4.96 moles of HBr to calculate the moles of hydrogen gas produced. This time, we are choosing the 4.96 moles of HBr.

$\frac{3\ \text{mol H}_2}{6\ \text{mol HBr}} = \frac{x\ \text{mol H}_2}{4.96\ \text{mol HBr}}$ x = 2.46 moles H_2 produced.

B. As determined, HBr is the limiting reactant.

C. Aluminum is the reactant in excess and we began with 2.48 moles of it. We determined that 1.65 moles of Al were used, and therefore, 0.83 mole of Al is left over.

2. A. $CuCl_2 + 2\ NaNO_3 \rightarrow Cu(NO_3)_2 + 2\ NaCl$

B. If you solve this stoichiometry problem using 15.0 grams of $CuCl_2$, you find that 13.0 grams of NaCl can be produced. If you solve this problem using 20.0 grams of $NaNO_3$, you find that 13.6 grams of NaCl can be formed. Since 13.0 g of NaCl is the smaller, number, that will be the answer.

C. Since the least amount of product was produced using the 15.0 g of $CuCl_2$, it tells us that $CuCl_2$ was the limiting reactant.

D. $\frac{15.0\ \text{g CuCl}_2}{134.5\ \text{g/mol}} = 0.112\ \text{mol CuCl}_2$

$\frac{1\ \text{mol CuCl}_2}{2\ \text{mol NaNO}_3} = \frac{0.112\ \text{mol CuCl}_2}{x\ \text{mol NaNO}_3}$ $x = 0.224\ \text{mol NaNO}_3$ used

grams $NaNO_3$ used = (0.224 mol)(85.0 g/mol) = 19.0 grams used

Therefore, 1.0 gram of $NaNO_3$ is left over.

Percent Yield

Lesson Objectives

- Define theoretical and actual yield.
- Explain the difference between theoretical and actual yield.
- Calculate percent yield (or reaction efficiency).

Introduction

The amount of product that should be formed when the limiting reactant is completely consumed is called the **theoretical yield** of that product. This is the maximum amount of the product that could form from the quantities of reactants used. In actual practice, this theoretical yield is seldom obtained because of side reactions, failure of the reaction to go to completion, and other complications. The actual amount of product produced in a laboratory or industrial reaction is called the **actual yield**. The actual yield is almost always less than the theoretical yield. The actual yield is often expressed as a percentage of the theoretical yield. This is called the **percent yield**.

Theoretical Yield Compared to Actual Yield

When we calculate the amount of product that can be produced from limiting reactants, we are determining the maximum theoretical amount of product we could obtain from the reaction. In other words, the ***theoretical yield*** is the maximum amount obtained when all of the limiting reactant has reacted in the balanced chemical equation.

Think about our sandwich maker. If our sandwich maker was given 10 slices of bread and 12 cheese slices, how many cheese sandwiches could he make with 2 slices of bread and 2 cheese slices?

The sandwich maker could actually only make 5 sandwiches because there are only 10 slices of bread and 5 × 2 = 10. Thus, the theoretical yield of sandwiches is 5.

The same idea can be translated into chemical equations. When Kerry-Sue worked in the laboratory with solutions of silver nitrate and potassium sulfide, she worked with the equation that is given below:

$$2\ \mathrm{AgNO_{3(aq)}} + \mathrm{K_2S_{(aq)}} \rightarrow \mathrm{Ag_2S_{(s)}} + \mathrm{KNO_{3(aq)}}$$

When Kerry-Sue added 5.00 g of the silver nitrate with 2.50 g potassium sulfide, what was her theoretical yield?

Notice that this is a limiting reagent problem because we are given two reactant amounts and we have to determine which of these reactants runs out first. We have to use the steps from the previous lesson in this section as well. We start with our first step to calculate the moles of each given reactant before we continue to determine the limiting reactant and then the mass of product or the theoretical yield.

$$2\ \mathrm{AgNO_{3(aq)}} + \mathrm{K_2S_{(aq)}} \rightarrow \mathrm{Ag_2S_{(s)}} + \mathrm{KNO_{3(aq)}}$$

Step 1: Determine the number of moles of each reactant in the chemical equation.

$$\text{mols } \mathrm{AgNO_3} = \frac{5.00\ \mathrm{g}}{170.\ \mathrm{g/mol}} = 0.0294\ \text{mol } \mathrm{AgNO_3} \qquad \text{mols } \mathrm{K_2S} = \frac{2.50\ \mathrm{g}}{110.\ \mathrm{g/mol}} = 0.0227\ \text{mol } \mathrm{K_2S}$$

Step 2: Determine the moles of $AgNO_3$ that are required to consume all the K_2S.

$$\text{mols of } \mathrm{AgNO_3} \text{ required to react with all the } \mathrm{K_2S} = (0.0227\ \text{mol } \mathrm{K_2S})\left(\frac{2\ mol\ AgNO_3}{1\ mol\ K_2S}\right) = 0.0454\ \text{mol } \mathrm{AgNO_3}$$

Step 3: Compare moles of $AgNO_3$ found in step 2 with actual amount given in step 1. If step 2 < step 1, $AgNO_3$ is limiting reagent. If step 2 > step 1, $AgNO_3$ is in excess.

We know that we have 0.0294 mol of $AgNO_3$ (Step 1)

We know that we need 0.0454 mol of $AgNO_3$ (Step 2) to use up the entire K_2S.

Since step 2 > step1, and $AgNO_3$ is the limiting reagent. This means that K_2S is the species in excess.

Now that we know which is limiting ($AgNO_3$), we can go on to answer the question: How much Ag_2S(s) can be formed? What is the theoretical yield?

$$2\ \mathrm{AgNO_3} + \mathrm{K_2S} \rightarrow \mathrm{Ag_2S} + \mathrm{KNO_3}$$

$$\text{mols } \mathrm{AgNO_3} = \frac{5.00\ \mathrm{g}}{170.\ \mathrm{g.mol}} = 0.0294\ \text{mol } \mathrm{AgNO_3}$$

$$\frac{x\ \text{mol } \mathrm{Ag_2S}}{0.0294\ \text{mol } \mathrm{AgNO_3}} = \frac{1\ \text{mol } \mathrm{Ag_2S}}{2\ \text{mol } \mathrm{AgNO_3}} \qquad x = 0.0147\ \text{mol } \mathrm{Ag_2S}$$

$$\text{grams } \mathrm{Ag_2S} = (\text{mols})(\text{molar mass}) = (0.0147\ \text{mol } \mathrm{Ag_2S})(248\ \mathrm{g/mol}) = 3.64\ \mathrm{g}\ \mathrm{Ag_2S}$$

Therefore, when Kerry-Sue did her experiment in the lab, her theoretical yield would have been 3.64 g of Ag_2S(s).

Alternatively using dimensional analysis:

$$5.00\text{ g AgNO}_3 \times \frac{1\text{ mol AgNO}_3}{170.\text{ g AgNO}_3} \times \frac{1\text{ mol Ag}_2\text{S}}{2\text{ mol AgNO}_3} \times \frac{248\text{ g Ag}_2\text{S}}{1\text{ mol Ag}_2\text{S}} = 3.64\text{ g Ag}_2\text{S}$$

Sample Question #1: Magnesium hydroxide reacts with hydrochloric acid according to the reaction below. Janet was working to determine the theoretical yield of magnesium chloride given that she started with 3.65g of magnesium hydroxide and 4.24 g of hydrochloric acid. The balanced equation is given below:

$$\text{Mg(OH)}_2 + 2\text{HCl} \rightarrow \text{MgCl}_2 + 2\text{H}_2\text{O}$$

$$\text{mols Mg(OH)}_2 = \frac{3.65\text{ g}}{58.3\text{ g/mol}} = 0.0626\text{ mol Mg(OH)}_2 \qquad \text{mols HCl} = \frac{4.24\text{ g}}{36.5\text{ g/mol}} = 0.116\text{ mol HCl}$$

Step 2: Determine the moles of Mg(OH)_2 that are required to consume all the HCl.

$$\text{mols Mg(OH)}_2 = (0.116\text{ mol HCl})\left(\frac{1\text{ mol Mg(OH)}_2}{2\text{ mol HCl}}\right) = 0.058\text{ mol Mg(OH)}_2$$

Step 3: Compare moles of Mg(OH)_2 found in step 2 with actual amount given in step 1. If step 2 > step 1, Mg(OH)_2 is limiting reagent. If step 2 < step 1, Mg(OH)_2 is in excess.

We know that we have 0.0626 mol of Mg(OH)_2 (Step 1)

We know that we need 0.0580 mol of Mg(OH)_2 (Step 2) to use up the entire HCl.

Since step 2 < step1, Mg(OH)_2 is in excess. This means that HCl is the limiting reagent.

Now that we know which is limiting (HCl), we can go on to answer the question: How much $\text{MgCl}_{2(aq)}$ can be formed? What is the theoretical yield?

$$\text{Mg(OH)}_{2(s)} + 2\text{ HCl}_{(aq)} \rightarrow \text{MgCl}_{2(aq)} + 2\text{ H}_2\text{O}_{(L)}$$

$$4.24\text{ g HCl} \times \frac{1\text{ mol HCl}}{36.5\text{ g HCl}} \times \frac{1\text{ mol MgCl}_2}{2\text{ mol HCl}} \times \frac{95.4\text{ g MgCl}_2}{1\text{ mol MgCl}_2} = 5.54\text{ g MgCl}_2$$

Therefore, Janet knows that the theoretical yield is 5.54 g for magnesium chloride given the above conditions for this reaction.

Sample question #2: Fire extinguishers that produce foam use aluminum hydroxide, Al(OH)_3, and CO_2 both to smother a fire. The foam that you normally see is the aluminum hydroxide. In the reaction below, calculate the amount of aluminum hydroxide produced from 500.0 g of baking soda and 250.0 grams of aluminum sulfate.

$$6\text{ NaHCO}_3 + \text{Al}_2(\text{SO}_4)_3 \rightarrow 3\text{ Na}_2\text{SO}_4 + 2\text{ Al(OH)}_3 + 6\text{ CO}_2$$

Solution:

$$\text{mols NaHCO}_3 = \frac{500.0\text{ g}}{84.1\text{ g/mol}} = 5.95\text{ mol NaHCO}_3 \qquad \text{mols Al}_2(\text{SO}_4)_3 = \frac{250.0\text{ g}}{342\text{ g/mol}} = 0.731\text{ mol Al}_2(\text{SO}_4)_3$$

Step 2: Determine the moles of NaHCO_3 that are required to consume all the $\text{Al}_2(\text{SO}_4)_3$.

$$\text{mols NaHCO}_3 = (0.731\text{ mol Al}_2(\text{SO}_4)_3)\left(\frac{6\text{ mol NaHCO}_3}{1\text{ mol Al}_2(\text{SO}_4)_3}\right) = 4.39\text{ mol NaHCO}_3$$

Step 3: Compare moles of $NaHCO_3$ found in step 2 with actual amount given in step 1. If step 2 > step 1, $NaHCO_3$ is limiting reagent. If step 2 < step 1, $NaHCO_3$ is in excess.

We know that we have 5.95 mol of $NaHCO_3$ (Step 1)

We know that we need 4.39 mol of $NaHCO_3$ (Step 2) to use up the entire $Al_2(SO_4)_3$.

Since step 2 < step1, $NaHCO_3$ is in excess. This means that $Al_2(SO_4)_3$ is the limiting reagent.

Now that we know the limiting reactant is $Al_2(SO_4)_3$, we can go on to answer the question: How much $Al(OH)_3$ can be formed? What is the theoretical yield?

$$6\ NaHCO_3 + Al_2(SO_4)_3 \rightarrow 3\ Na_2SO_4 + 2\ Al(OH)_3 + 6\ CO_2$$

We don't actually have to go all the way back to grams of aluminum sulfate for this calculation because we already converted the grams of aluminum sulfate to moles in an earlier part of the problem.

$$0.731\ \text{mol}\ Al_2(SO_4)_3 \times \frac{2\ \text{mol}\ Al(OH)_3}{1\ \text{mol}\ Al_2(SO_4)_3} \times \frac{78.0\ \text{g}\ Al(OH)_3}{1\ \text{mol}\ Al(OH)_3} = 114\ \text{g}\ Al(OH)_3$$

Therefore, the theoretical yield of aluminum hydroxide foam from the fire extinguisher is 114.0 g.

If you look at these calculations, there is nothing new. The only new part, to date, in this lesson has been the definition of the theoretical yield, or the amount that is calculated on the product side of the equation.

Stop for a moment and think of a situation where you are in the lab and conditions are not good. Have you ever had one of those days when things are just not going your way, where it just seems like conditions just aren't working for you? The same holds true for reactions. In other words, theoretical yields are the *optimum* yields. These are the yields that are calculated if conditions allow all 100% of the reactant to reacts. If, on the other hand, anything were to happen to jeopardize this, the actual yield will differ from the theoretical yield. The **actual yield** is the actual amount that is obtained from the experiment and is almost always less than the theoretical yield.

Now let's go back to the sandwich maker for a moment. What if, while making his sandwiches, his sister comes in and takes a piece of bread off the table and eats it. What does this do to the actual yield, the actual number of sandwiches the sandwich maker has produced? Does he still have 5 sandwiches? No, because during the process of the "reaction", or his sandwich making, the reaction conditions changed and the actual yield became less (down to 4 sandwiches) than the theoretical yield.

The actual yield is massed out at the end of the experiment and thus is provided as a data value. We often calculate how close this actual yield is to the theoretical yield. The percentage of the theoretical yield that is actually produced (actual yield) is known as the percent yield.

The Yield Efficiency Can be Found by Calculating Percent Yield

The efficiency of a chemical reaction can be measured in terms of their various yields. The efficiency of a chemical reaction is determined by the ***percent yield.*** The percent yield is found using the following formula.

$$\%\ \text{yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100$$

Remember the actual yield is measured and the theoretical yield is calculated. Let's look at a sample question. In the reaction shown below, a student was able to produce a actual yield of 5.12 g of calcium sulfate from 4.95 g of sulfuric acid and excess calcium hydroxide. What was her percent yield?

$$H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2\ H_2O$$

We can calculate the theoretical yield by regular stoichiometric means. The method employed below is the factor-label method.

$$4.95 \text{ g } H_2SO_4 \times \frac{1 \text{ mol } H_2SO_4}{98.1 \text{ g } H_2SO_4} \times \frac{1 \text{ mol } CaSO_4}{1 \text{ mol } H_2SO_4} \times \frac{136.2 \text{ g } CaSO_4}{1 \text{ mol } CaSO_4} = 6.88 \text{ g } CaSO_4$$

Once we have found the theoretic yield, we can use the actual yield given in the problem to find the percent yield.

$$\% \text{ yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100 = \frac{5.12 \text{ g}}{6.88 \text{ g}} \times 100 = 74.4\%$$

Sample question #1: Potassium hydrogen phthalate, $KHC_8H_4O_4$, is a compound used quite frequently in acid-base chemistry for a procedure known as standardization. Standardization has to do with the process of determining the concentration of a standard solution. In a certain experiment, 12.50 g of potassium hydroxide is mixed with 1.385 g of KHP. If 5.26 g of the product, $K_2C_8H_4O_4$, is produced, what is the percent yield?

$$KOH + KHC_8H_4O_4 \rightarrow K_2C_8H_4O_4 + H_2O$$

Solution:

$$\text{mols KOH} = \frac{1.385 \text{ g}}{56.1 \text{ g/mol}} = 0.0247 \text{ mol KOH} \qquad \text{mols } KHC_8H_4O_4 = \frac{12.5 \text{ g}}{204 \text{ g/mol}} = 0.0612 \text{ mol } KHC_8H_4O_4$$

Step 2: Determine the moles of KOH that are required to consume all the $KHC_8H_4O_4$.

mols KOH required to react with all the $KHC_8H_4O_4$ = $(0.0612 \text{ mol } KHC_8H_4O_4)\left(\frac{1 \text{ mol } KOH}{1 \text{ mol } KHC_8H_4O_4}\right)$ = 0.0612 mol KOH

Step 3: Compare moles of KOH found in step 2 with actual amount given in step 1. If step 2 > step 1, KOH is limiting reagent. If step 2 < step 1, KOH is in excess.

We know that we have 0.0247 mol of KOH (Step 1)

We know that we need 0.0612 mol of KOH (Step 2) to use up the entire $KHC_8H_4O_4$.

Since step 2 < step1, KOH is the limiting reagent. This means that $KHC_8H_4O_4$ is in excess.

Now that we know the limiting reactant is KOH, we can go on to answer the question: How much $K_2C_8H_4O_4$ can be formed? What is the theoretical yield?

$$0.0247 \text{ mol KOH} \times \frac{1 \text{ mol } K_2C_8H_4O_4}{1 \text{ mol KOH}} \times \frac{242.3 \text{ g } K_2C_8H_4O_4}{1 \text{ mol } K_2C_8H_4O_4} = 5.98 \text{ g } K_2C_8H_4O_4$$

Therefore, the theoretical yield of $K_2C_8H_4O_4$ is 5.98 g. Remember the actual yield given in the question was 5.26 g. Now to calculate the percent yield.

$$\% \text{ yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100 = \frac{5.26 \text{ g}}{5.98 \text{ g}} \times 100 = 88.0\%$$

Sample question #2: Zeanxanthin is a compound that has, as its claim to fame, the responsibility to cause the colors of the maple leaf to change in the fall. It has the formula $C_{38}H_{56}O_2$. In a combustion reaction of 0.95 g of zeanxanthin with excess oxygen, 2.2 g of carbon dioxide was produced. The other product was water. What is the percent yield of CO_2?

Solution:

$C_{38}H_{56}O_2 + 52\ O_2 \rightarrow 38\ CO_2 + 28\ H_2O$

$$\text{mols } C_{38}H_{56}O_2 = \frac{0.95\text{ g}}{544\text{ g/mol}} = 0.00174\text{ mol } C_{38}H_{56}O_2$$

$$\frac{x\text{ mol }CO_2}{0.00174\text{ mol }C_{38}H_{56}O_2} = \frac{38\text{ mol }CO_2}{1\text{ mol }C_{38}H_{56}O_2} \qquad x = 0.066\text{ mol }CO_2$$

grams CO_2 = (0.066 mol)(44 g/mol) = 2.9 g CO_2 *(theoretical yield)*

$$\%\text{ yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100 = \frac{2.2\text{ g}}{2.9\text{ g}} \times 100 = 76\%$$

Lesson Summary

- The percent yield of a reaction is the actual amount of product that is produced. The theoretical yield is the amount of product that is produced under ideal conditions.

Review Questions

1. Is it possible for the actual yield to be more than the theoretical yield? **(Intermediate)**

2. What happens when competing reactions occur when performing an experiment in the lab? **(Intermediate)**

3. If the actual yield is 4.5 g but the theoretical yield was 5.5 g, what is the percent yield for this data? **(Intermediate)**

4. Solid aluminum and sulfur come together in a reaction to produce 7.5 g of aluminum sulfide. If 5.00g of each solid react together, what is the percent yield? Remember to balance the reaction. **(Intermediate)**

$Al + S \rightarrow Al_2S_3$

(a) 32.0 %

(b) 53.4 %

(c) 96.2 %

(d) 100.0 %

5. In her experiment, Gerry finds she has obtained 3.65 g of lead(II) iodide. She knows her reaction was lead (II) nitrate that reacted completely with potassium iodide to produce lead (II) iodide and potassium nitrate. The potassium iodide produced is a brilliant yellow colored precipitate. **(Intermediate)**

$Pb(NO_3)_2(aq) + KI(aq) \rightarrow PbI_2(s) + KNO_3(aq)$

Gerry began with 5.00 g of potassium iodide. What was her percent yield? Remember to balance your equation first!

(a) 26.3%

(b) 36.0%

(c) 52.6%

(d) 72.0%

6. If a percentage yield in the reaction below was found to be 78.3% and the actual yield was 1.01g, what was the original mass of the limiting reagent, oxygen. **(Intermediate)**

$2S + 3O_2 \rightarrow 2SO_3$

(a) 0.515 g

(b) 0.773 g

(c) 1.01 g

(d) 1.29 g

7. Bromine pentafluoride can be produced from a reaction between liquid bromine and fluorine gas. If 3.25 g of fluorine reacts with 2.74 g of bromine to produce 4.83 g of bromine pentafluoride, what is the percent yield of the product? **(Intermediate)**

8. Ammonia can react with nitrogen in a reaction that is similar to a combustion reaction. The products, however, are nitrogen monoxide and water rather than carbon dioxide and water. In the reaction between ammonia and oxygen, 15 g of each reactant are placed in a container and 10.5 g of nitrogen monoxide was produced. What is the percent yield of the nitrogen monoxide? **(Intermediate)**

Further Reading / Supplemental Links

Website with lessons, worksheets, and quizzes on various high school chemistry topics.

- Lesson 16-6 is on Percent Yield.

http://www.fordhamprep.org/gcurran/sho/sho/lessons/lesson166.htm

Vocabulary

theoretical yield	The amount obtained when all of the limiting reactant has reacted in the balanced chemical equation.
actual yield	The actual amount that is obtained from the experiment and is always less than the theoretical yield.
percent yield	% yield = $\frac{\text{actual yield}}{\text{theoretical yield}}$ x 100
yield efficiency	The percent yield of the reaction compared to the optimal yield.

Review Answers

1. The theoretical yield is always greater than or equal to the actual yield, obviously because you cannot create matter. The theoretical yield tells you the maximum yield. It is possible for an inexperienced chemist to allow some water of hydration to remain in the product and thus it might appear that the actual yield is greater than the theoretical, but if the work is done correctly, the actual yield can never be greater than the theoretical.

2. Answers may vary but students may write about the aspect of the reduced yield that would occur due to the fact that a competing reaction would reduce the actual yield which would then reduce the percent yield.

3. 81.8%

4. (c) 96.2%

5. (c) 52.6%

6. (b) 0.773 g

7.

$Br_2 + 5\ F_2 \longrightarrow 2\ BrF_5$

mols $Br_2 = \frac{2.74\ g}{159.8\ g/mol} = 0.0171$ mol Br_2 mols $F_2 = \frac{3.15\ g}{38.0\ g/mol} = 0.0829$ mol F_2

mols Br_2 required to react with all the F_2 = (0.0829 mol F_2) $\left(\frac{1\ mol\ Br_2}{5\ mol\ F_2}\right)$ = 0.0166 mol Br_2

Therefore, the limiting reactant is F_2.

0.0829 mol F_2 x $\frac{2\ mol\ BrF_5}{5\ mol\ F_2}$ x $\frac{175\ g\ BrF_5}{1\ mol\ BrF_5}$ = 5.80 g BrF_5

% yield = $\frac{4.83\ g}{5.80\ g}$ x 100 = 83.2%

8.

$4\ NH_3 + 5\ O_2 \longrightarrow 4\ NO + 6\ H_2O$

mols $NH_3 = \frac{15.0\ g}{17.0\ g/mol} = 0.882$ mol NH_3 mols $O_2 = \frac{15.0\ g}{32.0\ g/mol} = 0.469$ mol O_2

mols NH_3 required to react with all the O_2 = (0.469 mol O_2) $\left(\frac{4\ mol\ NH_3}{5\ mol\ O_2}\right)$ = 0.375 mol NH_3

Therefore, the limiting reactant is O_2.

0.469 mol O_2 x $\frac{4\ mol\ NO}{5\ mol\ O_2}$ x $\frac{30.0\ g\ NO}{1\ mol\ NO}$ = 11.2 g NO

% yield = $\frac{10.5\ g}{11.2\ g}$ x 100 = 93.8%

Energy Calculations

Lesson Objectives

- Define endothermic and exothermic reactions in terms of energy and ΔH.
- Distinguish between endothermic and exothermic chemical changes.

- Write ΔH reactions for a given number of moles of reactants or products.

Introduction

Every sample of matter has energy stored in it. This energy is present in various forms. Some of the energy in a sample of matter is potential energy stored in the chemical bonds. Some of the energy is potential energy associated with the physical phase of the sample of matter and its pressure and volume. Some of the energy in a sample of matter is the kinetic energy due to the random motion of all the atoms and molecules in the material. The total of all these forms of energy is called the **heat content** of the substance.

It is not possible to measure or calculate the total heat content of a substance. All we can do is measure or calculate the amount of energy that a substance gains or loses. When a substance gains energy, its total heat content increases and when a substance loses energy, its total heat content decreases. This section of the chapter will show you how changes in heat content are measured, kept track of, and expressed in chemical notation.

Chemical Reactions Can be Either Exothermic or Endothermic

In the previous lessons, we concentrated on the Law of Conservation of Matter; that is, we learned how to make sure that the numbers and kinds of atoms and the total mass on the two sides of an equation were equal. Reactions also conserve energy during the conversion of reactants to products. The fact that energy is neither created nor destroyed in chemical changes is stated by the Law of Conservation of Energy. The ***Law of Conservation of Energy*** states that the energy of a closed system is constant. If one part of the system gains energy in some form, then another part of the system must lose the same amount of energy in some form. Energy is converted from one form to another in chemical reactions.

Different phases of matter contain different amounts of potential energy. A substance in the gaseous phase contains more potential energy than the same substance in the liquid phase. The same substance in the solid phase contains even less potential energy than it did in the liquid phase. When substances change phase, they must either gain or lose potential energy. The energy that is held by a substance due to its phase, since it is potential energy, cannot be measured with a thermometer. Thermometers only measure kinetic energy. If a substance changes from solid phase to liquid phase (melts), it must add potential energy to its structure and it takes this potential energy from the kinetic energy of its surroundings. If a substance changes from liquid phase to solid phase, it must give up some potential energy and this potential energy that is released becomes kinetic energy in the surroundings.

Chemical bonds also have potential energy associated with them. Some chemical bonds have more potential energy and some have less. During a chemical reaction, when some bonds are breaking and new bonds are being formed, the potential energy of the bonds must also change. If the bonds of the products need less potential energy than the bonds of the reactants, then there is excess potential energy left over and this energy is released during the reaction and becomes kinetic energy of the surroundings. If the bonds of the products need more energy than is available in the bonds of the reactants, the substances will absorb energy from the kinetic energy of the surroundings and put this energy (in the form of potential energy) into the bonds of the products.

Chemical and physical changes are said to absorb or release heat as they proceed from reactants to products. Changes that release energy are known as ***exothermic*** reactions. When an exothermic change occurs, the reactants lose potential bond energy. Let's first examine an ***exothermic chemical change.***

Have you ever held your hand just over the tip of a candle flame, or warmed your hands beside a burning campfire? The burning of the wax or the wood is an exothermic process causing the temperature of the surrounding air to increase. When the potential energy is released from the chemical bonds, the energy becomes kinetic energy of the surroundings and so the temperature of the surroundings will increase. Combustion is an excellent example of this energy change. Look at the reaction for the combustion of octane.

$$2\ C_8H_{18(L)} + 25\ O_{2(g)} \rightarrow 16\ CO_{2(g)} + 18\ H_2O_{(L)} + \text{energy}$$

Notice for exothermic reactions, the energy is listed on the product side of the equation. This means that, like the substances on the product side of the equation, kinetic energy is being produced.

When you are adding or removing heat to a system from an outside source, it can confuse the situation as to whether the reaction itself is giving off or gaining heat. That is, when you put a beaker containing a reaction over a flame or put the beaker into a freezer, it becomes difficult to tell whether the reaction itself is gaining or losing heat. Consider a simpler situation. If you have an acid dissolved in water and a base dissolved in water and you pour them together in a beaker to react, the immediate "surroundings" are the solution in the beaker and the beaker itself. Eventually heat may be transferred to the table the beaker is sitting on and to the air around the beaker but these are less immediate surroundings. If you mix an acid solution and a base solution in a beaker sitting on a lab table and you put a thermometer in the mixed solutions, the thermometer will tell you what energy transfers are occurring. If the temperature of the solution increases, it means that the reactants are giving up potential energy which enters the surroundings as kinetic energy - hence the increase in the temperature of the surroundings. If, when you mix the solutions, the temperature decreases, it means that the reactants are absorbing potential energy which is taken from the kinetic energy of the surroundings - hence the decrease in the temperature of the surroundings.

Physical changes can also be exothermic. However, in order not to get confused, be sure to always think back to the definition of exothermic: potential energy is being lost by the reactant. An example of an ***exothermic physical change*** is liquid water being put into the freezer to make ice cubes:

$$H_2O_{(L)} \longrightarrow H_2O_{(s)} + \text{energy}$$

Notice that in this equation the “energy” term also appears on the product side of the equation – meaning that potential energy is being given up by the reactants and the surroundings are gaining kinetic energy.

Another way to understand this concept is to return to the burning of the wax candle. First you light the candle and determine that it is an ***exothermic chemical change*** since it gives off heat and light, in other words, energy is being released. When you take some of the melted wax and drip onto a piece of plastic wrap, the liquid wax will cool and solidify; once again, energy is being released. This is an ***exothermic physical change.***

Reactions that absorb energy from reactants to products are known as **endothermic** reactions. Let’s first look at an example of an ***endothermic physical change.*** For instance, ice melting:

$$\text{energy} + H_2O_{(s)} \longrightarrow H_2O_{(L)}$$

In this change, the reactant, $H_2O(s)$, is absorbing energy. When you take an ice cube out of the freezer, it melts. The glass, or whatever it’s been placed in, will begin to get colder. This tells us that energy is being absorbed by the $H_2O(s)$ from its surroundings. For endothermic changes, the energy symbol or amount of energy is located on the left hand side of the equation. In other words, the energy is a reactant because it is being absorbed by the system. In this case, $H_2O_{(s)}$ is absorbing energy from the surroundings (the glass). The energy is absorbed as potential energy by the ice but the energy which is being lost by the surroundings is kinetic energy (measureable as temperature).

Finally let’s examine an **endothermic chemical change.** You have probably, at one time or another, added baking soda to vinegar. What happened? You should have gotten lots of bubbles that may have produced a bit of a mess. But did you also notice that the container you used got cold? [You can try this at home using a baggie. It works fine!]. Can you now explain what happened?

Baking soda + vinegar $\longrightarrow$ sodium acetate + water + carbon dioxide

$$\text{Energy} + NaHCO_{3(s)} + CH_3CO_2H_{(aq)} \longrightarrow NaCH_3CO_2\ (aq) + H_2O_{(L)} + CO_{2(g)}$$

Since a gas is given off, we know it is a chemical change. However, this is an **endothermic chemical change** because the reactants are absorbing energy – the surroundings are getting colder - in order to make the products.

The Heat of Reaction

The heat released or absorbed in a chemical reaction is known as the heat of the reaction, ΔH. The ***heat of the reaction,*** also known as the ***enthalpy*** of the reaction, is the measure of the difference in energy in the final state and the initial state. In the previous section, endothermic changes were described as ones that absorbed energy and exothermic as ones that release energy. In a chemical reaction, when bonds are broken, energy is required or absorbed. When bonds are formed, energy is released. The difference between the energy taken on to break bonds and the heat given off when new bonds are formed is the heat of the reaction. The ΔH for a reaction is defined by the equation:

$$\Delta H_{\text{reaction}} = \Delta H_{\text{products}} - \Delta H_{\text{reactants}}$$

From here on, the symbol ΔH_{rxn} will be used as a shorthand form for $\Delta H_{\text{reaction}}$. If more energy is taken on to break the bonds than is given off when new bonds form, then $\Delta H > 0$ and the reaction is endothermic. If more energy is given off by forming bonds than was required to break bonds, then $\Delta H < 0$ and the reaction is exothermic.

Look at the reaction for the partial decomposition of sulfur trioxide. Previously we could have written this reaction with the energy component in the equation as follows:

$$98.9\text{ kJ} + SO_{3(g)} \longrightarrow \frac{1}{2}\,SO_{2(g)} + O_{2(g)}$$

When the energy unit is written into the equation, it is called a thermochemical equation. We can also express the energy needed or given off in a reaction by what is called ΔH notation.

$$SO_{3(g)} \longrightarrow SO_{2(g)} + \frac{1}{2}\,O_{2(g)} \qquad \Delta H = +\,98.9\text{ kJ/mol}$$

When 1 mole of $SO_{3(g)}$ undergoes this decomposition reaction, 98.9 kJ of heat energy is required. This reaction is endothermic. This means that one mole of sulfur dioxide and one-half mole of oxygen gas must contain 98.9 kJ more energy than one mole of sulfur trioxide. This is because in order for the bonds in sulfur trioxide to form, 98.9 kJ of energy must be added.

If a reaction releases more energy when bonds are formed than is absorbed when the bonds are broken, then $\Delta H < 0$ and the reaction is exothermic.

$$H_{2(g)} + \frac{1}{2}\,O_{2(g)} \longrightarrow H_2O_{(L)} \qquad \Delta H = -285.8\text{ kJ/mol}$$

Therefore when 1 mole of liquid water is prepared from its elements, 285.8 kJ of energy is released. This means that the one mole of liquid water contains 285.8 kJ less energy than the one mole of hydrogen gas and the one-half mole of oxygen gas.

Sample question #1: For the following equations, if the equation is given in thermochemical form, convert into ΔH form and if it is in ΔH form, convert it into thermochemical form. In each case, state whether the reaction is endothermic or exothermic.

(a) $C_4H_{10(g)} + H_{2(g)} \longrightarrow 2\,C_2H_{6(g)} + 42\text{ kJ}$

(b) $H_{2(g)} + Cl_{2(g)} \longrightarrow HCl_{(g)} \qquad \Delta H = -\,92.3\text{ kJ}$

(c) $2\,Ag_{(s)} + Cu^{2+}{}_{(aq)} + 147.4\text{ kJ} \longrightarrow Cu_{(s)} + 2Ag^{+}{}_{(aq)}$

(d)$CO_{2(g)} + 2\ H_2S_{(g)} \longrightarrow CS_{2(L)} + 2H_2O_{(L)}$ ΔH -20.2 kJ

Solution:

(a) $C_4H_{10(g)} + H_{2(g)} \longrightarrow 2\ C_2H_{6(g)}$	$\Delta H = -42$ kJ	(exothermic)
(b) $H_{2(g)} + Cl_{2(g)} \longrightarrow 2\ HCl_{(g)} + 92.3$ kJ		(exothermic)
(c) $2\ Ag_{(s)} + Cu^{2+}{}_{(aq)} \longrightarrow Cu_{(s)} + 2\ Ag^{+}{}_{(aq)}$	$\Delta H = +147.4$ kJ	(endothermic)
(d) $CO_{2(g)} + 2\ H_2S_{(g)} \longrightarrow CS_{2(L)} + 2H_2O_{(L)} + 20.2$ kJ		(exothermic)

The Heat of Formation, ΔH_f, and Heat of Combustion, ΔH_c

A reaction in which exactly one mole of one compound is formed from its component elements in their standard state is called a **formation reaction**. Here are some example formation reactions.

$H_{2(g)} + \frac{1}{2}\ O_{2(g)} \longrightarrow H_2O_{(L)}$

$H_{2(g)} + S_{(s)} + 2\ O_{2(g)} \longrightarrow H_2SO_{4(L)}$

$8\ C_{(s)} + 9\ H_{2(g)} \longrightarrow C_8H_{18(L)}$

$Ca_{(s)} + C_{(s)} + \frac{3}{2}\ O_{2(g)} \longrightarrow H_2CO_{3(L)}$

The above are all formation reactions because one mole of a compound is formed from its elements. Here are some reactions that are NOT formation reactions.

$2\ H_{2(g)} + O_{2(g)} \longrightarrow 2\ H_2O_{(L)}$

This is not a formation reaction because two moles of product are formed. A formation reaction may have only one mole of the product.

$\frac{1}{2}\ H_{2(g)} + NO_{(g)} + O_{2(g)} \longrightarrow HNO_{3(L)}$

This is not a formation reaction because one of the reactants is a compound. All the reactants in a formation reaction must be elements. Formation reactions are special reactions and therefore, we use a special notation for the ΔH of a formation reaction. Instead of the general ΔH_{rxn} notation, we use ΔH_f for the heat of reaction of a formation reaction. Consider the following formation reaction.

$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} + 393.5$ kJ

One mole of carbon dioxide is being formed from its elements, so we can specify the energy change using ΔH_f. Therefore we can say this synthesis reaction has a $\Delta H_f = -393.5$ kJ/mole. The following table lists some compounds and their heats of formation.

substance	formula	ΔH_f
acetylene	C_2H_2	+227
ethane	C_2H_6	- 84.7

calcium carbonate	$CaCO_3$	-1206.9

Another special group of reactions are combustion reactions. Combustion reactions are reactions in which one mole of a substance is reacted with oxygen. The heat of reaction for a combustion reaction is sometimes indicated by ΔH_{com}. When you compare heats of combustion, you are comparing how much energy is released when one mole of the substance is burned.

type of fuel	formula	ΔH_c
carbon(s)	C	-393.5 kJ
methane(g)	CH_4	-890.3 kJ
octane(l)	$C_8H_{18}(l)$	-5,490 kJ

Comparing these three fuels (there are many more that are not listed), octane would obviously be the best choice to provide the most energy when one mole of this substance is burned.

Lesson Summary

- Chemical or physical changes that release energy are exothermic changes. Chemical or physical changes that absorb energy are endothermic changes. ΔH_{rxn} is the change in the energy of a reaction. ΔH_f is the heat of formation and represents the energy change when one mole of a compound is produced from its elements. ΔH_{com} is the heat of combustion and represents the energy change, always exothermic, when one mole of a fuel is burned.

Review Questions

1. How does the energy change of the bonds breaking compare to that of them forming? What happens with endothermic and exothermic reactions in terms of the energy? **(Intermediate)**

2. The Bombardier beetle defends itself by squeezing fluid from the inner compartment in its body to the outer compartment. When the fluid reaches the outer compartment, an exothermic reaction takes place using the enzymes present in the beetle's body to produce $C_6H_4O_2$, the defense spray compound. The reaction that takes place in the outer body is shown below. Is this reaction endothermic or exothermic? **(Beginning)**

$$C_6H_4(OH)_2(aq) + H_2O_2(aq) \longrightarrow C_6H_4O_2(aq) + 2H_2O(l) \quad \Delta H = -203.6 \text{ kJ/mol}$$

3. Ozone, $O_3(g)$, is in the news quite frequently due to the environmental concerns about the hole in the stratosphere. The ozone present in the stratosphere protects us from the Sun's harmful ultraviolet rays. Which of the following choices best expresses the equation below? **(Intermediate)**

$$3O_2(g) \longrightarrow 2O_3(g) \quad \Delta H = 286 \text{ kJ}$$

(a) ΔH = 143 kJ/mol and the reaction is endothermic

(b) ΔH = 143 kJ/mol and the reaction is exothermic

(c) ΔH = 286 kJ/mol and the reaction is endothermic

(d) ΔH = 286 kJ/mol and the reaction is exothermic

4. What can you say about the reaction below? **(Intermediate)**

$Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2(g)$ Δ H = - 24.8kJ

(a) it is endothermic and heat is absorbed

(b) it is exothermic and heat is absorbed

(c) it is endothermic and heat is released

(d) it is exothermic and heat is released

5. For the reactions below, convert the thermochemical equations into the ΔH form and convert those in ΔH form into thermochemical equations. **(Beginning)**

(a) $CH_4(g) + 2Cl_2(g) \longrightarrow CH_2Cl_2(g) + 2HCl(g) + 230kJ$

(b) $Fe(s) + Cu^{2+}(aq) \longrightarrow Cu(s) + Fe^{2+}(aq)$ ΔH = -152.3kJ

(c) $N_2(g) + O_2(g) + 91.3\text{ kJ} \longrightarrow NO(g)$

(d) $CH_3CH_2OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$ ΔH = 1367 kJ

6. Dodecane is the main ingredient in diesel fuel. It has a formula $C_{12}H_{26(L)}$. When it undergoes combustion, 7561 kJ of energy is released per mole of dodecane. Using your knowledge of chemical reactions, write the combustion reaction for dodecane in both thermochemical and ΔH forms. **(Intermediate)**

Vocabulary

law of conservation of energy	The energy of the universe is constant and is therefore conserved.
potential energy	Energy of position.
kinetic energy	Energy of motion.
endothermic	Energy is absorbed in the reaction, ΔH is positive or ΔH > 0.
exothermic	Energy is released in the reaction, ΔH is negative or ΔH < 0.
heat of reaction, ΔH_{rxn}	The change in energy from the products to the reactants ($\Delta H_{reaction} = H_{products} - H_{reactants}$).
enthalpy	A measure of the energy content of a system.
ΔH_f	Heat of Formation; the energy change when 1 mole of a substance is produced from its elements in their standard states.
ΔH_{com}	Heat of combustion; the energy change that occurs when 1 mole of a fuel is reacted with oxygen.

Review Answers

1. When bonds break, energy is absorbed from the surroundings to break the bonds. When bonds form energy is released to the surrounding as the new bonds form. For an exothermic reaction, more energy was given off when bonds formed that was absorbed when the bonds were broken. It is vice versa for endothermic

reactions.

2. The reaction is exothermic because of the negative ΔH. This means that 203.6 kJ of energy is released when the reactants form products or that there is 203.6 less energy in product formation than in reactant breakdown.

3. (a) ΔH = 143 kJ/mol and the reaction is endothermic

4. (d) it is exothermic and heat is released

5.

(a) $CH_4(g) + 2Cl_2(g) \longrightarrow CH_2Cl_2(g) + 2HCl(g)$	+ ΔH - 230 kJ	(exothermic)
(b) $Fe(s) + Cu^{2+}(aq) \longrightarrow Cu(s) + Fe^{2+}(aq) + 152.3kJ$		(exothermic)
(c) $N_2(g) + O_2(g) \longrightarrow NO(g)$	ΔH + 91.3 kJ	(endothermic)
(d) $CH_3CH_2OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l) + 1367$ kJ		(exothermic)

6. ΔH notation: $C_{12}H_{26}(l) + \frac{37}{2} O_2 \longrightarrow 12CO_2 + 13H_2O$ $\Delta H = -7561$ kJ/mol

thermochemical notation: $C_{12}H_{26}(l) + \frac{37}{2} O_2 \longrightarrow 12CO_2 + 13H_2O + 7561$ kJ/mol

18. The Kinetic-Molecular Theory

The Three States of Matter

Lesson Objectives

- The student will describe molecular arrangement differences among solids, liquids, and gases.
- The student will describe the basic characteristic differences among solids, liquids, and gases.

Introduction

The Kinetic Molecular Theory allows us to explain the existence of the three phases of matter. In addition, it helps explain the physical characteristics of each phase and how phases change from one to another. The Kinetic Molecular Theory is essential for the explanations of gas pressure, compressibility, diffusion, and mixing. Our explanations for reaction rates and equilibrium also rest on the concepts of the Kinetic-Molecular Theory.

The Assumptions of the Kinetic Molecular Theory

According to the Kinetic Molecular Theory, all matter is composed of tiny particles that are in constant, random, straight-line motion. This motion is constantly interrupted by collisions between the particles and between the particles and surfaces. The rate of motion of the particles is related to their temperature. The velocity of the particles is greater at higher temperatures and lower at lower temperatures. In our discussions of gases, we will be referring to what are called ideal gases. In **real gases,** there is some slight attraction between the gas molecules and the molecules themselves do take up a small amount of space. However, in an **ideal gas,** we assume there are no attractions between molecules and we assume the molecules themselves take up no space. Later in this chapter, real and ideal gases will be discussed again in more detail.

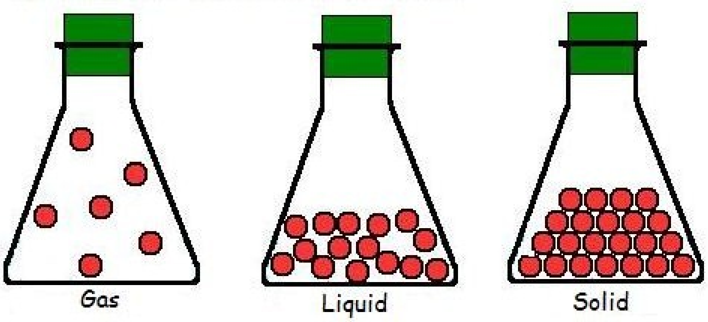


Figure 1: The three phases of matter. (*Created by:* Richard Parsons, *License:* CC-BY-SA)

The Characteristics of Solids

In a solid, the molecules are held in a tightly packed pattern (see Figure 1), in which molecules hold a set position in spite of random motion. Molecular motion is reduced to vibrating in place.

In a liquid, the molecules touch each other but are not held in a pattern. The liquid structure has holes in it, which allow molecules to pass each other and change position in the structure. In a gaseous substance, the molecules are completely separated from each other and move around independently. Most of the volume of a gas is empty space. The molecular arrangement in the three phases accounts for the various characteristics of the phases of matter.

In a liquid, the molecules touch each other but are not held in a pattern. The liquid structure has holes in it, which allow molecules to pass each other and change position in the structure. In a gaseous substance, the molecules are completely separated from each other and move around independently. Most of the volume of a gas is empty space. The molecular arrangement in the three phases accounts for the various characteristics of the phases of matter. For example, mixing of the particles in solids is almost non-existent. This is because the molecules cannot pass by one another in the tightly packed pattern. Solids are essentially incompressible because when a substance is compressed, it is the spaces between molecules that are compressed, not the molecules themselves. Since solids have almost no empty space in their structure, they do not compress. Solids have their own shape and volume as shown in **Figure 2.** A 25 mL rectangular piece of copper has the same shape and volume when it is resting on the table top as it does inside a beaker. The volume and shape of a solid is maintained by the particle structure of the solid which is a tightly held pattern of atoms.

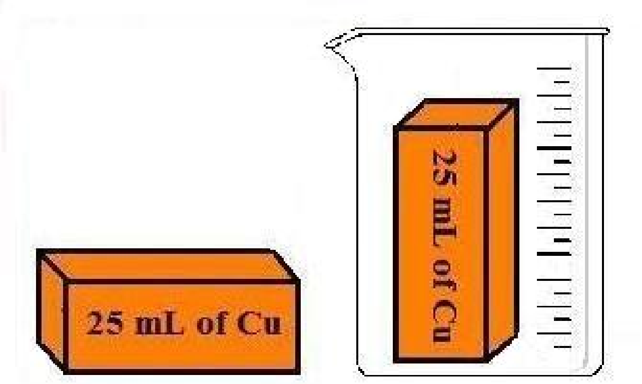


Figure 2: Solids maintain their own shape and their own volume. (*Created by:* Richard Parsons, *License:* CC-BY-SA)

The Characteristics of Liquids

In liquids, mixing occurs more readily because there are spaces between the molecules that allow molecules to pass each other. The spaces between the molecules in liquids are small and so liquids have very little compressibility. Liquids maintain their own volume but take their shape from the shape of the container.

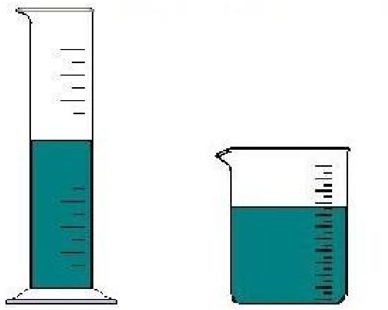


Figure 3: Liquids maintain their own volume but take the shape of their container.

(*Created by:* Richard Parsons, *License:* CC-BY-SA)

A 25 mL sample of liquid in a graduated cylinder has a volume of 25-mL and has the shape of a cylinder. If the 25 mL sample is placed in a beaker, it still has a volume of 25 mL but now it has the shape of the beaker. The structure of the liquid keeps the particles in touch with each other so the volume does not change but the particles can slide by each other so they can flow to the shape of the container.

The Characteristics of Gases

Mixing in gases is almost instantaneous because there are no inhibitions for particles to pass one another. The volume of a gas is nearly all empty space and so particles move completely freely. Gases are highly compressible because there is a great deal of empty space in gaseous structures which allows the particles to be pushed closer together. Gases do not have either their own volume or their own shape. They take both volume and shape from their container.

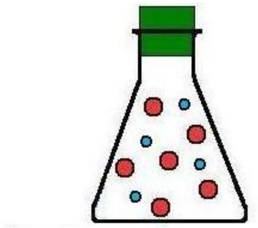


Figure 4: Gases mix readily. (*Created by:* Richard Parsons, *License:* CC-BY-SA)

Lesson Summary

- All matter is composed of tiny particles called atoms or molecules.
- These particles are in constant random motion at all temperatures above absolute zero.
- In the solid phase, the molecules are held in a highly organized, tightly-packed pattern.
- Due to the tightly-packed pattern of molecules in a solid, solids maintain their own shape and volume and do not mix readily.
- In the liquid phase, molecules are in touch with each other but they loosely packed and may move past each other easily.
- Due to the loosely packed structure of a liquid, liquids maintain their own volume but take the shape of their container and they are able to mix readily.
- In the gaseous phase, molecule are completely separate from each other.
- The volume of a gas is mostly empty space.
- Due to the structure of gases, they take both the volume and the shape of their container and they mix almost instantaneously.

Review Questions

1. Automobile brakes have a hose full of liquid connected to your brake pedal on one end and to the brake pads on the other end. When you press on the brake pedal, the force is transferred through the liquid and presses the brake pads against the wheels to slow or stop them. Brakes that use liquid in this fashion are called hydraulic brakes and the liquid is called hydraulic brake fluid. What don't they use air in the brake lines instead of liquid? **(Intermediate)**

2. Why would it cause a problem if some air got into your liquid-filled brake lines? **(Intermediate)**

3. If you had a 250 mL container full of helium gas and you transferred all of the gas into an empty 1.00 liter container, would the 1.00 liter container be full or only 1/4 full? If something seems odd about this question, what do you think it is? **(Challenging)**

Further Reading / Supplementary Links

http://learner.org/resources/series61.html'"

The ***learner.org*** website allows users to view streaming videos of the Annenberg series of chemistry videos. You are required to register before you can watch the videos but there is no charge. The website has one video that relates to this lesson called ***A Matter of State*** .

Vocabulary

phase	Any of the forms or states, solid, liquid, gas, or plasma, in which matter can exist, depending on temperature and pressure.
kinetic	The term "kinetic" refers to the motion of material bodies and the forces associated with them.
molecule	In the kinetic theory of gases, any gaseous particle regardless of composition

Review Answers

1. Gases due to the very large spaces between the molecules are highly compressible. Liquids, on the other hand, due to very small spaces between the molecules are not compressible. When you use liquid in a brake line, the force you exert on the brake pedal is transferred to the brakes pads and presses them against the wheel. If you had air in your brake line, the pressure you exert on the brake pedal would simply compress the air and would not transfer through to the brake pads. You would, essentially, have no brakes.

2. The answer is similar to that for question #1. Even a relatively small amount of air in the brake line would compress enough to allow the brake pedal to be pushed down without transferring the force to the brake pads.

3. Any sample of gas always completely fills any container it is in. That is because the gas will expand until it hits all the walls of the container – the spaces between the molecules simply get larger. Our definition of “full” apparently means that the substance contained touches all the walls. It seems odd that the same amount of material will exactly fill two containers of different size. Perhaps the oddity is due to the fact that the word “full” doesn’t apply well when gases are being discussed.

Gases

Lesson Objectives

- The student will describe the relationship between molecular motion and Kelvin temperature.
- The student will describe random motion of gaseous molecules and explain how their collisions with surfaces cause pressure on the surface.
- The student will state that zero kinetic energy of molecules corresponds to 0 K and that there is no lower temperature.

Introduction

Gases are tremendously compressible, can exert massive pressures, expand nearly instantaneously into a vacuum, and fill every container they are placed in regardless of size. All of these properties of gases are due to their molecular arrangement.

Gases Readily Change Volume

In dealing with gases, we lose the meaning of the word “full.” A glass of water may be ¼ full or ½ full or full, but a container containing a gaseous substance is always full. The same amount of gas will fill a quart jar, or a gallon jug, a barrel, or a house. The gas molecules separate farther from each other and spread out uniformly until they fill whatever container they are in. Gases can be compressed to small fractions of their original volume and expand to fill virtually any volume. If gas molecules are pushed together to the point that they touch, the substance would then be in the liquid form. One method of converting a gas to a liquid is to cool it and another method is to compress it.

Gases Exert Pressure

The constant random motion of the gas molecules causes them to collide with each other and with the walls of their container. These collisions of gas molecules with their surroundings exert a pressure on the surroundings. When you blow up a balloon, the air particles inside the balloon push against the elastic sides, the walls of the balloon are pushed outward and kept firm. This pressure is produced by air molecules pounding on the inside walls of the balloon.

When you look at the side of a blown-up balloon, the balloon wall is held out firmly and with no visible vibration or movement in its position. It is not apparent that the wall is being held in position by billions of collisions with tiny particles – but that is exactly what is happening. If you place a book on its edge and tilt it over slightly so that without support, it would fall, you can keep the book from falling by tapping it very rapidly with your finger on the underside. The book doesn't stay steady because you can't tap it fast enough to keep it exactly in one position. If you can imagine being able to tap it millions of times per second, you can see how a steady position could be maintained with many small collisions.

Gas Temperature and Kinetic Energy

Kinetic energy is the energy of motion and therefore, all moving objects contain kinetic energy. The mathematical formula for calculating the kinetic energy of an object is $KE = \frac{1}{2} mv^2$. This physics formula applies to all objects in exactly the same way whether we are talking about the moon moving in its orbit, a baseball flying toward home plate, or a gas molecule banging around in a bottle. All of these objects have kinetic energy and their kinetic energies can all be calculated with the same formula. As you can see from the formula, the kinetic energy is dependent on both the mass of the object and the velocity of the object. The kinetic energy of a 0.20 kg ball moving at 20. m/s would be $KE = \frac{1}{2}\ (0.20\ \text{kg})(20.\ \text{m/s})^2 = 40.$ Joules. The kinetic energy of a molecule would be calculated in exactly this same way. You should note that if the mass of an object is doubled while its velocity remains the same, the kinetic energy of the object would also be doubled. If, on the other hand, the velocity is doubled while the mass remains the same, the kinetic energy would be quadrupled because of the square in the formula.

It was mentioned at the beginning of this lesson that the molecular motion of molecules is related to their temperature. If you think of the average kinetic energy of a group of molecules and temperature measured in degrees Kelvin, the relationship is a direct proportion. When you measure the temperature of a group of molecules, what you are actually measuring is their average kinetic energy. They are the same thing but expressed in different units. The formula for this relationship is $KE_{ave} = 3/2\ RT$ where R is a constant of proportionality and T is the absolute temperature (Kelvin). When a substance is heated, the average kinetic energy of the molecules increases. Since the mass of the molecules cannot be increased by heating, it is clear that the velocity of the molecules is increasing. The relationship between the kinetic energy of an object and its velocity, however, is not linear. Because of the exponential dependence of the velocity in the formula for kinetic energy, when the absolute temperature is doubled, the average kinetic energy is also doubled but the velocity is increased only by a factor of 1.4.

It is absolutely vital that you keep in mind that the mathematical relationship between the temperature and the average kinetic energy of molecules only exists when the temperature is expressed in the Kelvin scale. In order for the direct proportion to exist, the molecules must have zero kinetic energy when the temperature is zero. It is surely apparent to you that molecules do NOT have zero kinetic energy at 0°C. Balloons and automobile tires do not go flat when the outside temperature reaches 0°C. The temperature at which molecular motion stops is 0 K (-273°C). If temperature is measured in Kelvin degrees, then the average kinetic energy of a substance at 100 K is exactly double the average kinetic energy of a substance at 50 K. Make sure all the work you do dealing with the kinetic energy of molecules is done with Kelvin temperatures.

Lesson Summary

- Gases are composed of tiny particles called molecules.

- Molecules of a gas are so far apart, on average, that the volume of the molecules themselves in negligible compared to the volume of the gas.
- Gas molecules are in constant, random, straight-line motion that is constantly interrupted by collisions with other molecules or with container walls.
- Molecular collisions with container walls cause the gas to exert pressure.

Review Questions

1. Ball A has a mass of 4 daltons and a speed of 16 meters per second. Ball B has a mass of 16 daltons. What velocity is necessary for ball B to have the same kinetic energy as ball A? **(Intermediate)**

2. Suppose you blow up a balloon, tie off the opening, and place the balloon in a freezer for one hour. When you take the balloon out of the freezer, what will the most significant difference be in its appearance from when you put it in the freezer? What do you think will happen to the this difference as the balloon sits out in the room for a while? **(Intermediate)**

3. Suppose you drive home from school on a hot day and when you get home, you check the pressure in your automobile tires. You find the tire pressure is over the manufacturer's recommended pressure and so you let some air out of the tires until the pressure is appropriate. What will the tire pressure be in the morning when you go out to go to school? **(Intermediate)**

4. Weather balloons are large balloons that are used to carry meteorological instruments up through the atmosphere and radio back measurements on temperature, pressure, humidity, etc. as it passes through many different altitudes. When these balloons are filled with helium before they are released from earth, they are only filled a little more than 10% full. This provides enough lift to carry the instruments but the balloon would have more lift if it were filled completely. Why don't they fill the weather balloons to maximum capacity? **(Challenging)**

Further Reading / Supplemental Links

Website with lessons, worksheets, and quizzes on various high school chemistry topics.

- Lesson 7-1 is on the Kinetic Theory of Gases.

http://www.fordhamprep.org/gcurran/sho/sho/lessons/lesson71.htm

Vocabulary

kinetic energy	Kinetic energy is the energy a body possesses due to it motion, $KE = 1/2\ mv^2$.
Kelvin temperature	The absolute temperature scale where 0 K is the theoretical absence of all thermal energy (no molecular motion).

Review Answers

1.

$$KE_A = \frac{1}{2} m_A v_A{}^2 = \frac{1}{2}(4)(16)^2 = 512$$

$$KE_B = \frac{1}{2} m_B v_B{}^2 = \frac{1}{2}(16)(x)^2 = 512 \quad \text{so} \quad x^2 = 64 \text{ and } x = 8 \text{ m/s}$$

2. As the air in the balloon cools down, the pressure inside the balloon will decrease and the balloon will shrink (outside air pressure will push it smaller). When you take the balloon out of the freezer it will be smaller than when you put it in. If you leave it sit around in the room for a while, the air in the balloon will warm up

and the balloon will expand.

3. Because of the hot day and the heat from friction of your tires rolling on the highway, the air in your tires have heated up and will exert a greater pressure. If you let some air out, then the next morning when your tires have cooled down, the air pressure in the tires will be too low.

4. If the weather balloons are filled to capacity, as they rise and the external air pressure decreases, the balloons will try to expand and will pop.

Gases and Pressure

Lesson Objectives

- The student will define pressure.
- The student will convert requested pressure units.
- The student will read barometers and open and closed-end manometers.
- The student will apply the gas laws to relationships between the pressure, temperature and volume of a gas.
- The student will state standard conditions for gases.

Introduction

The tremendous gas pressures that are possible are due to the pounding of trillions of tiny particles on a surface.

Pressure

Pressure is defined as the force exerted divided by the area over which the force is exerted.

$$\textbf{Pressure} = \frac{\textbf{Force}}{\textbf{Area}}$$

You must be careful when thinking about force and pressure. The concept of force is quite straightforward but the concept of pressure is a little trickier. Consider a large man and a smaller woman dressed to go out for an evening. The man weighs 200 pounds and is wearing normal man's shoes so that when he walks, at times, all his weight is exerted on the heel of one shoe. If that heel is 2 inches long and 2 inches wide, then his weight is exerted over an area of 4 inches^2 and the pressure exerted by the heel of his shoe would be

Pressure = $\frac{\text{Force}}{\text{Area}} = \frac{200.\ \text{pounds}}{4.0\ \text{inches}^2}$ **= 50. lbs/in^2** The woman, on the other hand weighs only 100 pounds but she is wearing high heels. If the heel on one of her shoes is ½ inch by ½ inch, then when she walks, at times, all her weight is exerted over an area of ¼ inch^2. The pressure exerted by one of her heels would be

Pressure = $\frac{\text{Force}}{\text{Area}} = \frac{100.\ \text{pounds}}{0.250\ \text{inches}^2}$ **= 400. lbs/in^2** This huge pressure has little to do with her weight but has a great deal to do with the area of the heels of her shoes. If these two people attempted to walk across the lawn, the 200 pound man would likely have no problem whereas the 100 pound woman might well have her heels sink into the grass. It is not uncommon for women wearing spike heels to put dents in hardwood flooring. Pressure is not just about the total force exerted but also about the area over which it exerted. This is the reason that nails and tent pegs and such things are sharpened on the end. If the end were blunt, the force exerted by a hammer would be insufficient to generate enough pressure to cause the object to be pounded into a piece of wood or the ground.

Figure 5: Reducing the area over which a force is exerted can greatly increase the pressure. (*Source:* CK-12 Foundation, *License:* CC-BY-SA)

Atmospheric Pressure

The tremendous pressure that can be exerted by gaseous molecules (because there are so many of them) was once demonstrated by a German physicist named Otto von Guericke who invented the air pump. Von Guericke placed two hemispheres about the size of dinner plates together and pumped the air out from between them. When both the inside and the outside of the hemispheres have air molecules, the pounding of the molecules on the plates is balanced on the two sides but when the air is removed from between the plates, there is no equalizing pounding of air molecules on the inside. Only the outside air molecules push on the plates and hold them together with amazing force. Teams of horses were unable to pull the hemispheres apart. The air molecules pounding on the outside of the hemispheres were exerting a greater pressure than the horses could produce trying to pull the hemispheres apart. When von Guericke opened a valve and allowed air inside, he could easily separate the hemispheres by hand.

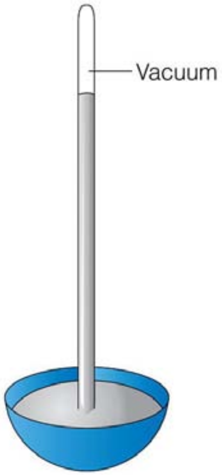


Figure 6: Barometer (*Source:* CK-12 Foundation, *License:* CC-BY-SA)

The air molecules in our atmosphere exert pressure on every surface that is in contact with air. The air pressure of our atmosphere at sea level is approximately 15 pounds/inch^2. This pressure is unnoticed because the air is not only outside the surfaces but also inside allowing the atmospheric air pressure to be balanced. The pressure exerted by our atmosphere will become quickly noticed, however, if the air is removed or reduced inside an object. A common demonstration of air pressure makes use of a one-gallon metal can. The can has a few drops of water placed inside and is then heated to boiling. The water inside the can vaporizes and expands to fill the can pushing the air out. The lid is then tightly sealed on the can. As the can cools, the water vapor inside condenses back to liquid water leaving the inside of the can with a lack of air molecules. As the water vapor condenses to liquid water, the air pressure outside the can slowly crushes the can flat. People, of course, also have atmospheric pressure pressing on them. An averaged sized person probably has a total force exerted on them from the atmosphere in excess of 25,000 pounds. Fortunately, people also have air inside them to balance the force. A device to measure atmospheric pressure, the barometer, was invented in 1643 by an Italian scientist named Evangelista Torricelli (1608 – 1647) who had been a student of Galileo. Torricelli's barometer was constructed by filling a glass tube, open at one end and closed at the other, with liquid mercury and then inverting the tube in a dish of mercury as shown in **Figure 6.** The empty tube was first turned so that the closed end was down and the tube was filled with liquid mercury. The dish was also filled two-thirds full of mercury. The open end of the mercury-filled tube was then covered and the tube was inverted. No mercury could flow out. The open end covered by the finger was then submerged completely beneath the mercury in the dish and the finger removed. Since the open end was under the surface, no air could get into the tube. When the finger was removed, the mercury in the tube fell to a height such that the difference between the surface of the mercury in the dish and the top of the mercury column in the tube was 760 millimeters. The volume of empty space above the mercury in the tube was a vacuum.

The explanation for why the mercury stays in the tube is that there are air molecules pounding on the surface of the mercury in the dish and there are no air molecules pounding on the top of the mercury in the tube. The weight of the mercury in the tube divided by the area of the opening in the tube is exactly equal to the atmospheric pressure. If you are quick with math, you will recognize that the diameter of the tube makes no difference. This is because doubling the diameter of the tube doubles the volume of mercury in the tube and doubles the weight of the mercury. It also doubles the area over which the force is exerted and therefore, the pressure will be the same for any size tube. No matter what diameter tube you might choose, the air pressure will hold the mercury to the same height.

The height to which the mercury is held would only be 760. millimeters when air pressure is normal and at sea level. The atmospheric pressure changes due to weather conditions and the height of the mercury in the barometer will change with it. Atmospheric pressure also varies with altitude. Higher altitudes have lower air pressure because the air is "thinner" – fewer air molecules per unit volume. In the mountains, at an altitude of 9600 feet, the normal atmospheric pressure will only support a mercury column of 520 millimeters.

Measuring Gas Pressure

For various reasons, chemistry has many different units for measuring and expressing gas pressure. You will need to be familiar with most of them so you can convert them into preferred units. Because instruments for measuring pressure often contain a column of mercury, the most commonly used units for pressure are based on the height of the mercury column that the gas can support. The original unit in chemistry for gas pressure was **mm of Hg** (millimeters of mercury). Standard atmospheric pressure at sea level is 760. mm of Hg. This unit is something of a problem because while it is a pressure unit, it looks a lot like a length unit. Students, in particular, occasionally leave off the "of Hg" and then it definitely appears to be a length unit. To eliminate this problem, the unit was given another name. It was called the **torr** in honor of Torricelli. 760

torr is exactly the same as 760 mm of Hg. For certain work, it became convenient to express gas pressure in terms of multiples of normal atmospheric pressure at sea level and so the unit atmosphere (atm) was introduced.

1.00 atm = 760. mm of Hg = 760. torr

Pressures expressed in mm of Hg can be converted to atmospheres using the conversion factor 1.00 atmosphere = 760. mm of Hg. In recent times, scientists decided that all branches of science should have the same units for measurements rather than each science using different units for the same measurement. The purest units are those from physics and therefore chemists have now added physics units for pressure. In physics, force is expressed in a unit called the Newton (N) and area is expressed in meters^2 (m^2). Therefore, pressure in physics is expressed in Newtons/meter^2 (N/m^2). This has also been renamed the **Pascal** (Pa).

1.00 atm = 101,325 N/m^2 = 101,325 Pa = 760 mm of Hg = 760 torr

As it happens, one Pascal is an extremely small pressure, so it is convenient to use kilopascals or kPa when expressing gas pressure in that unit. 1.00 atm = 101.325 kPa.

Pressure Unit Conversion Example 1

Convert 425 torr to atm.

Solution

The conversion factor is 760. torr = 1.00 atm.

$$(425\ \text{torr})\left(\frac{1.00\ atm}{760.\ torr}\right) = 0.559\ \text{atm}$$

Pressure Unit Conversion Example 2

Convert 425 torr to kPa.

Solution

The conversion factor is 760. torr = 101.325 kPa.

$$(425\ \text{torr})\left(\frac{101.325\ kPa}{760.\ torr}\right) = 56.7\ \text{kPa}$$

Pressure Unit Conversion Example 3

Convert 0.500 atm to mm of Hg.

Solution

The conversion factor is 1.00 atm = 760. mm of Hg.

$$(0.500\ \text{atm})\left(\frac{760.\ mm\ of\ Hg}{1.00 atm}\right) = 380.\ \text{mm of Hg}$$

Pressure Unit Conversion Example 4

Convert 0.500 atm to kPa.

Solution

The conversion factor is 1.00 atm = 101.325 kPa.

$(0.500 \text{ atm}) \left(\frac{101.325\ kPa}{1.00 atm}\right) = 50.7 \text{ kPa}$

You might notice if you wanted to measure a gas pressure that was around 2.0 atm with a barometer, you would need a glass column filled with mercury that was over 1.5 meters high. That would be a fragile and dangerous instrument since mercury fumes are toxic. If we used water (which is one-thirteenth as dense as mercury) in the tube to be free of toxicity, the column would have to be 50 feet high. Other instruments, called **manometers,** have been designed to measure gas pressure in flasks. There are two kinds of manometers in use, **open-end manometers** and **closed-end manometers.**

The closed-end manometer is easier to read so we will begin with it (see Figure 7). The empty tube above the mercury level for the outside tube contains a vacuum. Therefore, there are no molecules pounding on the surface of the mercury in the outside tube. In the manometer in Figure 7A, we represent a flask that contains no gas so that there are no molecules in the flask to exert pressure, $P_{gas} = 0$. The two mercury levels will be exactly even so the mercury level in the outside arm balances the mercury level in the inside arm. In Figure 7B, we represent a flask that contains a gas at 1.00 atm pressure. The mercury level in the outside tube will rise to a height of 760 mm of Hg so that the excess mercury in the outside tube balances the gas pressure in the flask. In the manometer in Figure 7C, we would read the gas pressure in the flask as 200. mm of Hg. In closed-end manometers, the excess mercury is always in the outside tube and the height difference in mercury levels will equal the gas pressure in the flask.

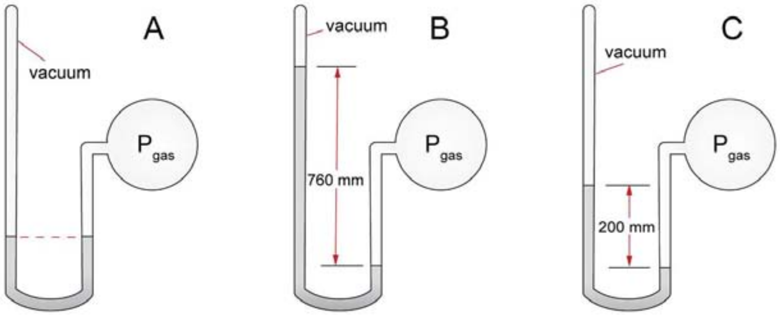


Figure 7: Closed-end manometers. (*Source:* CK-12 Foundation, *License:* CC-BY-SA)

In open-end manometers (Figure 8), the open-end of the tube allows atmospheric pressure to push down on the top of the column of mercury. In manometer A in Figure 8, the pressure inside the flask is equal to atmospheric pressure. The two columns of mercury are the same height and so they balance each other and therefore the atmospheric pressure pushing on the outside column of mercury must equal the gas pressure in the flask pushing on the inside column of mercury. In order to properly read an open end manometer, you must know the actual air pressure in the room because atmospheric pressure is not always 760 mm of Hg. In Figure 8B, the pressure

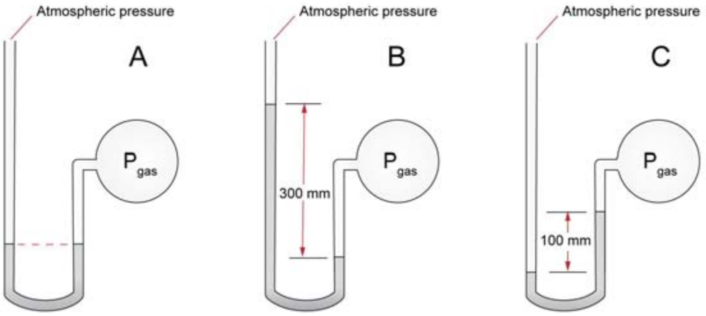


Figure 8: Open-end manometers. (*Source:* CK-12 Foundation, *License:* CC-BY-SA)

inside the flask is balancing the atmospheric pressure PLUS the pressure of 300. mm of Hg. If the actual atmospheric pressure is 750. mm of Hg, then the pressure in the flask is 1050 mm of Hg. In the flask in Figure 8C, the pressure in the flask is less than the atmospheric pressure so the excess mercury is in the inside arm of the manometer. If the atmospheric pressure is 750. mm of Hg, then the pressure in the flask is 650. mm of Hg. For open-end manometers, when the excess mercury is in the outside arm, the height difference is added to atmospheric pressure and when excess mercury is in the inside arm, the height difference is subtracted from atmospheric pressure.

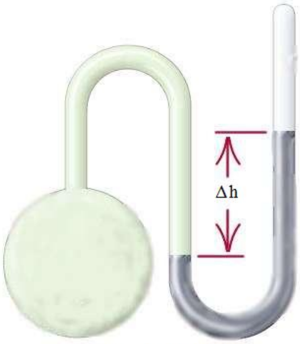
Scientists also use mechanical pressure gauges on occasion. These instruments use the stretching or compression of springs to turn dials or something similar. While such instruments seem to be less trouble, they must all be calibrated against mercury column instruments and they are more susceptible to reactive gases.

Lesson Summary

- Because of the molecular motion of molecules, they possess kinetic energy at all temperatures above absolute zero.
- The collisions between molecules are perfectly elastic. The phrase "perfectly elastic collision" means that kinetic energy is conserved in the collisions.
- The molecules of an ideal gas have no attraction or repulsion for each other.
- At any given moment, the molecules of a gas have different kinetic energies. We deal with this variation by considering the average kinetic energy of the molecules. The average kinetic energy of a group of molecules is measured by temperature.

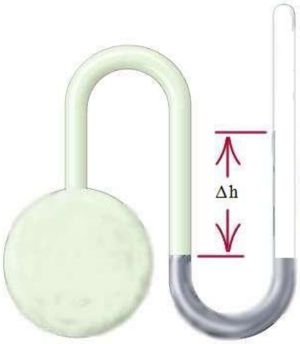
Review Questions

1. The manometer shown at right is an closed-end manometer filled with mercury. If the atmospheric pressure in the room is 760. mm of Hg and Δ h is 65 mm of Hg, what is the pressure in the flask? **(Intermediate)**



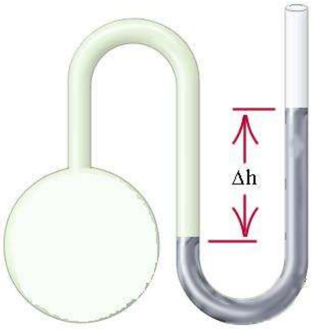
Closed-end Manometer

2. The manometer shown at right is an closed-end manometer filled with mercury. If the atmospheric pressure in the room is 750. mm of Hg and Δ h is 0 mm of Hg, what is the pressure in the flask? **(Intermediate)**



Closed-end Manometer

3. The manometer shown at right is an open-end manometer filled with mercury. If the atmospheric pressure in the room is 750. mm of Hg and Δ h is 65 mm of Hg, what is the pressure in the flask? **(Intermediate)**



4. The manometer shown at right is an open-end manometer filled with mercury. If the atmospheric pressure in the room is 760. mm of Hg and Δ h is 0 mm of Hg, what is the pressure in the flask? **(Intermediate)**

Open-end Manometer

5. Explain why at constant volume, the pressure of a gas decreases by half when its Kelvin temperature is reduced by half. **(Intermediate)**

Vocabulary

barometer	A barometer is an instrument used to measure atmospheric pressure.
manometer	A manometer is a liquid column pressure measuring device.

Review Answers

1. 65 mm of Hg

2. 0 mm of Hg

3. 815 mm of Hg

4. 760. mm of Hg

5. Gas pressure is determined by dividing the total force exerted by molecular collisions by the area over which the force is exerted. If we reduce the total force by half (reduce Kelvin temperature by half) and keep the same area (constant volume), then the pressure will be halved.

Gas Laws

Lesson Objectives

- The student will state Boyle's' Law, Charles' Law, and Gay-Lussac's Law.
- The student will solve problems using Boyle's' Law, Charles' Law, and Gay-Lussac's Law.
- The student will state the combined gas law.
- Using the combined gas law, $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$, and given any five of the six variables, the student will solve for the sixth variable.

Introduction

The gas laws are mathematical relationships that exist for gases between the volume, pressure, temperature, and quantity of gas present. They were determined experimentally over a period of 100 years. They are logically derivable from our present day definitions of pressure, volume, and temperature.

Boyle’s Law

Gases are often characterized by their volume, temperature, and pressure. These characteristics, however, are not independent of each other. Gas pressure is dependent on the force exerted by the molecular collisions and the area over which the force is exerted. The force exerted by the molecular collisions is dependent on the absolute temperature and so forth. The relationships between these characteristics can be determined both experimentally and logically from their mathematical definitions.

The relationship between the pressure and volume of a gas was first determined experimentally by an Irish chemist named Robert Boyle (1627-1691). The relationship between the pressure and volume of a gas is commonly referred to as **Boyle’s Law.**

When we wish to observe the relationship between two variables, it is absolutely necessary to keep all other variables constant so that the change in one variable can be directly related to the change in the other. Therefore, when the relationship between gas volume and gas pressure is investigated, the quantity of gas and its temperature must be held constant so these factors do not contribute to any observed changes.

You may have noticed that when you try to squeeze a balloon, the resistance to squeezing is greater as the balloon becomes smaller. That is, the pressure inside the balloon becomes greater when the volume is reduced. This phenomenon can be studied more carefully with an apparatus like that in Figure 9. This is a cylinder tightly fitted with a piston that can be raised or lowered. There is also a pressure gauge fitted to the cylinder so that the gas pressure inside the cylinder can be measured. The amount of gas inside the cylinder cannot change and the temperature of the gas is not allowed to change.

In the picture on the left in Figure 9, the volume of the gas is 4.0 liters and the pressure exerted by the gas is 2.0 atm. If the piston is pushed down to decrease the volume of the gas to 2.0 liters, the pressure of the gas is found to be 4.0 atm. The piston can be moved up and down to positions for several different volumes and the pressure of the gas read at each of the volumes. Several trials would generate a data set like that shown in Table 1. **Table 1: PV Data**

Trial	Volume	Pressure
1	8.0 liters	1.0 atm
2	4.0 liters	2.0 atm
3	2.0 liters	4.0 atm
4	1.0 liters	8.0 atm

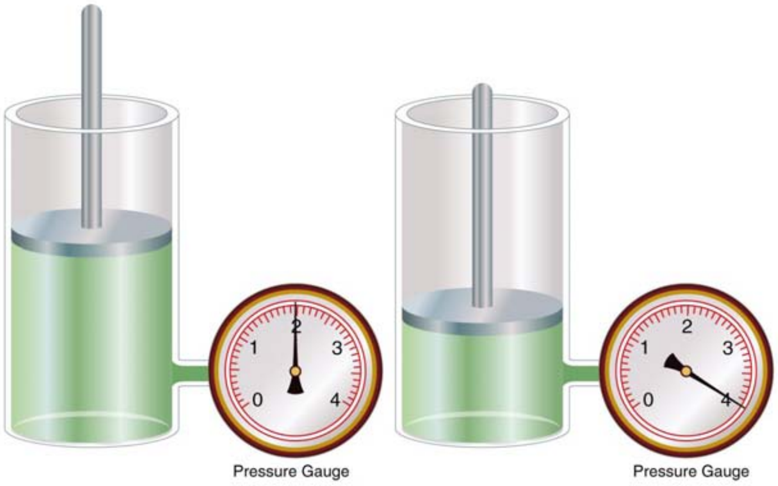


Figure 9: Boyle's Law Apparatus. (*Source:* CK-12 Foundation, *License:* CC-BY-SA)

Trial	Volume	Pressure
1	8.0 liters	1.0 atm
2	4.0 liters	2.0 atm
3	2.0 liters	4.0 atm
4	1.0 liters	8.0 atm

We might note from casual observation of the data that doubling volume is associated with the pressure being reduced to half and if we move the piston to cause the pressure to double, the volume is halved. We can analyze this data mathematically by adding a fourth column to our table – namely, a column showing the product of multiplying pressure times volume for each trial (see Table 2).

Table 2: PV Data

Trial	Volume	Pressure	Pressure x Volume
1	8.0 liters	1.0 atm	8.0 liters-atm
2	4.0 liters	2.0 atm	8.0 liters-atm
3	2.0 liters	4.0 atm	8.0 liters-atm
4	1.0 liters	8.0 atm	8.0 liters-atm

The data in the last column shows that with constant temperature and quantity of gas, the pressure times the volume of this sample of gas yields a constant. A mathematical constant (often represented by ***k***) is a number that does not change even when other quantities in the formula do change. The value of ***k*** will change if a different quantity of gas is used or if the trials are carried out at a different temperature, but for a particular mass of a particular gas at a particular temperature, the value of ***k*** will always be the same. This relationship can be shown in a mathematical equation.

PV = K

This equation is a mathematical statement of Boyle's Law. This particular equation is what is called an inverse proportionality. When one of the variables is increased, the other variable will decrease by exactly the same factor (see Figure 10). This result is the same as we would draw from logic. If the pressure a gas exerts is equal to force divided by the area over which it is exerted and we decrease the area but keep the force constant, we would expect the pressure to increase. Similarly, if we maintain the same number of molecules of gas and we keep the same temperature, the total force exerted by the molecules will be the same, and if we then expand the volume of the gas so that the area over which the force is exerted increased, we would expect the pressure to decrease.

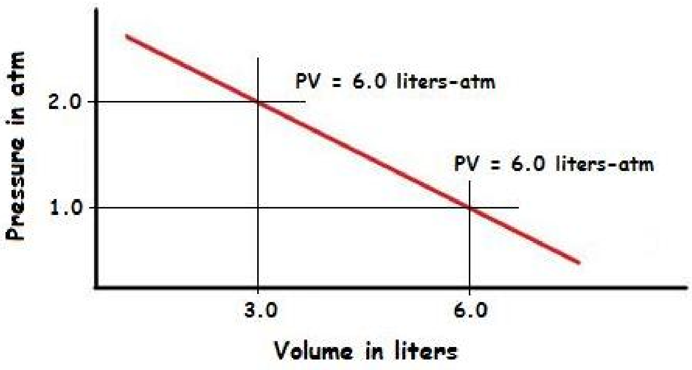


Figure 10: Graph of Boyle's Law data. (*Created by:* Richard Parsons, *License:* CC-BY-SA)

Charles's Law

The relationship between the volume and temperature of a gas was investigated by a French physicist, Jacques Charles (1746-1823). (As a piece of trivia, Charles was also the first person to fill a large balloon with hydrogen gas and take a solo balloon flight.) The relationship between the volume and temperature of a gas is often referred to as **Charles's Law.**

An apparatus that can be used to study the relationship between the temperature and volume of a gas is shown in Figure 11. Once again, we have a sample of gas trapped inside a cylinder so no gas can get in or out. Thus we have a constant mass of gas. We also have a mass set on top of a moveable piston to keep a constant force pushing against the gas. This guarantees that the gas pressure in the cylinder will be constant because if the pressure inside increases, the piston will be pushed up expanding inside volume until the inside pressure becomes equal to outside pressure again. Similarly, if the inside pressure decreases, the outside pressure will push the cylinder down, decreasing volume, until the two pressures again become the same. This system guarantees constant gas pressure inside the cylinder. With this set up, we can adjust the temperature to various temperatures and measure the volume at each temperature to produce a data table in the same way we did for pressure versus volume. The picture on the left in Figure 11 shows the volume of a sample of gas at 250 K and

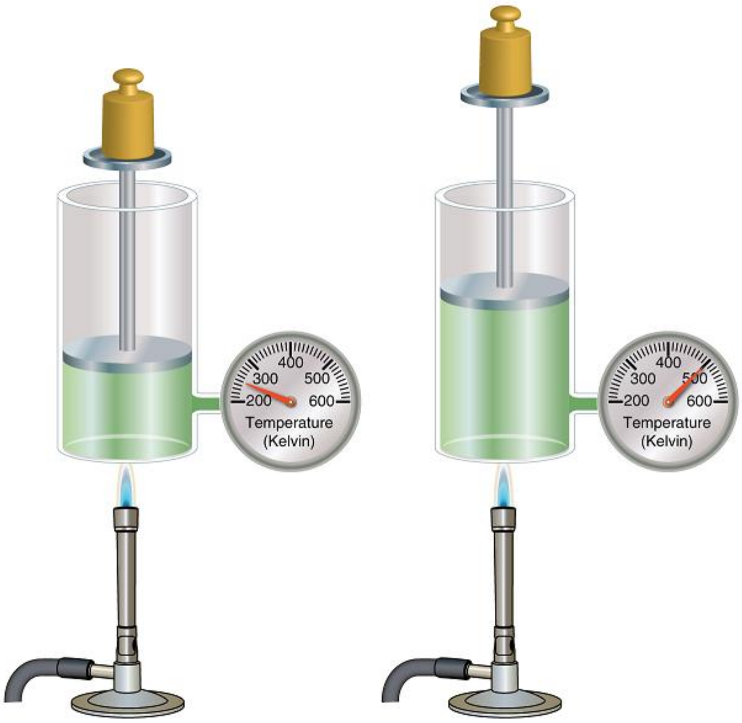


Figure 11: Charles' Law Apparatus. (*Source:* CK-12 Foundation, *License:* CC-BY-SA)

the picture on the right shows the volume when the temperature has been raised to 500 K. After two more trials, the data is shown in Table 3.

Table 3: Charles's Law Data

Trial	volume	Temperature	Volume/Temp
1	1000.mL	250.K	4.00 mL/K
2	1200.mL	300.K	4.00 mL/K
3	2000.mL	500.K	4.00 mL/K
4	2400.mL	600.K	4.00 mL/K

In order to find a constant form this data, it was necessary to divide volumes by corresponding Kelvin temperatures. The mathematical expression for Charles's Law is

$$\frac{\mathbf{V}}{\mathbf{T}} = \mathbf{K}$$

This relationship would also be expected when we recognize that we are increasing the total force of molecular collisions with the walls by raising the temperature and the only way to keep the pressure from increasing is to increase the area over which that larger force is exerted. This mathematical relationship is known as a direct proportionality. When one variable is increased, the other variable also increases by exactly the same factor.

Gay-Lussac's Law

The relationship between temperature and pressure was investigated by the French chemist, Joseph Gay-Lussac (1778-1850). An apparatus that could be used for this investigation is shown in Figure 12. In this case, the cylinder does not have a moveable piston because it is necessary to hold the volume constant as well as the quantity of gas. This apparatus allows us to alter the temperature of a gas and measure the pressure exerted by the gas at each temperature. After a series of temperatures and pressures have been measured, a data table like the others can be produced. **Table 4: Pressure vs. Temperature Data**

Trial	Temperature	Pressure	Pressure/Temp
1	200.K	600.torr	3.00 torr/K
2	300.K	900.torr	3.00 torr/K
3	400.K	1200.torr	3.00 torr/K
4	500.K	1500.torr	3.00 torr/K

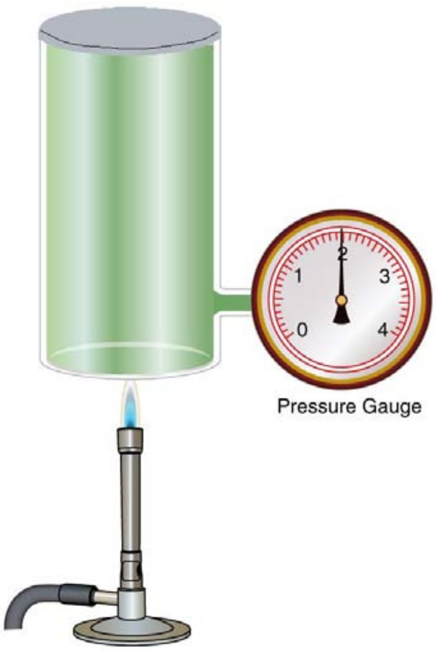


Figure 12: Apparatus for Gay-Lussac's Law. (*Source:* CK-12 Foundation, *License:* CC-BY-SA)

Trial	Temperature	Pressure	Pressure/Temp

1	200.K	600.torr	3.00 torr/K
2	300.K	900.torr	3.00 torr/K
3	400.K	1200.torr	3.00 torr/K
4	500.K	1500.torr	3.00 torr/K

Like Charles's Law, in order to produce a constant when operating on the data in Table 4, we must divide pressure by temperature. The relationship, again like Charles's Law is a direct proportionality.

The mathematical form of Gay-Lussac's Law is:

$$\frac{P}{T} = K$$

This relationship is also logical since by increasing temperature, we are increasing the force of molecular collision and keeping the area over which the force is exerted constant requires that the pressure increases.

Standard Temperature and Pressure (STP)

It should be apparent by now that expressing a quantity of gas simply by stating its volume is totally inadequate. Ten liters of oxygen gas could contain any mass of oxygen from 4,000 grams to 0.50 grams depending on the temperature and pressure of the gas. Chemists have found it useful to have a standard temperature and pressure with which to express gas volume. The standard conditions of temperature and pressure (STP) were chosen to be 0°C (273 K) and 1.00 atm (760 mm of Hg). You will commonly see gas volumes expressed as *1.5 liters of gas under standard conditions or 1.5 liters of gas at STP.* Once you know the temperature and pressure conditions of a volume of gas, you can calculate the volume at other conditions and you can also calculate the mass of the gas if you know the formula.

The Combined Gas Law

Boyle's Law shows how the volume of a gas changes when its pressure is changed (temperature held constant) and Charles's Law shows how the volume of a gas changes when the temperature is changed (pressure held constant). Is there a formula we can use to calculate the change in volume of a gas if both pressure and temperature change? The answer is "yes", we can use a formula that combines Boyle's Law and Charles's Law.

Boyle's Law states that for a sample of gas at constant temperature, every *volume times pressure* trial will yield the same constant. If we use subscripts of "1" to represent one set of conditions and subscripts of "2" to represent a second set of conditions,

$$P_1V_1 = P_2V_2 \quad \text{and} \quad V_2 = V_1 \times \frac{P_1}{P_2}$$

Charles' Law is similar.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad \text{and} \quad V_2 = V_1 \times \frac{T_2}{T_1}$$

Combining the two equations yields

$$V_2 = V_1 \times \frac{P_1}{P_2} \times \frac{T_2}{T_1}$$

This equation is most commonly written in the from shown below and is known as the **Combined Gas Law**.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

The majority of problems you will solve with this equation will be of the type where known values will be given to you for five of the six variables and you will be asked to solve for the sixth. When solving problems with the combined gas law, temperatures must always be in Kelvin. The units for pressure and volume may be any appropriate units but the units for each value of pressure must be the same and the units for each value of volume must be the same.

Sample Problem 1

A sample of gas has a volume of 400. liters when its temperature is 20.°C and its pressure is 300. mm of Hg. What volume will the gas occupy at STP?

Solution:

STEP 1: Assign the known values for each of the variables representing them.

P_1 = 300. mm of Hg

V_1 = 400. liters

T_1 = 20.°C + 273 = 293 K

P_2 = 760. mm of Hg (standard pressure)

V_2 = x liters (the unknown)

T_2 = 0°C + 273 = 273 K

STEP 2: Solve the combined gas law for the unknown variable.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \quad \text{so} \quad V_2 = \frac{P_1V_1T_2}{P_2T_1}$$

STEP 3: Substitute the known values into the formula and solve for the unknown.

$$V_2 = \frac{(300.\ \text{mm of Hg})(400.\ \text{L})(273\ \text{K})}{(760.\text{mm of Hg})(293\ \text{K})} = 147 \text{ liters}$$

Sample Problem 2

A sample of gas occupies 1.00 liter under standard conditions. What temperature would be required for this sample of gas to occupy 1.50 liters and exert a pressure of 2.00 atm?

STEP 1

P_1 = 1.00 atm (standard pressure in atmospheres)

V_1 = 1.00 liter

T_1 = 273 K (standard temperature)

P_2 = 2.0 atm

V_2 = 1.50 liters

T_2 = x (the unknown)

STEP 2

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \quad \text{so} \quad T_2 = \frac{P_2V_2T_1}{P_1V_1}$$

STEP 3

$$T_2 = \frac{(2.00\ \text{atm})(1.50\ \text{L})(273\ \text{K})}{(1.00\ \text{atm})(1.00\ \text{L})} = 819\ \text{K}$$

Sample Problem 3

A 1.00 liter sample of oxygen gas under standard conditions has a density of 1.43 g/L. What is the density of oxygen gas at 500. K and 760. torr?

Solution:

You can find the mass of oxygen in the 1.00 liter sample by multiplying volume times density which yields a mass of 1.43 grams. Changing the temperature and/or pressure of a sample of gas changes its volume and therefore density BUT it does NOT change the mass. Therefore, when the new volume of the gas is found, the mass of oxygen gas in it will still be 1.43 grams. The density under the new conditions can be found by dividing the mass by the volume the gas now occupies.

P_1 = 760.torr	P_2 = 760.torr
V_1 = 1.00 L	V_2 = unknown
T_1 = 273 K	T_2 = 500.K

$$V_2 = \frac{P_1V_1T_2}{P_2T_1} = \frac{(760.\ \text{torr})(1.00\ \text{L})(500.\ \text{K})}{(760.\ \text{torr})(273\ \text{K})} = 1.83\ \text{liters}$$

$$D_{O2@500\ K} = \frac{\text{mass}}{\text{volume}} = \frac{1.43\ \text{g}}{1.83\ \text{L}} = 0.781\ \text{g/L}$$

Lesson Summary

- Because of the molecular motion of molecules, they possess kinetic energy at all temperatures above absolute zero.
- The collisions between molecules are perfectly elastic. The phrase “perfectly elastic collision” comes from physics and means that kinetic energy is conserved in collisions.
- The molecules of an ideal gas have no attraction or repulsion for each other.
- At any given moment, the molecules of a gas have different kinetic energies. We deal with this variation by considering the average kinetic energy of the molecules. The average kinetic energy of a group of

molecules is measured by temperature.

- For a fixed sample of ideal gas at constant temperature, volume is inversely proportional to pressure.
- For a fixed sample of ideal gas at constant pressure, volume in directly proportional to temperature.
- For a fixed sample of ideal gas at constant volume, pressure is directly proportional to temperature.
- The volume of a mass of gas is dependent on the temperature and pressure. Therefore, these conditions must be given along with the volume of a gas.
- Standard conditions of temperature and pressure are 0°C and 1.0 atm.

Review Questions

1. When a sample of gas is placed in a larger container at the same temperature, what happens to the total FORCE of the molecules hitting the walls? **(Intermediate)**

2. When a sample of gas is placed in a larger container at the same temperature, what happens to the pressure exerted by the gas? **(Intermediate)**

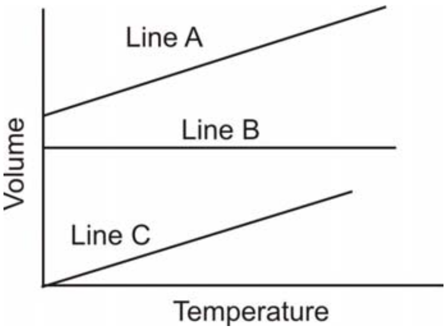
3. If molecules of H_2 (mol. mass = 2), O_2 (mol. mass = 32), and N_2 (mol. mass = 28) are all placed in the same container at the same temperature, which molecules will have the greatest average kinetic energy? **(Intermediate)**

4. If molecules of H_2 (mol. mass = 2), O_2 (mol. mass = 32), and N_2 (mol. mass = 28) are all placed in the same container at the same temperature, which molecules will have the greatest velocity? **(Intermediate)**

5. If X and Y are quantities that are related to each other by inverse proportion, what will the value of Y become when the value of X is increased by a factor of five? **(Intermediate)**

6. Under what conditions will the value for the constant, K, change in the equation for Boyle's Law, PV = K. **(Intermediate)**

7. A sample of gas has a volume of 500. mL under a pressure of 500. mm of Hg. What will be the new volume of the gas if the pressure is reduced to 300. mm of Hg at constant temperature? **(Intermediate)**



8. A graph is made illustrating Charles's Law. Which line in the picture at right would be appropriate assuming temperature is measured in Kelvin? **(Intermediate)**

9. At constant pressure, the temperature of a sample of gas is decreased. Will the volume of the sample (a) increase (b) decrease (c) remain the same? **(Intermediate)**

10. A sample of gas has its temperature increased from -43°C to 47°C at constant pressure. If its volume at -43°C was 500. mL, what is its volume at 47°C? **(Intermediate)**

11. A gas is confined in a rigid container and exerts a pressure of 250. mm of Hg at a temperature of 17°C. To what temperature must this gas be cooled in order for its pressure to become 216 mm of Hg? Express

this temperature in °C. **(Intermediate)**

12. What is the abbreviation used to indicate standard conditions of temperature and pressure? **(Beginning)**

13. A sample of gas has a volume of 500. mL at standard conditions. Find its volume at 47°C and 800. torr. **(Intermediate)**

14. A sample of gas has a volume of 100. L at 17°C and 800. torr. To what temperature must the gas be cooled in order for its volume to become 50.0 L at a pressure of 600. torr? **(Intermediate)**

Further Reading / Supplemental Links

Website with lessons, worksheets, and quizzes on various high school chemistry topics.

- Lesson 7-6 is on the Combined Gas Law.

http://www.fordhamprep.org/gcurran/sho/sho/lessons/lesson31.htm

Vocabulary

barometer	An instrument used to measure atmospheric pressure.
dalton	The unified atomic mass unit, or Dalton, is a unit of mass used to express atomic and molecular masses. It is the approximate mass of a hydrogen atom, a proton, or a neutron. The precise definition is that it is one-twelfth of the mass of an unbound carbon-12 atom at rest.
manometer	A liquid column pressure measuring device.

Review Answers

1. Since the number of molecules remain the same and the temperature of the molecules remain the same, the total force will remain the same.

2. Even though the total force remains the same, the area over which the force is exerted is increased and therefore, the pressure will be lower.

3. Temperature is a measure of average kinetic energy. If they all have the same temperature, they will all have the same kinetic energy.

4. In order to have the same kinetic energy, the more massive molecules must be moving slower and the less massive molecules must be moving faster. Since hydrogen molecules are the lightest, they will have the greatest velocity at the same temperature.

5. The value of Y will decrease by a factor of five.

6. PV = K requires that quantity of gas and temperature remain constant. If either of those change, K will change. If those two conditions remain constant, K will not change.

7. $P_1V_1 = P_2V_2$

(500. mm of Hg)(500. mL) = (300. mm of Hg)(x mL)

x = 833 mL

8. Line C because theoretically the pressure and volume of a gas become zero at zero Kelvin.

9. (b) decrease Charles’s Law tells us that the volume and temperature of a gas are directly proportional when pressure is held constant.

10.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\frac{500.\ \text{mL}}{230.\ \text{K}} = \frac{x}{320.\ \text{K}}$$

x = 696 mL

11.

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$\frac{250.\ \text{mm of Hg}}{290.\ \text{K}} = \frac{216\ \text{mm of Hg}}{x\ \text{K}}$$

x = 251 K = -22°C

12. STP

13.

$$V_2 = \frac{P_1V_1T_2}{P_2T_1} = \frac{(760.\ \text{mm of Hg})(500.\ \text{mL})(320.\ \text{K})}{(800.\ \text{mm of Hg})(273\ \text{K})} = 557\ \text{mL}$$

14.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \quad \text{so} \quad T_2 = \frac{P_2V_2T_1}{P_1V_1} = \frac{(600.\ \text{torr})(50.0\ \text{L})(290.\ \text{K})}{(800.\ \text{torr})(100.\ \text{L})} = 109\ \text{K}$$

Universal Gas Law

Lesson Objectives

- The student will solve problems using the Universal Gas Law, PV = nRT.
- The student will state Avogadro’s Law of equal molecules in equal volumes.
- The student will calculate molar mass from mm = gRT/PV given mass, temperature, pressure, and volume.

Introduction

The individual gas laws and the combined gas law all require that the quantity of gas remain constant. The Universal Gas Law (also sometimes called the Ideal Gas Law) allows us to make calculations on different quantities of gas as well.

Avogadro’s Law

Avogadro’s Law was known as Avogadro’s hypothesis for the first century of its existence. Since Avogadro's hypothesis can now be demonstrated mathematically, it was decided that it should be called a law instead of a hypothesis. Avogadro’s Law postulates that ***equal volumes of gas under the same conditions of temperature and pressure contain the same number of molecules.***

If we think about the definitions of gas volumes, pressures, and temperatures, we can develop Avogadro's conclusion. Suppose we have a group of toy robots that are all identical in strength. They don't all look the same and they are not all the same size but they all have exactly the same strength at an assigned task. We arrange a tug-of-war between groups of our robots. We arrange the rope they will be pulling on so that we can see one end but the other end disappears behind a wall. On the visible end, we place eight robots to pull. On the other end, an unknown number of robots will pull. When we say "go," both sides pull with maximum strength but the rope does NOT move. How many robots are pulling on the hidden end of the rope? Since each robot has exactly the same strength to pull, to balance eight robots on one end, there MUST be eight robots on the other end. If we can think of molecules as robots and we recognize that molecules at the same temperature have exactly the same striking power when they collide, then equal volumes of gas with equal pressures and equal temperatures must contain an equal number of molecules.

In the early 1800s, the first attempts to assign relative atomic weights to the atoms were accomplished by decomposing compounds to determine the mass ratios in the compounds and assigning hydrogen to have an atomic mass of 1.0. Some atomic weights found in this way were accurate but many were not. In the 1860s, Stanislao Cannizzaro refined relative atomic weights using Avogadro's Law. If gas X and gas Y were heated to the same temperature, placed in equal volume containers, and some gas was released from one of the containers until the two containers had the same pressure, Avogadro's conditions would be present. Cannizzaro could conclude that the two containers had exactly the same number of molecules. The mass of each gas was then determined with a balance (subtracting the masses of the containers) and the relationship between the masses would be the same as the mass relationship of one molecule of X to one molecule of Y. That is, if the total mass of gas X was 10. grams and the total mass of gas Y was 40. grams, then Cannizzaro knew that one molecule of Y must have four times as much mass as one molecule of X. If an arbitrary value such as 1.0 Dalton was assigned as the mass of gas X, then Y's mass on that same scale would be 4.0 Daltons.

The Universal Gas Law Constant

We have considered three laws that describe the behavior of gases.

Boyle's Law, $V = \frac{k_1}{P}$ at constant temperature and constant moles of gas, where k_1 is a constant.

Charles's Law, $V = k_2T$ at constant pressure and constant moles of gas, where k_2 is a constant.

Avogadro's Law, $V = k_3\,\mathbf{n}$ at constant temperature and pressure, where n is the number of moles of gas and k_3 is a constant.

These three relationships, which show how the volume of a gas depends on pressure, temperature, and the number of moles of gas, can be combined to form **PV = nRT,** where R is the combination of the three constants. The equation is called the **Universal Gas Law** (or the Ideal Gas Law) and R is called the **universal gas law constant.** When the pressure is expressed in atmospheres and the volume in liters, R has the value **0.08206 L**

·

atm/mol

·

K. You can convert the value of R into values for any set of units for pressure and volume. Moles, of course, always have the unit moles and temperature must always be Kelvin.

In our analysis of gas behavior, we have used a pair of assumptions that are usually true but not always true. We have assumed that the volume of the actual molecules in a gas is insignificant compared to the volume of the empty space between molecules. We have operated as if the molecules were geometric points and took up no space. For most gases, for most of the time, this assumption is true and the gas laws work well. If, however, a gas is highly compressed (at very high pressure), the molecules will be pushed very close together and much of the empty space between molecules will have been removed. Under such circumstances, the volume of the molecules themselves becomes significant and some calculations with the gas laws will be slightly off.

Another assumption we use is that the molecules are not attracted to each other so that every collision is a perfectly elastic collision, i.e. no energy is lost during the collision. This assumption also works out well most of the time. Even though the molecules do have some attraction for each other, usually the temperature is high enough that the molecular motion readily overcomes any attraction and the molecules move around as if there were no attraction. If, however, we operate with gases at low temperatures (temperatures near the phase change temperature of the gas), the molecular attractions have enough effect to put our calculations slightly off. If a gas follows the ideal gas laws, we say that the gas behaves ideally. Gases behave ideally at low pressure and high temperature. At low temperatures or high pressures, gas behavior may become non-ideal. As a point of interest, if you continue your study of chemistry, you will discover at the next level, there is yet another gas law equation for these non-ideal situations.

Sample Problem 4

A sample of nitrogen gas (N_2) has a volume of 5.56 liters at 0°C and 1.50 atm pressure. How many moles of nitrogen are present in this sample?

Solution:

STEP 1: Assign known values to variable.

P = 1.50 atm

V = 5.56 L

n = unknown

T = 0°C + 273 = 273 K

R = 0.08206 L · atm/mol · K

STEP 2: Solve the universal gas law for the unknown variable.

$PV = nRT \quad \text{so} \quad n = \frac{PV}{RT}$

STEP 3: Substitute the know values into the equation and solve.

$n = = \frac{PV}{RT} = \frac{(1.50\ \text{atm})(5.56\ \text{L})}{(0.08206\ \text{L}\cdot\text{atm/mol}\cdot\text{K})(273\ \text{K})} = 0.372\ \text{mol}$

Sample Problem 5

2.00 moles of methane gas (CH_4) are placed in a rigid 5.00 liter container and heated to 100.°C. What pressure will be exerted by the methane?

Solution:

P = unknown

V = 5.00 liters

N = 2.00 moles

T = 100.°C + 273 = 373 K

R = 0.08206 L · atm/mol · K

$$P = \frac{nRT}{V} = \frac{(2.00\ \text{mols})(0.08206\ \text{L}\cdot\text{atm/mol}\cdot\text{K})(373\ \text{K})}{(5.00\ \text{L})} = 12.2\ \text{atm}$$

Sample Problem 6

A sample gas containing 0.300 moles of helium at a pressure of 900. torr is cooled to 15°C. What volume will the gas occupy under these conditions?

Note: If we are to use 0.08206 L · atm/mol · K for the value of R, then the pressure must be converted from torr to atm.

P = (900.torr)(1.00 atm/760.torr) = 1.18 atm

V = unknown

N = 0.300 mole

T = 15°C + 273 = 288 K

R = 0.08206 L · atm/mol · K

$$V = \frac{nRT}{P} = \frac{(0.300\ \text{mols})(0.08206\ \text{L}\cdot\text{atm/mol}\cdot\text{K})(373\ \text{K})}{(1.18\ \text{atm})} = 6.01\ \text{liters}$$

Molar Mass and the Universal Gas Law

The universal gas law can also be used to determine the molar mass of an unknown gas provided the pressure, volume, temperature and mass are known. The number of moles of a gas, n, can be expressed as grams/molar mass. If we substitute g/mm for n in the universal gas law, we get PV = (g/mm)RT which can be re-arranged to mm = gRT/PV.

Sample Problem 7

20.0 grams of an unknown gas occupy 2.00 L under standard conditions. What is the molar mass of the gas?

Solution:

$$\text{molar mass} = \frac{gRT}{PV} = \frac{(20.0\ \text{g})(0.08206\ \text{L}\cdot\text{atm/mol}\cdot\text{K})(273\ \text{K})}{(1.00\ \text{atm})(2.00\ \text{L})} = 224\ \text{g/mol}$$

Density and the Universal Gas Law

The density of a gas under a particular set of conditions is the mass of the sample of gas divided by the volume occupied at those conditions, D = m/V. In the universal gas law, both the mass of the sample of gas and the volume it occupies are represented. We can substitute density for g/V where it appears in the equation and produce an equation that contains density rather than mass and volume. For example, in the equation mm = gRT/PV, mass appears in the numerator and volume appears in the denominator so we can substitute d for those two variables producing the equation mm = dRT/P.

Sample Problem 8

The density of a gas was determined to be 1.95 g/mL at 1.50 atm and 27°C. What is the molar mass of the gas?

Solution

molar mass = $\frac{\mathrm{dRT}}{\mathrm{P}} = \frac{(1.95\ \mathrm{g/L})(0.08206\ \mathrm{L{\cdot}atm/mol{\cdot}K})(300.\ \mathrm{K})}{(1.50\ \mathrm{atm})}$ = 32.0 g/mol

Lesson Summary

- Avogadro's Law: Equal volumes of gases under the same conditions of temperature and pressure contain equal numbers of molecules.
- The Universal Gas Law: PV = nRT.
- The universal gas law is often used along with laboratory data to find the molar mass of an unknown substance.

Review Questions

1. What volume will 2.00 moles of hydrogen gas occupy at 2.62 atm of pressure and 300.°C? **(Intermediate)**

2. How many moles of gas are required to fill a volume of 8.00 liters at 2.00 atm and 273 K? **(Intermediate)**

3. What is the molar mass of a gas if its density is 1.30 g/L at STP? **(Challenging)**

Vocabulary

universal gas law constant, R	**R** is a constant equal $\frac{\mathrm{PV}}{\mathrm{nT}}$ where the pressure, volume, moles, and temperature of the gas are P, V, n, and T, respectively. The value and units of R depend on the units of P and V. Commonly used values of R include; 82.055 $\mathrm{mL^3\ atm\ K^{-1}\ mol^{-1}}$, 0.082055 $\mathrm{L\ atm\ K^{-1}\ mol^{-1}}$, 8.314 $\mathrm{J\ K^{-1}\ mol^{-1}}$, 8.314 $\mathrm{Pa\ m^3\ K^{-1}\ mol^{-1}}$.

Review Answers

1. V = $\frac{\mathrm{nRT}}{\mathrm{P}} = \frac{(2.00\ \mathrm{mols})(0.0821\ \mathrm{L{\cdot}atm/mol{\cdot}K})(573\ \mathrm{K})}{2.62\ \mathrm{atm}}$ = 35.9 liters

2. n = $\frac{\mathrm{PV}}{\mathrm{RT}} = \frac{(2.00\ \mathrm{atm})(8.00\ \mathrm{L})}{(0.0821\ \mathrm{L{\cdot}atm/mol{\cdot}K})(273\ \mathrm{K})}$ = 0.714 mole

3. molar mass = $\frac{\mathrm{dRT}}{\mathrm{P}} = \frac{(1.30\ \mathrm{g/L})(0.08206\ \mathrm{L{\cdot}atm/mol{\cdot}K})(273\ \mathrm{K})}{(1.00\ \mathrm{atm})}$ = 29.1 g/mol

Molar Volume

Lesson Objectives

- The student will apply the relationship 1.00 mole of any gas at standard conditions will occupy 22.4 L.
- The student will convert gas volume at STP to moles and to molecules and vice versa.

- The student will apply Dalton's Law of Partial Pressures to describe the composition of a mixture of gases.

Introduction

When molecules are at the same temperature, they have the same kinetic energy regardless of their mass. They all exert the same force when they strike a wall. In this sense, all molecules are created equal (as long as they are at the same temperature). Since equal numbers of molecules at the same temperature will exert the same force of collision, then when such groups of molecules are trapped in identical containers, they will exert exactly the same pressure. This is the logic of Avogadro's Law. If we alter this situation a little and say we have the same number of molecules at the same temperature and insist they exert the same pressure, then similar logic allows us to conclude that these groups of molecules must be in equal size containers.

Molar Volume of Gases at STP

As you know, 1.00 mole of any substance contains 6.02 x 10^{23} molecules. With a sort of a reverse use of Avogadro's Law, we also know that 6.02 x 10^{23} molecules of any gas will occupy the same volume under the same conditions of temperature and pressure. Therefore, we can say that 1.00 mole of any gas under the same conditions will occupy the same volume. You can find the volume of 1.00 mole of any gas under any conditions by plugging the values into the universal gas law, PV = nRT, and solving for volume. We are particularly interested in the volume occupied by 1.00 mole of any gas under standard conditions. We can calculate that volume using PV = nRT.

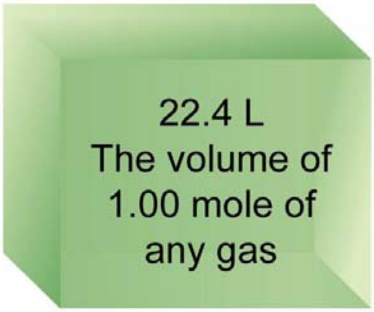


Figure 13: The molar volume of any gas at STP. (*Source:* CK-12 Foundation, *License:* CC-BY-SA)

This is the volume that 1.00 mole of any gas will occupy at STP. You will be using the number to convert gas volumes at STP to moles and vice versa. You will use it often enough to make it worth memorizing.

$$V = \frac{nRT}{P} = \frac{(1.00\ \text{mols})(0.08206\ \text{L·atm/mol·K})(273\ \text{K})}{(1.00\ \text{atm})} = 22.4\ \text{liters}$$

Sample Problem 9

How many moles are present in 100. L of hydrogen gas at STP?

Solution:

$$(100.\ \text{L})\left(\frac{1.00\ mol}{22.4\ L}\right) = 4.46\ \text{liters}$$

Sample Problem 10

What volume will 100. grams of methane gas (CH_4, molar mass = 16.0 g/mol) occupy at STP?

Solution:

$$(100.\ \text{g})\left(\frac{1.00\ mol}{16.0\ g}\right)\left(\frac{22.4\ L}{1.00\ mol}\right) = 140.\ \text{liters}$$

Dalton’s Law of Partial Pressures

The English chemist, John Dalton, in addition to giving us the atomic theory, also studied the pressures of gases when gases were mixed with each other but did not react chemically. His conclusion is **Dalton’s Law of Partial Pressures.**

For a mixture of gases in a container, the total pressure exerted is the sum of the pressures that each gas would exert if it were alone.

This can be expressed as: $P_{TOTAL} = P_1 + P_2 + P_3 + ...$

In the last section, molecules were described as robots. The robots were identical in their ability to exert force. When a group of diverse molecules are at the same temperature, this analogy works well. In the case of molecules, they don’t all look alike but they have the same average kinetic energy and therefore they exert the same force when they collide. If we have 10,000 gaseous molecules at 100°C in a container and they exert a pressure of 0.10 atm, then adding another 10,000 gaseous molecules of any substance at the same temperature to the container would increase the pressure to 0.20 atm. If there are 200 molecules in a container (and at the same temperature), each single molecule is responsible for 1/200th of the total pressure. In terms of force of collision, it doesn’t make any difference if the molecules have different masses. At the same temperature, the little ones are moving faster and the big ones are moving slower so that the striking force is the same. It is this ability to exert force that is measured by temperature. We can demonstrate that different sized objects can have the same kinetic energy by calculating the kinetic energy of a golf ball and the kinetic energy of a bowling ball at appropriate velocities. Suppose a 100. gram golf ball is traveling at 60. m/s and a 7,200 gram bowling ball is traveling at 7.1 m/s.

$$KE_{GOLF} = \tfrac{1}{2}mv^2 = \tfrac{1}{2}(0.100\ \text{kg})(60.\ \text{m/s})^2 = 180\ \text{Joules}$$

$$KE_{BOWL} = \tfrac{1}{2}mv^2 = \tfrac{1}{2}(7.2\ \text{kg})(7.1\ \text{m/s})^2 = 180\ \text{Joules}$$

The kinetic energies are the same. If these balls were invisible and were to strike a pressure plate, they would exert exactly the same force and we would not be able to determine which one had struck the plate. So it is with molecules at the same temperature.

Suppose we have three one-liter containers labeled A, B, and C. Container A holds 0.20 mole of O_2 gas at 27°C, container B holds 0.50 mole of N_2 gas at 27°C, and container C holds 0.30 mole of He gas at 27°C. The pressure of each gas in the separate containers can be calculated with PV = nRT.

$$P_{O2} = \frac{nRT}{V} = \frac{(0.20\ \text{mols})(0.08206\ \text{L·atm/mol·K})(300.\ \text{K})}{(1.00\ \text{L})} = 4.92\ \text{atm}$$

$$P_{N2} = \frac{nRT}{V} = \frac{(0.50\ \text{mols})(0.08206\ \text{L·atm/mol·K})(300.\ \text{K})}{(1.00\ \text{L})} = 12.3\ \text{atm}$$

$$P_{He} = \frac{nRT}{V} = \frac{(0.30\ \text{mols})(0.08206\ \text{L·atm/mol·K})(300.\ \text{K})}{(1.00\ \text{L})} = 7.39\ \text{atm}$$

The sum of these three pressures is 24.6 atm.

If all three gases are placed in one of the containers still at 27°C, the pressure in the single container can also be calculated with PV = nRT. (Remember that with all three gases in the same container, the number of moles is 0.20 + 0.50 + 0.30 = 1.00 mole.

$$P_{MIXTURE} = \frac{nRT}{V} = \frac{(1.00\text{ mols})(0.08206\text{ L}\cdot\text{atm/mol}\cdot\text{K})(300.\text{ K})}{(1.00\text{ L})} = 24.6\text{ atm}$$

You can quickly verify that the total pressure in the single container is the sum of the individual pressures when the gases were alone in their own container. The pressure exerted by each of the gases in a mixture is called the **partial pressure** of that gas. Hence, Dalton's Law is the law of partial pressures.

Graham's Law of Diffusion

In a previous section, it was mentioned that gases will spread out and occupy any and all space available. This spreading out and mixing of a substance is called **diffusion.** The small spaces available in liquid structure allows diffusion to occur only slowly. A drop of food coloring in a glass of water (without stirring) might take half an hour or more to spread through the water evenly. With solid structure we would expect no diffusion or mixing at all but there is a story of lead and gold bricks stacked together for many years that showed a few molecules exchanged in the surfaces. Even if the story is true, diffusion in solids is negligible. In gases, of course, diffusion is very rapid. Not even the presence of other gases offer much obstacle to gases spreading out throughout their container. If someone opens a bottle of perfume or ammonia across the room from you, it is only a matter of minutes until you smell it. The molecules evaporate from the liquid in the bottle and spread out through the room quickly.

It turns out that the diffusion of gases is not all the same. If bottles of strong smelling substances are opened across the room from you at the same time, the odors will not reach you at the same time. If we pick the strong smelling substances ammonia (NH_3) and acetone (C_3H_6O) and open bottles of these substances across the room from you, you will always smell the ammonia before the acetone. If we had thought about this a little, we probably would have predicted it. With the two liquids in the same room, they are probably the same temperature so the molecules will have the same kinetic energy. Remember that when molecules have the same kinetic energy, big ones move slower and little ones move faster. If we consider the molar mass of these two substances, the molar mass of ammonia is 17 g/mol and the molar mass of acetone is 58 g/mol; so we would have realized that the ammonia molecules are traveling quite a bit faster than the acetone molecules in order for them to have the same kinetic energy. We would have expected the ammonia to diffuse through the room faster.

A demonstration commonly used to show the different rates of diffusion for gases is to dip one cotton ball in an ammonia solution and another cotton ball in a dilute HCl solution and stuff the cotton balls in the opposite ends of a glass tube. When NH_3 and HCl react, they form NH_4Cl, a white powdery substance. Molecules of NH_3 and HCl will escape the cotton balls at opposite ends of the tube and diffuse through the tube toward each other. Since the molar mass of HCl is slightly more than double that of NH_3, the NH_3 will travel further down the tube than the HCl by the time they meet.

Figure 14: A Diffusion Tube.

(*Source:* CK-12 Foundation, *License:* CC-BY-SA)

The white cloud of NH_4Cl always forms nearer the HCl end. If this experiment is done carefully and the distances are measured accurately, a reasonable ratio for the molar masses of these compounds can be determined.

Thomas Graham (1805-1869), an English chemist, studied the rates of diffusion of different gases and was able to describe the relationships quantitatively in what is called **Graham's Law.**

Under the same conditions of temperature and pressure, gases diffuse at a rate inversely proportional to the square root of the molecular masses.

The velocity of particle one is to the velocity of particle two as the square root of the molecular mass of particle two is to the square root of the molecular mass of particle one.

$$\frac{V_1}{V_2} = \sqrt{\frac{mm_2}{mm_1}}$$

Lesson Summary

- At STP, one mole of any gas occupies 22.4 liters.
- When gases are mixed and do not react chemically, the total pressure of the mixture of gases will be equal to the sum of the partial pressures of the individual gases.
- Gases diffuse at rates that are inversely proportional to the square roots of their molecular masses.
- Real gases tend to deviate from ideal gases at high pressures and low temperatures.

Review Questions

1. A 1.00 L container of helium gas at 1.00 atm pressure and a 1.00 L container of hydrogen gas at 2.00 atm are both transferred into a 1.00 L container containing nitrogen gas at 3.00 atm. What is the final pressure in the final container holding all three gases (assuming no temperature change)? **(Challenging)**

2. For the situation described in problem #1, what will be the partial pressure of the helium in the final container? **(Challenging)**

3. What conditions of temperature and pressure cause gases to deviate from ideal gas behavior? **(Beginning)**

4. At STP, how many molecules are in 89.6 liters of gas? **(Intermediate)**

5. If 1.00 liter of gas A at STP and 1.00 liter of gas B at STP are both placed into a 2.00 liter evacuated container at STP, what will the pressure be in the 2.00 liter container? **(Intermediate)**

6. Consider the gases CO and N_2. Which of the following will be nearly identical for the two gases at 25°C and 1.0 atm? **(Challenging)**

I. average molecular speed

II. rate of effusion through a pinhole

III. density

A. I only B. III only C. I and II only D. II and III only E. I, II, and III

7. The density of an unknown gas at 2.0 atm and 25°C is determined to be 3.11 g/L. Which of the following gases is the unknown most likely to be? **(Intermediate)**

A. CH_4 B. F_2 C. N_2O_4 D. O_2 E. CF_2Cl_2

Vocabulary

diffusion	The movement of particles from areas of higher concentration to areas of lower concentration of that particle.
partial pressure	The pressure that one component of a mixture of gases would exert if it were alone in a container.
molar volume	The volume occupied by one mole of a substance in the form of a solid, liquid, or gas.

Review Answers

1. Each gas will exert pressure as if it were in the container alone and the total pressure will be the sum of the individual (partial) pressures. Therefore, the total pressure will be 6.00 atm.

2. 1.00 atm

3. high temperature and low pressure

4. 89.6 liters of gas at STP is four molar volumes and therefore contains three moles of gas.

$(4)(6.02 \times 10^{23} \text{ molecules}) = 2.41 \times 10^{24}$ molecules

5. The number of molecules has been doubled but the volume has also been doubled, so the pressure will be 1.00 atm.

6. E The two gases have the same molar mass. At constant temperature and pressure, all the listed quantities depend primarily on the molar mass of the gas.

7. *Choice B*

$$\text{molar mass} = \frac{dRT}{P} = \frac{(3.11\ \text{g/L})(0.08206\ \text{L}\cdot\text{atm/mol}\cdot\text{K})(298\ \text{K})}{(2.00\ \text{atm})} = 38.0\ \text{g/mol}$$

Of the molar masses of the choices, F_2 is the closest.

Stoichiometry Involving Gases

Lesson Objectives

- The student will solve stoichiometry problems involving gas volume at STP to moles and vice versa.
- The student will solve stoichiometry problems involving gas volume to gas volume.

Introduction

The knowledge of the molar volume of gases at STP and the other gas laws allows us to work stoichiometry problems from gas volumes as well as masses.

Volumes, Moles, and Molecules

Avogadro's Law tells us that under the same conditions of temperature and pressure, equal volumes of gases will contain equal numbers of molecules. By logical extension, we can say that under the same conditions of temperature and pressure, equal numbers of molecules will occupy equal volumes. For example, 1.00 mole of hydrogen gas will occupy the same volume as 1.00 mole of oxygen gas if their temperatures and pressures are the same. With the same logical extension, we can say that at the same temperature and pressure, 2.00 moles of oxygen gas will occupy twice the volume of 1.00 mole of hydrogen gas. This logic allows us an additional way to read an all gaseous chemical equation.

$$2\ H_{2(g)} + O_{2(g)} \rightarrow 2\ H_2O_{(g)}$$

The first way we learned to read this equation was: 2 molecules of hydrogen gas react with 1 molecule of oxygen gas to yield 2 molecules of gaseous water. After we learned about moles, we could also read this equation as: 2 moles of hydrogen gas react with 1 mole of oxygen gas to yield 2 moles of gaseous water. Now, we have a third way we can read this all gaseous equation: 2 volumes of hydrogen gas react with 1 volume of oxygen gas to yield 2 volumes of gaseous water if all substances are at the same temperature and pressure. The reacting ratio indicated by the coefficients in this equation are true for molecules, moles, and volumes for an all gaseous reaction if the gases are all under the same conditions.

Sample Problem 11

What volume of oxygen gas is necessary to react with 100. L of hydrogen gas assuming all volumes are measured at the same temperature and pressure?

Solution

The reacting ratio indicated by the coefficients from the equation are true for gas volumes under equal conditions.

$$2\ H_{2(g)} + O_{2(g)} \rightarrow 2\ H_2O_{(g)}$$

The coefficients of the balanced equation indicate that 2 molecules of hydrogen will require 1 molecule of oxygen to react completely so 100. L of hydrogen will required 50. L of oxygen to react completely.

$$\frac{2 \text{ mols } H_2}{1 \text{ mol } O_2} = \frac{100. \text{ L of } H_2}{x \text{ L of } O_2} \qquad x = 50.0 \text{ L of } O_2$$

Volume-Volume Calculations at STP

When you first learned to solve stoichiometry problems, one of the steps was to convert known quantities to moles. In those early problems, the known quantity was also given in mass and you converted mass to moles by dividing grams by molar mass. Later, known quantities may have been given to you as the molarity and volume of a solution. To convert a volume of solution at known molarity to moles, you multiplied molarity times solution volume in liters.

From now on, you may also be given known quantities as a volume of gas either at STP or at some other conditions of temperature and pressure. You already know how to convert a volume of gas at STP to moles. At STP, one mole of any gas occupies 22.4 liters. If you are given a volume of gas at STP as a known, you convert it to moles by dividing by 22.4 L/mol. If you are given a volume of gas at conditions other than STP, you must use PV = nRT to calculate the number of moles.

Sample Problem 12

$$N_{2(g)} + 3\ H_{2(g)} \rightarrow 2\ NH_{3(g)}$$

According to this equation, how many liters of ammonia can be formed from 50.0 L of nitrogen gas, N_2. Assume all gases are at STP.

Solution:

Since both the given substance and the requested substance are gases under the same conditions of temperature and pressure, the reacting ratio indicated by the coefficients in the equation are true for volumes.

$$\frac{1\ N_2}{2\ NH_3} = \frac{50.0\ L\ of\ N_2}{x\ L\ of\ NH_3} \qquad x = 100.\ L\ of\ NH_3$$

Sample Problem 13

$$N_{2(g)} + 3\ H_{2(g)} \rightarrow 2\ NH_{3(g)}$$

According to this equation, how many grams of ammonia can be formed from 30.0 L of hydrogen gas at STP?

Solution:

Since the hydrogen gas volume is given at STP, we can convert the volume to moles by dividing by 22.4 L/mol. Once we have the given quantity in moles, the remainder of the problem is the same as other stoichiometry problems.

$$(30.0\ L)\left(\frac{1.00\ mol}{22.4\ L}\right) = 1.34\ mols\ H_2$$

$$\frac{3\ H_2}{2\ NH_3} = \frac{1.34\ mol\ H_2}{x\ mol\ NH_3} \qquad x = 0.893\ mol\ NH_3$$

$$grams\ NH_3 = (moles)(molar\ mass) = (0.893\ mol)(17.0\ g/mol) = 15.2\ grams$$

Sample Problem 14

$$N_{2(g)} + 3\ H_{2(g)} \rightarrow 2\ NH_{3(g)}$$

According to this equation, how many liters of ammonia gas at STP can be formed from 25.0 g of hydrogen gas?

Solution:

The solution steps are to convert the grams of H_2 to moles, use the ratio from the equation to solve for moles of ammonia gas and then convert the moles of ammonia to liters of gas at STP. The moles of ammonia gas is converted to liters at STP by multiplying by 22.4 L/mol.

$$(25.0\ g)\left(\frac{1.00\ mol}{2.02\ g}\right) = 12.4\ mols\ H_2$$

$$\frac{3\ H_2}{2\ NH_3} = \frac{12.4\ mol\ H_2}{x\ mol\ NH_3} \qquad x = 8.27\ mol\ NH_3$$

$$liters\ NH_3 = (moles)(molar\ mass) = (8.27\ mol)(22.4\ L/mol) = 185\ liters$$

Mole-Volume or Volume-Mole Calculations Not at STP

When volumes involved in chemical reactions are not given at standard conditions, the conversion between moles of gas and volume of gas can be determined by using the universal gas law, PV = nRT.

Sample Problem 15

1,000. grams of calcium carbonate are heated and reacts according to the following equation.

$$CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2(g)}$$

If the carbon dioxide is collected at 500. K and 2.00 atm, what volume will it occupy under these conditions?

Solution:

$$(1000.\ \text{g})\left(\frac{1.00\ mol}{100.\ g}\right) = 10.0 \text{ mols } CaCO_3$$

Since the reacting ratio between calcium carbonate and carbon dioxide in the equation is 1 to 1, the 10.0 mols of calcium carbonate will form 10.0 mols of carbon dioxide. We use PV = nRT to find the volume of 10.0 mols of gas under these conditions.

$$V = \frac{nRT}{P} = \frac{(10.0\ \text{mols})(0.08206\ \text{L}\cdot\text{atm/mol}\cdot\text{K})(500.\ \text{K})}{(2.00\ \text{atm})} = 205 \text{ liters}$$

Lesson Summary

- In a balanced gaseous equation, the coefficients apply to molecules, moles, and volumes of gas if the gases are under the same conditions of temperature and pressure.

Review Questions

1. How many liters of hydrogen gas are required to react with 25.0 L of nitrogen gas according to the following equation? $N_{2(g)} + 3\ H_{2(g)} \longrightarrow 2\ NH_{3(g)}$ **(Intermediate)**

2. How many grams of ammonia will be formed from 25.0 L of nitrogen gas measured at STP according to the equation in question 29? **(Intermediate)**

Further Readings / Supplementary Links

Chemistry, 5th Edition, chapter 5: Gases, Steven S. Zumdahl and Susan A. Zumdahl, Houghton Mifflin Company, 2000.

http://www.chm.davidson.edu/chemistryapplets/kineticmoleculartheory/basicconcepts.html

http://en.wikipedia.org/wiki/Kinetic_theory;

http://www.chm.davidson.edu/chemistryapplets/kineticmoleculartheory/basicconcepts.html

Review Answers

1. 75 liters

2. 37.9 grams

19. The Liquid State

The Properties of Liquids

Lesson Objectives

- The student will explain the basic behavior and characteristics of liquids using the molecular arrangement in liquids.

Introduction

Liquids and solids differ from gases in two important ways. The particles (atoms, molecules, or ions) are much closer together so the total volume of a liquid or solid is much closer to the sum of the volumes of the molecules. Also, attractive forces between the particles in liquids and solids are much stronger. The strength of these forces of attraction between particles is a major reason that the substance is in the liquid or solid state rather than gaseous.

Liquids Maintain Their Volume But Take the Shape of Their Container

The arrangement of the molecules in a liquid structure accounts for most of the physical properties of liquids.

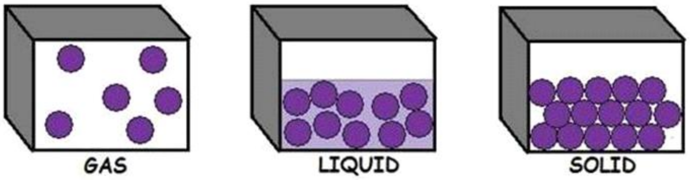


Figure 1: The Three Phases of Matter.

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Liquids have much less space between molecules and stronger attractive forces than gases. In the liquid state, attractive forces between molecules are a major factor in the behavior of the liquids. Although liquid structure has small spaces so the molecules can move past one another, the attraction between particles keep them from getting very far apart. Therefore, liquids maintain their own volume but take the shape of their container. 100 mL of liquid will be 100 mL in any container but because the liquid molecules are not held in a tightly packed pattern (like solids), the molecules can move past one another and so liquids will flow to fit the shape of their container

Liquids Have Greater Densities Than Gases

In gases, the distance between the molecules is so great that the size of the molecules themselves become inconsequential. A gas is considered to be essentially empty space. (If the picture above were realistic of gas structure, the molecules would be so small you couldn't see them.) If we consider the volumes of 6.02×10^{23} molecules of oxygen gas (O_2) and 6.02×10^{23} molecules of Freon gas (CF_4) both at STP, we know that the volumes will be the same, 22.4 liters. This is because the sizes of the molecules themselves are negligible compared to the empty space in a gas. The fact that the Freon molecules are several times larger than the oxygen molecules makes no difference. In a gas, you are measuring the volume of the empty space. If we consider the volume of 6.02×10^{23} molecules of *liquid* oxygen and 6.02×10^{23} molecules of *liquid* Freon both at STP, we find the volume of the oxygen is about 28 mL and the volume of the Freon is about 55 mL.

In the case of liquids, the volumes of the molecules themselves make a difference. In liquids, the volume of a group of molecules is related to the volume of the individual molecules and so equal moles of liquids DO NOT occupy equal volumes under the same conditions. Since liquids have many more molecules in a smaller volume, they will have much greater densities than gases.

Liquids Are Almost Incompressible

When a substance is compressed, it is not the molecules themselves that are compressed; it is the space between the molecules that is compressed. Gases have lots of empty space and so are easily compressed. A pressure of 3.0 atm compresses a gas to one-third its volume at 1.0 atm. Liquids have very little space between molecules and do not compress easily – a pressure of 3.0 atm will have virtually no effect on the volume of a liquid. Liquids are used in hydraulic systems because of their ability to flow to fit their container and their incompressibility.

Liquids Diffuse More Slowly Than Gases

Diffusion in gases (mixing) is nearly instantaneous. If you release a colored gas in a container of non-colored gas, the color spreads evenly throughout the container in a second or two. In liquids, diffusion is a much slower process. The smaller spaces to move through and the almost constant collisions cause the molecules to require much more time to move from one side of the container to the other.

Lesson Summary

- Molecules in the liquid phase have some freedom of movement but their motion is much more restricted than that of gases.
- Liquids are only slightly compressible.
- Liquids diffuse more slowly than gases.

Review Questions

1. The molar volumes of solid silicon and solid bromine under the same conditions are different and the molar volumes of liquid silicon and liquid bromine under the same conditions are different, but the molar volumes of gaseous silicon and gaseous bromine under the same conditions are exactly the same. Explain. **(Intermediate)**

Vocabulary

incompressible	The terms compressibility and incompressibility describe the ability of molecules in a fluid to be compacted (made more dense).

Review Answers

1. In solids and liquids (so-called condensed phases), the space between the molecules is less significant than in gases. Most of the volume of solids and liquids consists of the actual molecules of solid and liquid. Therefore, the fact that the molecules have different volumes causes the overall volume to be different. In gases, however, the volume of the gaseous molecules are insignificant compared to the volume of the empty space between the molecules. Therefore, the volumes of the molecules in a gas do not affect the overall volume of the gas. The volume of a gas is essentially the empty space between the molecules and under the same conditions, all gases have the same volume of empty space.

Forces of Attraction

Lesson Objectives

- The student will identify liquids whose intermolecular forces of attraction are due to London dispersion forces, polar attractions, and hydrogen bonding.
- The student will describe some of the unique properties of water that are due to hydrogen bonding.
- The student will select from comparative compounds, the ones most likely to form hydrogen bonds.
- The student will select from comparative compounds whose intermolecular forces are London dispersion forces, the one most likely to have the strongest intermolecular forces.

Introduction

Forces on the molecular level are divided into two categories – the forces inside a molecule holding atoms together to form the molecule and the forces between molecules holding the molecules in the liquid or solid state. The forces *inside* the molecule are called intramolecular forces and the forces *between* molecules are called intermolecular forces. You can relate them to bus systems where intracity buses move people around inside one city and intercity buses move people from one city to another.

Intramolecular Forces

Intramolecular forces refer to the forces inside a molecule that holds the atoms together to form molecules. Essentially, there is only one force in this category and that is covalent chemical bonds.

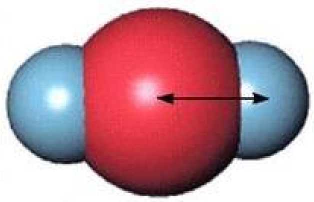

Figure 2: The only intramolecular forces are covalent chemical bonds.

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Even though we sometimes write ionic compounds in equations and call the equations "molecular equations", ionic compounds are not considered to form molecules. Ionic compounds in the solid state from crystal lattices in which each ion is equally attracted to more than one oppositely charged ion. The only true molecules are in covalently bonded compounds.

Intermolecular Forces of Attraction

We will consider three types of intermolecular forces of attraction. These are the forces that hold molecules in the condensed states (liquid and solid).

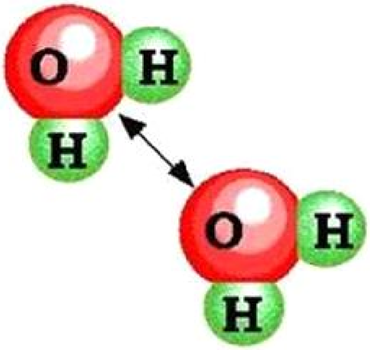

Figure 3: Intermolecular forces of attraction are the forces between molecules that hold them in the liquid or solid state.

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When a substance changes phase as in a solid melting to liquid or a liquid vaporizing to gas, the intermolecular forces must be overcome. Therefore, the stronger the intermolecular forces of attraction, the greater the molecular motion (temperature) that will be required to overcome them. The liquids with the strongest intermolecular forces of attraction will have the highest boiling points and vice versa.

London Dispersion Forces

The weakest type of intermolecular force is called **London dispersion forces.** London dispersion forces occur between all atoms and molecules but they are so weak, they are only considered when there is no other intermolecular force. For example, London dispersion forces exist between water molecules but water molecules also have a permanent polar attraction so much stronger than the London dispersion forces that the London dispersion force is insignificant and not mentioned.

The cause of London dispersion force is not obvious. Although we usually assume the electrons of an atom are uniformly distributed around the nucleus, this is apparently not true at every instant. As the electrons move around the nucleus, at a given instant, more electrons may be on one side of the nucleus than the other side. This momentary nonsymmetrical electron distribution can produce a temporary dipolar arrangement of charge. This temporary dipole can induce a similar dipole in a neighboring atom and produce a weak, short-lived attraction.

The cases where London dispersion forces would be considered as the intermolecular force of attraction would be in the noble gases and non-polar molecules such as H_2, N_2, Cl_2, CH_4, CCl_4, CO_2, SF_6 and so forth. Since non-polar molecules do not have a permanent dipole and no further bonding capacity, their only means of attracting each other is through London dispersion forces. Some of the substances whose intermolecular forces of attraction are London dispersion forces are held in the liquid state very weakly and therefore, would have the lowest melting points of all substances.

Boiling Points of Some London Dispersion Forces Liquids

Substance	**Boiling Point (°C)**
Helium, He	-269.7
Neon, Ne	-248.6
Argon, Ar	-189.4
Krypton, Kr	-157.3
Xenon, Xe	-111.9
Hydrogen, H_2	-253

Oxygen, O_2	-182
Methane, CH_4	-161
Carbon Dioxide, CO_2	-78

The temporary dipoles that cause London dispersion forces are affected by the molar mass of the particle. The greater the molar mass of the particle, the greater is the force of attraction caused by London dispersion forces. The molar masses of H_2, N_2, and O_2 are 2, 28, and 32 g/mol, respectively, and their boiling points increase in similar fashion; H_2 is -253°C, N_2 is -196°C, and O_2 is -183°C. When the molar masses of London dispersion force liquids become high enough, the substances will be liquid even at room temperature and above. Carbon tetrachloride, molar mass 154 g/mol, and bromine, molar mass 160 g/mol, boil at +77°C and +59°C, respectively. Many long carbon chain, non-polar substances such as gasoline and oil remain liquids at common temperatures.

Polar Attractions

When covalent bonds form between identical atoms such as in H_2, N_2, O_2, and so on, the electrons shared in the bonds are shared exactly equally. The two atoms have the same electronegativity and therefore, the same pull on the shared electrons.

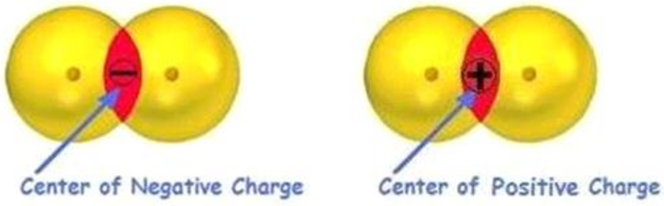

Figure 4: The centers of positive and negative charge.

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The center of negative charge for the entire molecule will be in the exact center of the molecule. This will coincide with the center of positive charge for the molecule. When the center of negative charge and the center of positive charge coincide, there is no charge separation and no dipole.

If the two atoms sharing the bonding pair of electrons are not of the same element, the atom with the greater electronegativity will pull the shared electrons closer to it. Because of the resulting uneven distribution of electrons, the center of negative charge will not coincide with the center of positive charge and a dipole is created on the molecule. When the centers of positive and negative charge do not coincide, a charge separation exists and a dipole is present.

The end of the molecule with the more electronegative atom will have a partial negative charge and the end of the molecule with the more electropositive atom will have a slight positive charge. The symbols δ+ and δ- are used because these are not full 1+ and 1- charges.

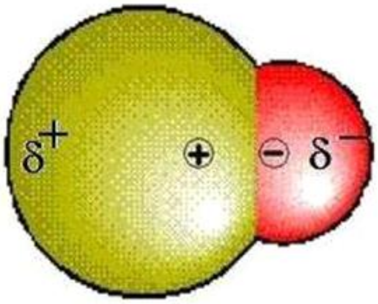

Figure 5: The polar molecule.

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This polarity is much less of a charge separation than in an ionic bond. These charges are only fractions of full 1+ and 1- charges. How much polarity a bond will experience depends on the difference in the electronegativities of the atoms.

In the case of a symmetrical molecule with polar bonds, the symmetry of the electron displacements of two or more electron pairs will keep the center of negative charge in the center of the molecule coincident with the center of positive charge and so no dipole will occur.

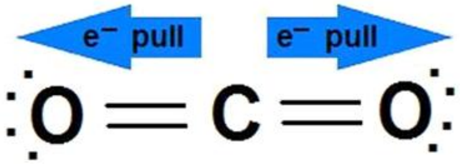

Figure 6: When the electron shift in polar bonds is symmetrical over the entire molecule, there will be no dipole.

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For example, in the CO_2 molecule, both carbon-oxygen bonds are polar, but the shift of bonding electrons toward the oxygen is the same on both sides of the carbon atom and the center of negative charge remains in the center.

For molecules that have a permanent dipole, the attraction between oppositely charged ends of adjacent molecules are the dominant intermolecular force of attraction.

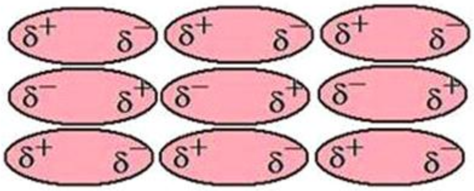

Figure 7: Polar attractions in a solid hold the molecules together.

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Figure 7 represents a polar solid, a polar liquid would look similar except the molecules would be less organized. On the average, these polar attractions are stronger than London dispersion forces so polar molecules, in general, have higher boiling points than London dispersion liquids. There is significant overlap, however, between the boiling points of the stronger London dispersion molecules and the weaker polar molecules.

The organization of a substance composed of polar molecules depends on the competition between the strength of the polar attractions and the molecular motion of the molecules. At higher temperatures, the molecular motion of the molecules is strong enough to disrupt the polar attractions but at low temperatures, the molecular motion is reduced and the polar attractions can hold the molecules in a structured arrangement. In liquid and gaseous forms, the molecules can also turn freely. If a pair of polar molecules in liquid form are aligned positive end to positive end, it is no problem for one of the molecules to spin around and align its negative end to the positive end of the other molecule.

This turning of polar molecules toward an attractive force can be seen in a macroscopic situation as well. If we allow a very thin stream of water to run from a faucet and we bring a charged object (rubber comb run through hair, balloon rubbed on wool sweater, etc) near the stream of liquid, the stream will bend its path toward the charged object. It doesn't make any difference if the charged object is positively or negatively charged because the water molecules in the stream will turn their oppositely charged end toward the charged object. In the sketch at right, the path of a non-polar liquid is not deflected by the charged rod but the path of the water stream is deflected by the charged rod.

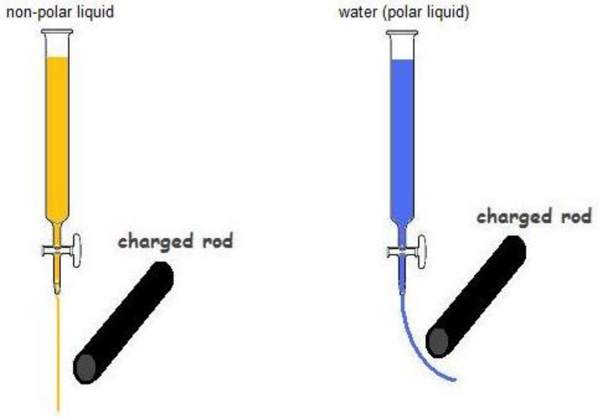
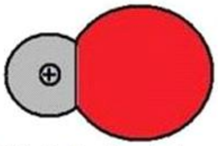


Figure 8: A stream of polar liquid will bend toward a charged rod. (*Created by:* Richard Parsons, *License:* CC-BY-SA)

Hydrogen Bonds

There are several polar molecules whose polar bonds are so strong they merit separate attention. These are the polar attractions that occur in molecules where hydrogen is bonded to nitrogen, oxygen, or fluorine. The polar attractions in these molecules are nearly 10 times as strong as regular polar attractions. These extra strong polar attractions that occur with the H-N, H-O, and H-F bonds are called **hydrogen bonds** which distinguishes them from regular polar attractions but keep in mind that they are, in fact, polar attractions, albeit very strong ones.

There is more than one explanation for why these three combinations form hydrogen bonds. There are only ten elements that have greater electronegativity than hydrogen and only four that have a significantly greater electronegativity than hydrogen. Three of the elements that have significantly greater electronegativity than hydrogen are nitrogen, oxygen, and fluorine – the three elements that form hydrogen bonds in compounds with hydrogen. When hydrogen bonds with atoms whose electronegativities are less than or equal to the electronegativity of hydrogen, the other atom cannot pull the shared electrons away from hydrogen.


In HBr, the bonding electrons remain partially around the hydrogen and shield its nucleus.

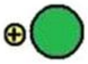

In HF, the bonding electrons are pulled away leaving an unshielded nucleus.

Figure 9: With highly electronegative non-metals, the electron shift away from the hydrogen atom leaves an unshielded proton.

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Therefore, the hydrogen nucleus (a single proton) is shielded by electrons in its electron cloud. When hydrogen chemically bonds with nitrogen, oxygen, or fluorine, the very high electronegativities of these atoms CAN pull the electrons far away from the hydrogen atom, thus removing the shielding electrons from the proton nucleus of hydrogen. When the polar attractions between HF molecules or other hydrogen bonding compounds set up, the negative end of a molecule can get very close to the proton on the positive end of another molecule because there are no electrons for shielding. The closeness of the charges causes the extra strong polar attractions in these compounds. The characteristics of a liquid that forms hydrogen bonds are significantly different from similar compounds that do not form hydrogen bonds. In the case of water, this is very important to life on earth.

A homologous series of compounds are compounds of the elements of a family, each bonded to the same other element. For example, family 4A in the periodic table consists of carbon, silicon, germanium, and tin. If each of these is bonded to hydrogen, it would produce a homologous series, CH_4, SiH_4, GeH_4, and SnH_4. If we graph the boiling points of this homologous series, we would get the graph sketched in Figure 10. The large majority of graphs of the boiling points of homologous series would look like this in that the boiling points increase as molar mass increases. If we graph the boiling points of the homologous series of family 6A combined with hydrogen, we get a quite different graph.

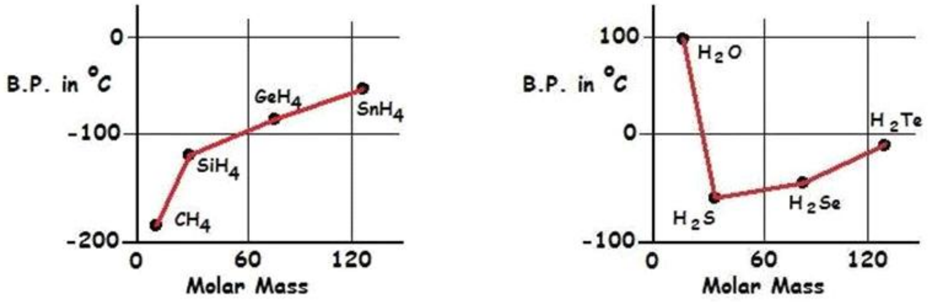

Figure 10: Boiling point comparisons: family 4A hydrogen compounds to family 6A hydrogen compounds.

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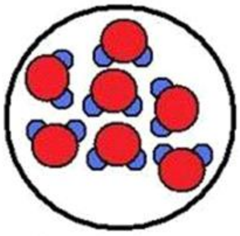
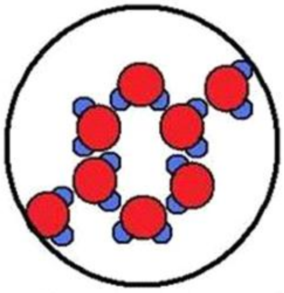
The higher molar mass compounds in the series follow the normal pattern of decreasing boiling points as the molar mass decreases. But, when we get to water, suddenly the boiling point is way out of line – it is more than 150 degrees too high. The explanation for why liquid water is held together far more tightly than expected – hydrogen bonds. Graphs of the boiling points of the homologous series of hydrogen with 5A family members and hydrogen with 7A family members would be similar. The boiling point of NH_3 and HF are greatly different from what would be expected.



Water with no significant hydrogen bonding.



Water with significant hydrogen bonding.

Figure 11: Significant hydrogen bonding causes water molecules to line up end-to-end.

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The fact that water forms hydrogen bonds has effects so large that it is impossible in this text to delineate them all. We will consider a few but there are many more not in this list.

1) The normal boiling point of water is 100°C. If water did not form hydrogen bonds and instead had a regular polar attraction between molecules, its boiling point would be somewhere around -60°C. The average temperature of the surface of the earth is 15°C. If water did not form hydrogen bonds, the oceans and lakes would vaporize and earth would not be a water planet. Therefore, it would likely not be a planet with life on it.

2) If you gathered 100 substances of all types (ionic, metals, regular polar substances, London dispersion substances) and water and you arranged to have each of these substances in both solid and liquid form and you dropped pieces of solid into the corresponding liquid, you would find exactly one compound whose solid floated in the liquid. For all the other compounds, the pieces of solid would sink to the bottom of the liquid. Only water would have the solid floating on the liquid. The reason for this is that as you cool the liquid of almost all substances to freeze them, the substance contracts as it cools – the molecules move around slower and intermolecular forces pull the molecules closer together. As a result, the solids are denser than the liquids and the solids will sink in the liquids. Water, of course, is the exception. When water cools to its freezing point and solidifies, it expands. When water molecules are at or above 4°C, the molecular motion is sufficient to keep the hydrogen bonds from locking water molecules into an end-to-end molecular complex with large holes in the structure. When water is cooled below 4°C, the molecular motion is inadequate to break up this complex structure – so water molecules begin forming end-to-end chains and the water expands because of the holes in the structure. Therefore, solid water is less dense than liquid water and ice floats on water. You have seen ice cubes floating in water a thousand times and you have probably never seen any other substance where you see the solid interacting with the liquid, so the ice floating looks normal to you. If you were familiar with the behavior of all other substances in this situation and then you saw someone place ice cubes in water for the first time, you would probably think they had just done a magic trick.

One of the effects of the fact that ice floats on water is that when cold weather comes to areas in the northern and southern parts of the earth, the cold air contacts the water on the surface of lakes and freezes that surface water. If water were like other substances and the solid sank to the bottom, then the cold air would freeze the new surface and it would sink and so on until the entire lake would be frozen top to bottom. No water dwelling animals would survive such an occurrence. But, actually, when the cold air freezes the surface of a lake, the ice floats, stays on top and insulates the rest of the rest of the water from the cold air. Only the surface freezes and the animals that live in the water survive the winter.

3) One of the factors in the weathering of rocks in geographical areas that have winter is that rain water enters rocks through cracks and then freezes and expands, fracturing the rock.

4) Some biologically active molecules such as DNA require a particular shape for their function. If you think of a long-chain molecule as something similar to a string, how can such a molecule have and hold a shape. At points along its length, the molecule can be linked to itself with different types of attractions – one of which are hydrogen bonds.

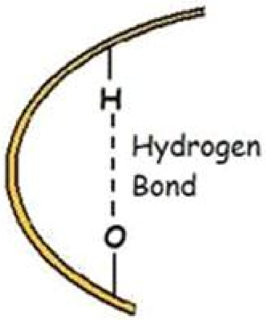

Figure 12: Hydrogen bonds form links to maintain shapes of molecules.

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5) As long as water is above 4°C, when it is cooled, like other substances, it contracts and becomes denser. When water passes through 4°C, significant hydrogen bonding begins to form and the water expands and becomes less dense. The maximum density for water is at 4°C. Many animals that live in water and require oxygen, use oxygen that is dissolved in the water. Water in lakes becomes oxygenated (has dissolved oxygen) by the action of wind and waves at the surface. For deep lakes, diffusion is inadequate to move the oxygenated water to the bottom of the lake. Once the oxygen was used up in the water at the bottom of a lake, oxygen using animals would be unable to live there. For lakes in northern climates, the surface passes through the temperature 4°C twice per year, once as it cools in the fall and once as it warms in the spring. During these two times, the water at the surface would sink to the bottom because it is denser and the sinking water would be oxygenated. These periods are called spring and fall “turnovers.” The turnovers provide oxygenated water at the bottom of the lakes.

Ionic Liquids

Ionic compounds may also exist in liquid form. The intermolecular forces of attraction in ionic liquids would, of course, be the electrostatic attraction between oppositely charged ions. The charges on ions are complete charges of 1+, 2+, 1-, 2- and so on. The attractions due to these charges are much greater than those of polar molecules, even the especially strong polar attractions of hydrogen bonds, and so the boiling points of ionic liquids would be much higher than the molecular liquids discussed previously. Sodium chloride, for example, boils at 1465°C.

Metallic Liquids

Metals may also exist in the liquid state. The bonding and therefore, the intermolecular forces of attraction for metals will be covered in the next chapter.

Lesson Summary

- Molecules are held together in the liquid phase by intermolecular forces of attractions.
- London dispersion forces are a very weak intermolecular force of attraction caused by a temporary electrostatic attraction between the electrons of one molecule or atom and the nucleus of another.
- Polar attractions are an intermolecular force of attraction caused by the electrostatic attraction between permanent dipoles that exists on polar molecules.
- Hydrogen bonds are an exceptionally strong type of polar attraction that occurs between molecules that have H-F bonds, H-O bonds, or H-N bonds.

- Ionic substances also exist in liquid form; the attractions between the ions are the attractions between ionic charges and are much stronger than polar attractions or hydrogen bonds.

Review Questions

1. Which of the following molecules would you expect to have the higher melting point? Why? **(Intermediate)**

A. CH_4 or H_2S

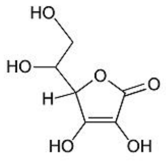
B. H_2O or H_2S

C. HCl or Cl_2

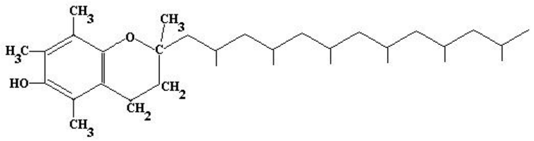
D. NaI or NH_3

E. SF_4 or CH_4

2.



Vitamin C



Vitamin E

The structures of vitamins C and E are shown above. Which of the following statements is correct? **(Intermediate)**

A. Vitamin E has more opportunities for hydrogen bonds than vitamin C.

B. The melting point of vitamin E is likely to be higher than that of vitamin C.

C. Vitamin C is likely to be very soluble in a non-polar solvent.

D. Vitamin C should have a higher solubility in water than vitamin E.

E. Vitamin C would be described as a "fat-soluble" vitamin.

Vocabulary

hydrogen bond	The exceptionally strong polar attraction between a hydrogen atom in one molecule and a highly electronegative atom (N, O, F) in another molecule.
London dispersion forces	Electrostatic attractions of molecule or atoms for nearby atoms or molecules caused by the temporary unsymmetrical distribution of electrons in electron clouds.

Review Answers

1.

A. H_2S because H_2S is polar whereas CH_4 is non-polar and therefore would be held together with London dispersion forces.

B. H_2O because while both are polar, H_2O will form hydrogen bonds and H_2S does not.

C. HCl because it is polar and Cl_2 is non-polar.

D. NaI because it is ionic whereas NH_3 is polar and ionic attractions are much stronger than polar attractions.

E. SF_4 because it is polar (distorted tetrahedron) whereas CH_4 is non-polar.

2. D

Vapor Pressure

Lesson Objectives

- The student will be able to describe the processes of evaporation and condensation.
- The student will be able to describe vapor pressure equilibrium.

Introduction

The phase of a substance is essentially the result of two forces acting on the molecules. The molecules of a substance are pulled together by intermolecular forces of attraction that were discussed in the previous section. Some of these intermolecular forces are weak and some are strong. The molecules of a substance also have kinetic energy so that the molecules are in constant random motion and are in almost constant collisions with each other. The motion and collisions of molecules push them away from each other. Without intermolecular forces of attraction, the molecules of all substances would move away from each other and there would be no condensed phases (liquids and solids).

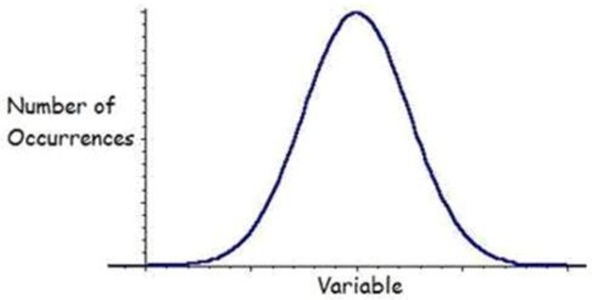
If the forces caused by molecular motion are much greater than and dominate the intermolecular forces of attraction, the molecules will separate and the substance will be in the gaseous state. If the intermolecular forces of attraction are dominantly stronger than the molecular motion, the molecules will be pulled into a closely packed pattern and the substance will be in the solid state. If there is some balance between molecular motion and intermolecular forces of attraction, the substance will be in the liquid state.

When substances are heated or cooled, their average kinetic energy increases or decreases, their molecular motion increases or decreases, and the substance may change phase. A substance in the solid phase (intermolecular forces dominate) can be heated until the molecular motion balances the intermolecular forces and the solid will melt to liquid. The liquid may be heated until the molecular motion completely overcomes the intermolecular forces and the liquid will vaporize to the gaseous state.

When you open a jar of perfume, your nose detects the substance almost immediately. You can see that the substance is in liquid form and it is not boiling, yet some of that material obviously entered the gaseous state and reached your nose.

Evaporation

The temperature of a beaker of water is a measure of the average kinetic energy of the molecules in the beaker. That does not mean that all the molecules in the beaker have exactly the same kinetic energy. Most of the molecules will be within a few degrees of the average but a few molecules may be considerably hotter or colder than the average. The kinetic energy of the molecules in the breaker will have a distribution curve similar to a standard distribution curve for most naturally occurring phenomena.



A standard distribution curve like this could represent the length of grasshopper legs in a random sample of grasshoppers or the distribution of IQ for a random sample of humans.

Figure 13: Standard Distribution Curve

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Naturally occurring phenomena usually have most of the instances near the average and the number of instances become less as the value gets farther from the average.

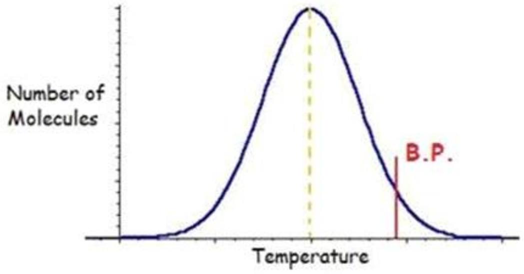

Figure 14: The distribution of temperature among the molecules of a beaker of water.

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In the case of a beaker of water, some of the molecules will have an average temperature below the boiling point and some of the molecules will have a temperature above the boiling point (see Figure 13). The dashed yellow line is the average temperature of the molecules and would be the temperature shown on a thermometer inserted into the liquid. The red line represents the boiling point of water (100°C at 1.00 atm pressure) and the area under the curve to the right of the red line represents the molecules of water that are above the boiling point. In order for a molecule of liquid that is above the boiling temperature to escape from the liquid, it must either be on the surface or it must be adjacent to many other molecules that are above the boiling point so that the molecules can form a bubble and rise to the surface.

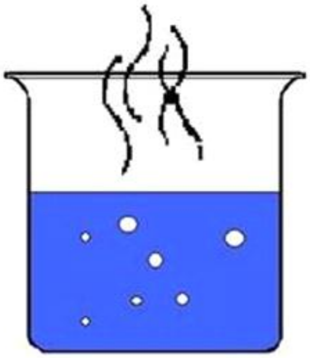

Figure 15: Water boils only when a sufficient number of adjacent molecules are above the boiling point and can form bubbles of gaseous water.

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The only circumstance when there are enough molecules above the boiling point to form bubbles is when the average temperature is at the boiling point. For single molecules above the boiling point, they must wait until their random motion gets them to the surface and then the molecule can leave the liquid and enter into the gaseous phase. This process of molecules escaping to the gaseous phase from the surface of a liquid when the average temperature of the liquid is below the boiling point is called **evaporation.**

The process of phase change is a little more complicated than just having the molecules reach the boiling point. Objects that attract each other and are separated have potential energy due to that attraction and separation. An object held above the earth is attracted to the earth by earth's gravity and has potential energy due to the attraction and separation. The amount of potential energy can be calculated by multiplying the force of attraction times the distance of separation. Two oppositely charged objects that are separated have potential energy. Objects with opposite magnetic poles that are separated have potential energy. A stretched rubber band has potential energy. Gaseous molecules that have a force of attraction between them but are separated have potential energy. Molecules in the liquid state and the same molecules in the gaseous state at the same temperature DO NOT have the same total energy. If they are at the same temperature, they have the same kinetic energy but the gaseous molecules have potential energy that the liquid molecules do not. Molecules in the liquid state that are hot enough to exist in the gaseous state must absorb energy from their surroundings to provide that potential energy as they change phase. This potential energy is called the **heat of vaporization** and it is absorbed by evaporating or vaporizing molecules from the kinetic energy of the liquid.

You are at least somewhat familiar with evaporation. You know that if you leave a saucer of water sitting out on the countertop, the water will slowly disappear – and yet, at no time is the temperature of the water ever at the boiling point. The water in an open container continues to evaporate until it is all in the vapor state. When molecules of a liquid are evaporating, it is clear that it is the hottest molecules that are evaporating. It might seem that once the molecules whose temperature was above the boiling point are gone, no more evaporation would occur. Here's the reason evaporation continues. The temperature of the liquid is the average temperature of all the molecules. When the hottest molecules evaporate, the average temperature of those molecules left behind is lower and the molecules left behind have also contributed to the heat of vaporization to the evaporating molecules. The process of evaporation causes the remaining liquid to cool significantly. Heat flows from warmer objects to colder objects and so when the liquid cools due to evaporation, the surroundings will give heat to the liquid thus raising its temperature back up equal to the surroundings thus producing more hot molecules. This process can continue in an open container until the liquid is all evaporated.

Many years ago, when people lived without electricity, they figured out that if they placed the butter dish on the dinner table in a shallow container of water, evaporation would cool the water and therefore the butter dish, enough to keep the butter from melting to a liquid. They also knew that if you put a container of water or milk in a fabric sack, soaked the sack in water, and swung the sack around in the air, the evaporation of the water from the sack would cool it and cool the container of milk or water to make it nicer to drink. Many hikers today use fabric canteen holders that they soak in water while hiking so that the water in the canteen will be cooler when they drink it.

The rate of evaporation is related to the strength of the intermolecular forces of attraction, to the surface area of the liquid, and to the temperature of the liquid. As the temperature of liquids get closer to the boiling point, more of the molecules have temperatures above the boiling point and so evaporation is faster. Substances with weak intermolecular forces of attraction evaporate more quickly than those with strong intermolecular forces of attraction. Substances that evaporate readily are called **volatile** and those that hardly evaporate at all are called **non-volatile.**

Condensation

Liquids will usually evaporate to dryness in an open container. What happens, however, if the container is closed? When a lid is put on the container, the molecules that have evaporated are now kept in the space above the liquid. This makes it possible for a gaseous molecule to collide with another molecule or a wall and **condense** (the gas to liquid phase change) back to liquid. Molecules at the boiling point can exist in either liquid phase or gaseous phase – the only difference between them is the amount of potential energy they hold.

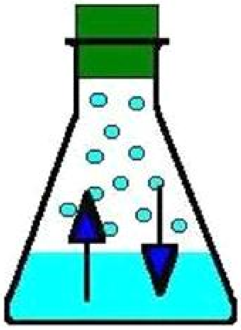

Figure 15: Evaporation and condensation both occur in a closed container.

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For a liquid molecule with adequate temperature to exist in the gaseous phase, it is necessary for the molecule to gain the heat of vaporization. It does this by collision with adjacent molecules. For a gaseous molecule to return to the liquid phase, it must give up the same amount of potential energy that it gained. That amount of potential energy is called the **heat of vaporization** when it is being gained and it is called the **heat of condensation** when it is being lost – but it is exactly the same amount of energy.

As more and more molecules evaporate in a closed container, the partial pressure of the gas in the space above the liquid increases. The rate at which molecules evaporate is determined by the temperature, the surface area, and what substance is involved. Once the substance, the surface area, and the temperature are established, the rate of evaporation will be constant. The rate at which the gas condenses is determined by the partial pressure of the gas, the surface area, and what substance is involved. Once the substance and surface area is established, the rate of condensation will only vary depending on the partial pressure of the gas. As the partial pressure of the gas in the space above the liquid increases, the rate of condensation will increase.

In the section on evaporation, it was pointed out that as a liquid evaporates, the remaining liquid cools because the hottest molecules are leaving so the average decreases and the heat of vaporization is being absorbed from the remaining molecules. For similar reasons, when a gas is undergoing condensation, the temperature of the remaining gas increases because the coolest molecules are condensing, thus raising the average of those left behind, and the condensing molecules must give up the heat of condensation.

Vapor Pressure Equilibrium

You can follow the progress of the two activities (evaporation and condensation) in a thought experiment. Suppose we place some liquid water in an Erlenmeyer flask and seal it. No water has evaporated yet so the partial pressure of water vapor in the space above the liquid is zero. As a result, there will be no condensation. As the water evaporates (at a constant rate since the temperature and surface area are constant), the partial pressure of the water vapor increases. Now that some vapor exists, condensation begins. Since the partial pressure of the water vapor is low, the rate of condensation will be low. Over time, more and more water evaporates and the partial pressure of the water vapor increases. Since the partial pressure increases, the rate of condensation increases. Eventually, the rate of condensation will become high enough that it is equal to the rate of evaporation. Once this happens, the rate of molecules of water going into the vapor phase and the number of molecules condensing back to liquid are exactly the same and so the partial pressure no longer increases. When the partial pressure of the water vapor becomes constant, the rate of condensation is constant and is exactly EQUAL to the rate of evaporation. A condition called **vapor pressure equilibrium** has been established. As time goes on from this point, the amount of liquid cannot change, the amount of gas cannot change; neither the rate of evaporation nor the rate of condensation can change. Everything remains exactly the same, BUT the two activities continue. Evaporation continues and condensation continues at exactly the same rate. Each different liquid at each temperature will have an exact partial pressure of vapor that will be present when vapor pressure equilibrium is established. The pressure of the vapor in the space above the liquid is called the **vapor pressure** of that liquid at that temperature.

Vapor Pressure of Water at Various Temperatures

Temperature in °C	**Vapor Pressure in Torr**
0	4.6
10	9.2
20	17.5
30	31.8
40	55.3
50	92.5
60	149.4
70	233.7
80	355.1
90	525.8
100	760.0

Volatile liquids would have higher vapor pressures than water at the same temperature and non-volatile liquids would have lower vapor pressures at the same temperature. The amount of volume for the space above the liquid makes no difference. The partial pressures of the gases will reach the equilibrium value – if the space is small, it will take little gas to produce the pressure and if the space is large, it will take much more gas to produce the pressure. As long as you introduce enough liquid into the container so that vapor pressure equilibrium will be reached, then the precise vapor pressure will be attained.

You might have noticed a subtle switch in vocabulary sometimes referring to the substance in the gaseous state as a gas and sometimes as a vapor. Chemists have agreed that a substance in the gaseous phase at temperatures above the boiling point of its liquid should be called a gas and if the temperature of the substance is below the boiling point, it should be called a vapor.

You should also note that the equilibrium vapor pressure of a liquid is the same regardless of whether or not another gas is present in the space above the liquid. If the space above liquid water contains air at 760 torr, and the liquid water evaporates until its equilibrium vapor pressure (25 torr) is reached, then the total pressure in the space above the liquid will be 785 torr. The presence of the air in no way affects the vapor pressure.

Vapor Pressure Correction

When gaseous substances are produced from chemical reactions and collected in the laboratory, they are usually collected over water. The "collection over water" technique is inexpensive and allows gaseous substances to be collected without having air mixed in. The process involves filling a collecting jar with water and inverting the jar in a pan of water without letting any water out or air in.

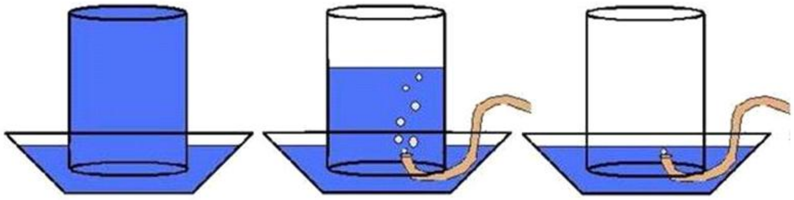

Figure 16: Gas Collection Over Water.

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In Figure 16, the picture on the far left represents the collecting jar full of water and inverted in a pan of water. A tube runs from the reaction vessel where the gas is produced and is tucked under the edge of the collecting jar. As the gas is produced and comes out the end of the tube, it bubbles up through the water and pushes the water out of the jar. When the water in the collecting jar and the pan are exactly level, as in the picture at the far right, the pressure inside the collecting jar and the atmospheric pressure in the lab are equal. Using the pressure in the lab and the temperature in the lab and the volume of the jar to the water level, you can calculate how much gas you produced. (Plug P, V, T, and R into PV = nRT, and solve for n.) It turns out, however, that you must make a correction before you plug in the pressure value. Since the collecting jar is a closed container and it has liquid water in the bottom of it, then it will contain the vapor pressure of water at this temperature. So the outside pressure in the lab tells you the pressure inside the collecting jar but it doesn't tell you how much of that pressure is due to the gas collected and how much is due to water vapor. You must get a table of the vapor pressure of water at each temperature and look up the vapor pressure of water at the temperature of your lab and then subtract that pressure from the total pressure in the collecting jar. The result will be the actual pressure of the gas collected.

Example

Some hydrogen gas was collected over water in the lab on a day that the atmospheric pressure was 755 torr and the lab temperature was $20^{\circ}C$. Hydrogen gas was collected in the collecting jar until the water levels inside and outside the jar was equal. What was the partial pressure of the hydrogen in the collecting jar?

Solution

The total pressure in the collecting jar is 755 torr and is equal to the sum of the partial pressure of hydrogen in the jar and the vapor pressure of water at $20^{\circ}C$. From the table, the vapor pressure of water at $20^{\circ}C$ is 17.5 torr.

Partial pressure of H_2 = 755 torr – 17.5 torr = 737 torr

Lesson Summary

- Molecules of liquid may evaporate from the surface of a liquid.
- When molecules of a liquid evaporate, the remaining liquid cools.
- Gas molecules in contact with their liquid may condense to liquid form.

- If a liquid is placed in a closed container, eventually vapor pressure equilibrium will be reached.

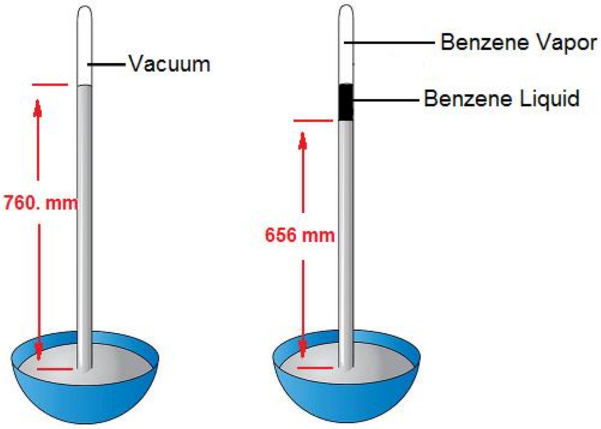
Review Questions

1. A flask half-filled with water is sealed with a stopper. The space above the water contains hydrogen gas and water vapor in vapor pressure equilibrium with the liquid water. The total pressure of the two gases is 780. mm of Hg at 20.°C. The vapor pressure of water at 20.°C is 19 mm of Hg. What is the partial pressure of the hydrogen gas in the flask? **(Intermediate)**

2. Describe all the reasons that the remaining liquid cools as evaporation occurs. **(Challenging)**

3. Describe all the reasons that the remaining gas gets hotter as condensation occurs. **(Challenging)**

4.



The apparatus above can be used to determine the vapor pressure of benzene. With a vacuum in the top of the tube, the mercury rises to the height shown. When a small amount of liquid benzene is injected into the space at the top of the tube, it floats on the mercury. The benzene will evaporate and eventually reach vapor pressure equilibrium. The mercury in the tube will pushed down further by the pressure of the benzene vapor in the tube. Neglecting the effect of the liquid benzene, what would be the calculated vapor pressure of benzene? **(Intermediate)**

5. Water vapor and hydrogen gas are sealed in a cylinder fitted with a piston at 60°C. The partial pressure of the hydrogen gas is 0.35 atm and the vapor pressure of the water is 0.20 atm at this temperature. The total pressure in the cylinder is 0.55 atm. If the piston is pushed down until the volume is half the original volume, what will be the pressure in the cylinder? **(Challenging)**

Vocabulary

condensation	The process whereby a gas or vapor is changed to a liquid.
equilibrium vapor pressure	The pressure that is exerted, at a given temperature, by the vapor of a solid or liquid in equilibrium with the vapor.
evaporation	The escape of molecules from a liquid into the gaseous state at a temperature below the boiling point.
heat of condensation	The quantity of heat released when a unit mass of a vapor condenses to liquid at constant temperature.
heat of vaporization	The quantity of heat required to vaporize a unit mass of liquid at constant temperature.

vapor	The gaseous phase of a substance that exists even though the temperature is below the boiling point of the substance.

Review Answers

1. (Total pressure) – (vapor pressure of water) = partial pressure of hydrogen 780. mm of Hg – 19 mm of Hg = 761 mm of Hg

2. Since the hotter molecules are evaporating, the average temperature of the ones left behind will be lower. Also, the molecules leaving the liquid and becoming gas absorb the necessary heat of vaporization from the other molecules in the liquid.

3. The molecules that are condensing are the cooler ones so the average temperature of the remaining gas will increase. Furthermore, the condensing molecules give up the heat of condensation to the surroundings which include the remaining gas.

4. The atmospheric pressure is 760. mm of Hg as demonstrated by the barometer on the left. The total pressure (mercury + benzene vapor pressure) in the tube on the right must therefore be equal to 760. mm of Hg. Since the mercury column in the tube on the right is 656 mm of Hg, the vapor pressure of benzene must be 104 mm of Hg.

5. The hydrogen gas is well above its boiling point and therefore, it will behave as a gas and follow the gas laws. Its new pressure will be double its original pressure or 0.70 atm. The water, however, it below its boiling point and will follow the rules of vapor pressure. As long as the temperature remains the same, the vapor pressure will remain the same. Therefore, when the piston is pushed down and the pressure of the water vapor increases, some of the water vapor will condense to liquid and only enough water vapor will remain to produce a vapor pressure of the same 0.20 atm. The total pressure in the cylinder will be 0.90 atm.

Boiling Point

Lesson Objectives

- The student will know the relationship between boiling point, vapor pressure, and ambient pressure.
- Given a vapor pressure table for water, and the ambient pressure, the student will be able to determine the boiling point of water for those conditions.

Introduction

If you want hard-boiled eggs at home, you can probably put the eggs in boiling water for about eight minutes to accomplish it. If you go camping in the Rocky Mountains at an altitude of 10,000 feet, you will find that an egg placed in boiling water for eight minutes is not hard boiled. In fact, even after twelve minutes in boiling water, the egg may still be a little too runny for your tastes.

Normal Boiling Point

Imagine you are boiling water in a place where the atmospheric pressure is 1.00 atm. In the boiling water, a large bubble forms near the surface of the liquid water and remaining at the same size rises to the top of the water and the gas escapes into the air. If the pressure of the gas inside that bubble had been less than 1.00 atm, the outside pressure of the atmosphere would have crushed the bubble and it would not have existed. If the pressure of the gas inside that bubble had been greater than 1.00 atm, the bubble would have expanded to a larger size instead of remaining at the same size. The fact that the bubble remained at the same size indicates that the gas pressure inside that bubble was the same as the atmospheric pressure.

When you are heating water in an effort to boil it, gas bubbles cannot form until the water can produce a vapor pressure equal to the surrounding air pressure. The hotter the water gets, the higher its vapor pressure becomes but only when that vapor pressure equals the surrounding atmospheric pressure can the water form bubbles in the process we call boiling. A liquid cannot boil until its vapor pressure is equal to the pressure on the surface of the liquid. The actual definition of boiling point is ***that temperature at which the vapor pressure of the liquid equals the surrounding pressure.***

If you are measuring boiling points at the normal sea level atmospheric pressure of 1.00 atm, a liquid more volatile than water such as chloroform will boil at 61.3°C. This is because the vapor pressure of chloroform is 1.00 atm at 61.3°C. The vapor pressure of ethanol reaches 1.00 atm at a temperature of 78.4°C and therefore, that is the normal boiling point of ethanol.

Boiling Points Change with Changes in Pressure

Since liquids boil when their vapor pressure becomes equal to surrounding pressure, then if the surrounding pressure is lower, liquids will boil at lower temperatures. At higher altitudes, atmospheric pressure is lower. In cities whose altitude is around 5,000 feet, water boils at 95°C instead of at 100°C and at 10,000 feet, water boils around 90°C. The water boils in normal fashion but its temperature is lower and therefore, cooking in boiling water takes a longer time. In situations where boiling is used to purify water or sterilize equipment, the lower temperature of boiling water requires concern.

If a container of water is placed in a bell jar and a vacuum pump attached so that the air pressure around the water can be greatly reduced, water may be made to boil at very low temperatures.

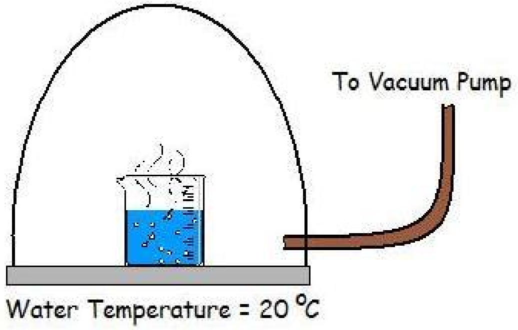


Figure 17: A beaker of water under a bell jar with lowered pressure.

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At room temperature, 20°C, the vapor pressure of water is 17.5 mm of Hg so if the pressure in the bell jar is reduced to 17.5 mm of Hg, water will boil at 20°C. The appearance of the boiling water is the same as it is at 100°C, with steam coming off and so on, but the water can be removed from the bell jar and poured on your hand and the temperature is only 20°C. When you look up the boiling point of a liquid, the reference will be to the **normal boiling point** which means the boiling point when the surrounding pressure is 1.00 atm.

If the surrounding pressure is less than 1.00 atm, the boiling points of liquids will be lower. Conversely, if the surrounding pressure is greater than 1.00 atm, the boiling points of liquids will be higher. It's fairly unusual to find atmospheric pressures greater than 1.00 atm except during storms, but it's easy enough to raise the surrounding pressure in a laboratory situation. If we use a strong container with a lid that screws on very tight, we can boil water in the container and as water vaporizes and the temperature of both the air and the water vapor increase, the gas pressure in the container will increase. As the pressure in the container increases, the boiling point of the water increases. The vapor pressure of liquid water at 120°C is 2.0 atm. Therefore, if we can raise the pressure inside a sealed container to 2.0 atm, water will not boil in the container until its temperature is 120°C. This is the concept that is used in pressure cookers and rice cookers. The cooking pot has a lid that can be sealed tightly and a valve in the lid that will open slightly when the pressure inside the container reaches 2.0 atm. Water and whatever food you wish to cook is placed inside the pressure cooker and it is set on the stove. The pressure and therefore the boiling point of water increases inside the container until the pressure reaches 2.0 atm. If the pressure goes beyond 2.0 atm, the little valve opens and lets out some gas so that the pressure remains at 2.0 atm. The valve can be opened and closed any number of times to keep the inside pressure at 2.0 atm. The temperature of the boiling water inside will be 120°C under these conditions and the food will cook in as little as one-third the normal time.

Lesson Summary

- The boiling point of a liquid is the temperature at which the vapor pressure of the liquid becomes equal to the surrounding pressure.
- The **normal** boiling of a liquid is the temperature at which the vapor pressure of the liquid becomes equal to 1.00 atmosphere.

Review Questions

1. What happens to the boiling point of a liquid if the pressure exerted on the surface of the liquid is increased? **(Beginning)**

2. How can you make water boil without heating it? **(Intermediate)**

Vocabulary

boiling point	The temperature at which the vapor pressure of a liquid equals the surrounding pressure.
normal boiling point	The temperature at which the vapor pressure of a liquid equals 1.00 atmosphere.

Review Answers

1. The boiling point will increase because the vapor pressure of the water must be higher (to equal surrounding pressure) for the water to boil.

2. Water will boil when its vapor pressure equals the surrounding pressure so you can boil it by lowering pressure instead of raising temperature.

Heat of Vaporization

Lesson Objectives

- The student will be able to calculate energy changes during phase changes.
- The student will be able to explain the slopes of various parts of heating and cooling curves.

Introduction

In order to vaporize a liquid, heat must be added to raise the kinetic energy (temperature) to the phase change temperature and then more heat must be added to provide the necessary potential energy to separate the molecules in the liquid form to the gaseous form.

The Potential Energy Stored in Gases

The difference between the liquid phase and the gas phase of a substance is essentially the distance between the molecules. Since the molecules attract each other and they are separated by a greater distance in the gaseous phase than in the liquid phase, the molecules in gaseous phase possess more potential energy than in the liquid phase. When a substance changes from the liquid phase to the gaseous phase, work (the physics kind of work as in force times distance) must be done on the molecules to pull them away from each other. The work done separating the molecules is stored in the molecular structure as potential energy. If the molecules are allowed to go back together as in the liquid phase, the potential energy is released – exactly the same amount that was needed to separate the molecules. This potential energy stored in molecules in the gaseous phase is called the **heat of vaporization**. The heat of vaporization (ΔH_{VAP}) for water is 540 calories/gram (2.26 kJ/g) at the normal boiling point. Because of the strength of the polar attractions holding water molecules together in the liquid form, water has a fairly high heat of vaporization. Ammonia, NH_3, and ethanol, C_2H_5OH, which are also polar molecules have heats of vaporization of 1.38 kJ/g and 0.84 kJ/g respectively.

Example

How much heat in kJ is necessary to vaporize 100. grams of ammonia at its boiling point?

Solution

Heat, $Q = (\text{mass})(\Delta H_{VAP}) = (100.\text{ g})(1.38\text{ kJ/g}) = 138\text{ kJ}$

The boiling point of ammonia is $-33^\circ C$. It is very important to understand that the ammonia is at the boiling point before the heat of vaporization is added and after the heat of vaporization is added, the ammonia is STILL at the boiling point. All the energy involved in the heat of vaporization is absorbed by the substance as potential energy – none of it goes into kinetic energy and therefore, the temperature cannot change. A common question asked of students to determine if they understand this point is to ask which would produce a more severe burn, spilling boiling water at $100^\circ C$ on your skin or being burned by gaseous water at $100^\circ C$? It may seem at first that since they are both at the same temperature, they would do the same damage, but in fact, the gaseous water would first deliver a tremendous amount of heat to your skin as the gas condensed to water (giving up the heat of vaporization) and after you had a burn from that, then you would have $100^\circ C$ boiling water on the skin that was already burned.

Heating and Cooling Curves

The addition of heat before, during, and after a phase transition can be analyzed with the help of a heating curve. In the heating curve below, a sample of water at $20^\circ C$ and 1.00 atm pressure had equal quantities of heat added to it per unit time.

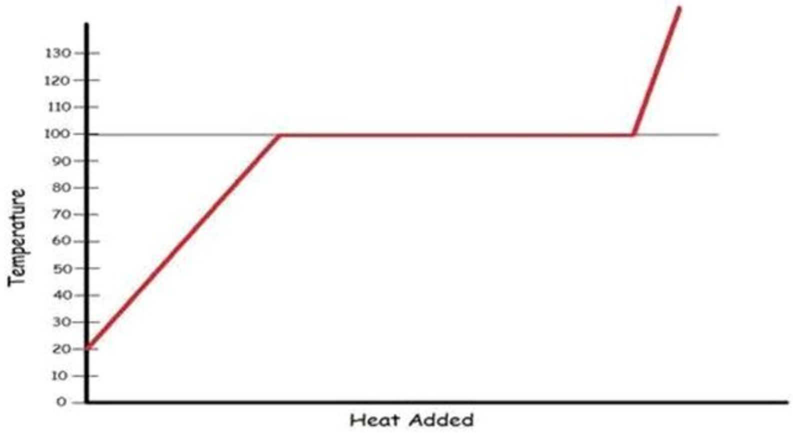


Figure 18: The heating curve for water at normal pressure.

(*Created by:* Richard Parsons, *License:* CC-BY-SA)

Between the temperatures of 20°C and 100°C, all the heat added was absorbed as kinetic energy and therefore the temperature increased. Once the water reached the boiling point, even though the same amount of heat was added per unit time, the temperature did not increase. Thus, this energy added to the water DID NOT become kinetic energy. All the heat added to the sample during the time the slope of the line is zero went into potential energy. This energy represents the heat of vaporization and was used to do the work of separating the liquid molecules into the gaseous form (greater distance between molecules). During this flat line period, an observer would see that the water was changing into gas but all of it, both the part in liquid form and the part in gaseous form, would be at exactly 100°C. The temperature cannot increase until all the liquid has been converted to gas. At 1.00 atm pressure, it is impossible to get water hotter than 100°C. No matter how much heat you add to it, all that happens is that the water boils faster and converts to gas faster but its temperature will never exceed 100°C. It is sort of like the water decides where the heat goes, and the water decides that ALL the heat added will be used to change phase and none of it will be used to raise temperature. Once all the water is in the gaseous form, the heat once again becomes kinetic energy and the temperature of the gas rises. When the gas is cooled, it follows this same curve in reverse. As it is cooled, the same flat line appears while the heat of vaporization (heat of condensation now) is removed, and then the temperature may go down again.

Specific Heat

Thermodynamic data (melting point, boiling point, heat of melting, heat of vaporization) for almost all elements and thousands of compounds are determined by laboratory activity and placed in reference books. Much of this thermodynamic data is also available now on the internet. Another piece of useful thermodynamic data about substances is called **specific heat.** The specific heat for a substance is the amount of heat required to raise 1.00 gram of the substance by 1.00°C. The symbol C is used for specific heat and the value for liquid water is 4.18 J/g°C.

Example

How much heat is required to raise the temperature of 25 grams of water from 15°C to 55°C?

Solution

$Q = (\text{mass})(\ C\ )(\Delta t) = (25\text{ g})(4.18\text{ J/g.}^\circ\text{C})(40.^\circ\text{C}) = 4180\text{ J} = 4.18\text{ kJ}$

Example

How much heat is required to raise 25 g of water from 25°C to gaseous water at 100°C?

Solution

In this problem, you have to calculate the heat to raise the temperature from 25°C to 100°C and then calculate the heat of vaporization for the 25 g of water.

Heat$_{\text{raising temp}}$ = (mass)(specific heat)(Δt) = (25 g)(4.18 J/g.°C)(75°C) = 7840 J = 7.48 kJ

Heat$_{\text{vaporizing}}$ = (mass)(heat of vaporization) = (25 g)(2.26 kJ/g) = 57 kJ

Total heat = 7.48 kJ + 57 kJ = 64 kJ

Lesson Summary

- The heat of vaporization of a liquid is the quantity of heat required to vaporize a unit mass of that liquid at constant temperature.
- The energy released when a gas condenses to a liquid is called the heat of condensation.
- The specific heat of a substance is the amount of heat required to raise the temperature of one gram of the substance by 1.0°C.

Review Questions

1. How much heat is required to vaporize 200. grams of water at 100.°C and 1.00 atm pressure? ΔH_{VAP} for water is 2.25 kJ/g. **(Beginning)**

2. How much heat is required to raise 80.0 grams of water from 0°C to 100.°C with no phase change occurring? The specific heat of water is 4.18 J/g.°C. **(Beginning)**

Further Reading / Supplemental Links

Chemistry, Matter and Its Changes, Fourth Edition, Chapter 12: Intermolecular Attractions and the Properties of Liquids and Solids, James E. Brady and Fred Senese, John Wiley & Sons, Inc. 2004.

http://www.sparknotes.com/testprep/books/sat2/chemistry/chapter5section5.rhtml

http://www.kentchemistry.com/links/matter/heatingcurve.htm

Vocabulary

heat of condensation	The quantity of heat released when a unit mass of a vapor condenses to liquid at constant temperature.
heat of vaporization	The quantity of heat required to vaporize a unit mass of liquid at constant temperature.

Review Answers

1. Q = (mass)(ΔH_{VAP}) = (200. g)(2.25 kJ/g) = 451 kJ

2. Q = mCΔT = (80. g)(4.18 J/g.°C)(100.°C) =33,400 J = 33.4 kJ

20. The Solid State

The Molecular Arrangement in Solids Controls Solid Characteristics

Lesson Objectives

- The student will describe the molecular arrangement of solids.
- The student will use the molecular arrangement in solids to explain the incompressibility of solids.
- The student will use the molecular arrangement in solids to explain the low rate of diffusion in solids.
- The student will use the molecular arrangement in solids to explain the ability of solids to maintain their shape and volume.

Introduction

There are many ways to classify solids but the broadest categories are **crystalline solids,** those with a highly regular arrangement of their particles, and **amorphous solids**, those with considerable disorder in their structures. The regular arrangement of the particles in a crystalline solid produces the beautiful, characteristic shapes of crystals. These structures are represented by a crystal lattice, a three-dimensional system of points designating the positions of the component particles (atoms, ions, or molecules). There are also many important amorphous solids. An example is glass, which is best represented as a solid where the components were frozen in place before they could get into the organized structure of a crystal. Because of the disorder in glass, some chemists have referred to glass as a super-cooled liquid.

The Molecular Arrangement in Solids

The molecular arrangement in a solid is one where the molecules (or atoms, or ions) are held in a tightly packed, highly organized pattern, as in Figure 1.

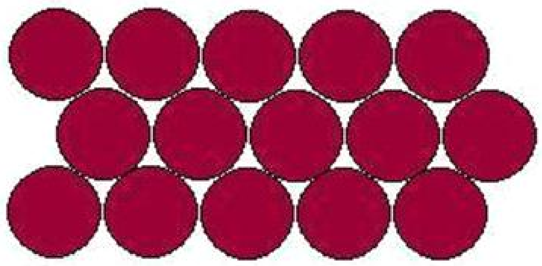


Figure 1: The molecular arrangement in a solid.

(*Created by:* Richard Parsons, *License:* CC-BY-SA)

In a solid, the intermolecular forces of attraction have completely overcome molecular motion and the movement of the particles has been reduced to vibration in place. There are only tiny spaces between the molecules, not nearly enough space for the particles to move past one another.

The Characteristics of Solids

The intermolecular forces of attraction in solids hold the particles so tightly in place that they cannot pull away from each other to expand their volume nor can they flow past one another to change shape. Therefore, solids hold their own shape and volume regardless of their container. There is very little empty space in the solid structure so solids are virtually incompressible and since molecules can't pass each other in the structure, diffusion is essentially non-existent beyond the surface layer.

Lesson Summary

- Molecules in a solid maintain both their own shape and their own volume.
- Solids are virtually incompressible and have little diffusion beyond the surface layer.
- The molecular arrangement in solids is a highly organized, tightly-packed pattern with small spaces and molecular motion reduced to vibration in place.

Review Questions

1. Fill in the types of phase changes left blank in the chart below. **(Beginning)**

Solid → Liquid ____________________

Liquid → Gas ______________________

Solid → Gas _____Sublimation_____

Liquid → Solid ____________________

Gas → Liquid ______________________

Gas → Solid _____Deposition_____

Review Answers

1. Fill in the types of phase changes left blank in the chart below.

Solid → Liquid ____Melting___

Liquid → Gas _____Boiling or Vaporization___

Solid → Gas _____Sublimation_____

Liquid → Solid ____Freezing or Fusion___

Gas → Liquid _____Condensing___

Gas → Solid _____Deposition___

Melting

Lesson Objectives

- The student will explain why it is necessary for a solid to absorb heat during melting even though no temperature change is occurring.
- Given appropriate thermodynamic data, the student will calculate the heat required to raise temperatures of a given substance with no phase change.
- Given appropriate thermodynamic data, the student will calculate the heat required to melt specific samples of solids with no temperature change.

- Given appropriate thermodynamic data, the student will calculate the heat required to produce both a phase change and temperature change for a given sample of solid.

Introduction

The melting point of a substance, like its boiling point, is directly related to the strength of the forces of attraction between molecules. Low melting points are typical of substances whose forces of attraction are very weak, such as hydrogen gas whose melting point is -259°C. High melting points are associated with substances whose forces of attraction are very strong, such as elemental carbon whose melting point is greater than 3500°C.

Melting Points

Solids, like liquids, have vapor pressure. The vapor pressure of a solid is generally very low because the forces of attraction in solids dominate molecular motion. The vapor pressure of solids, also like liquids, increases with temperature. The vapor pressure of liquid water is 760 mm of Hg at 100°C and decreases as the temperature decreases (non-linearly) to 4.6 mm of Hg at 0°C. Solid water (ice) has very low vapor pressures because of both strong forces holding the molecules together and the fact that our interaction with ice is usually at low temperatures. For example, at -83°C, the vapor pressure of ice is 0.00025 mm of Hg. As ice is heated, its vapor pressure increases. At 0°C, the vapor pressure of ice is 4.6 mm of Hg which also happens to be the vapor pressure of water at 0°C. In fact, for all substances, their solids and liquids have the same vapor pressure at the melting point. The melting point of a solid is defined as the temperature at which the vapor pressure of the solid and liquid are the same.

Heat of Fusion

The phase change from solid to liquid, melting, has many similarities to vaporization. The solid must reach its melting point before the molecules can enter the liquid phase. The molecules in liquid phase, however, are farther apart than the molecules in the solid phase. Since the molecules attract each other, increasing the distance between them (from solid structure to liquid structure) requires work. Force must be exerted to pull the molecules away from each other. The work done in separating the molecules is stored in the molecules as potential energy in the liquid phase. This is the same process that occurs when the heat of vaporization must be added to liquid molecules to get them into the gaseous phase. In the case of melting, this potential energy is called the **heat of fusion** or the heat of melting.

The word ‘fusion’ is used several times in science with different meanings. You need to note the context of the use of the word to know which meaning is intended. In this case, fusion is the name of the liquid to solid phase change. When a solid melts, the heat of fusion must be added and when a liquid freezes (fuses) back to solid, the heat of fusion is given off. The heat of fusion for water is 334 Joules/gram.

Example 1

How much heat must be added to 25 grams of ice at 0°C to convert it to liquid water at 0°C?

Solution

$Q = (\text{mass})(\Delta H_{\text{FUSION}}) = (25\text{ g})(334\text{ J/g}) = 8350\text{ J} = 8.4\text{ kJ}$

Heating Curves

Phase changes are often analyzed with the help of a heating curve. The heating curve for water at 1.00 atm pressure appears in Figure 2. Many substances will have heating curves similar to the one for water. The differences will be in the length of flat lines and the slopes of the inclined lines.

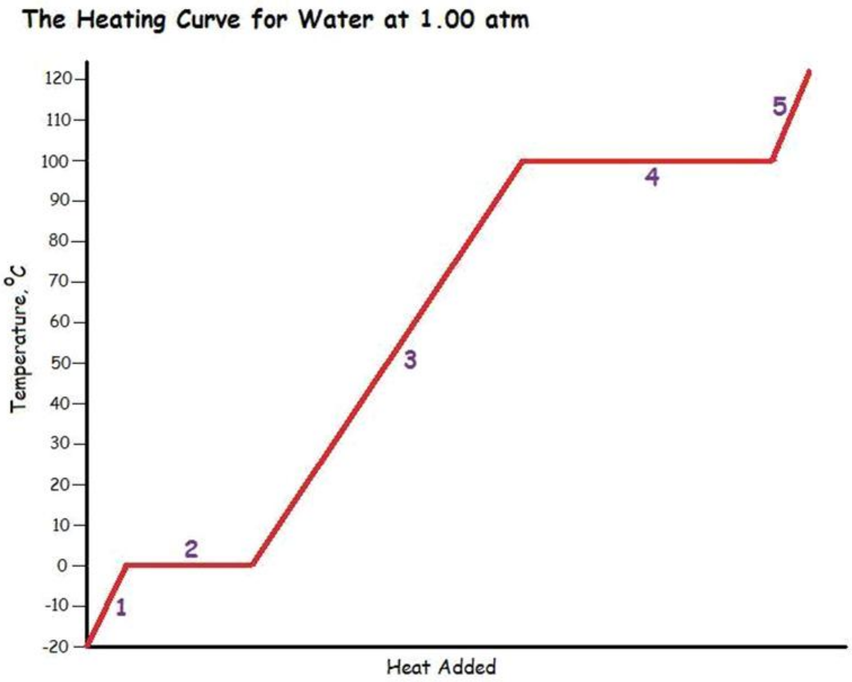


Figure 2: The heating curve for water.

(*Created by:* Richard Parsons, *License:* CC-BY-SA)

The section of the curve labeled "1" represents the time the sample is completely in the form of ice and is being heated. All the heat added is going into kinetic energy and so the temperature of the ice is increasing. The slope of the line is related to the specific heat of ice – the amount of heat required to raise 1.00 gram of ice by 1.00°C. When the sample reaches 0°C, that is, the melting point, all the heat added starts going into potential energy. During the section of the graph labeled "2," the sample is being converted from solid to liquid. Both solid and liquid are present at this time, but all of the sample, both solid and liquid are at 0°C. No heat will go into kinetic energy until the entire sample is converted to liquid. Therefore, the temperature remains constant during this period. The total amount of heat added during section "2" would represent the heat of melting for this sample. Once the entire sample has been converted to liquid, the added heat would once again go into kinetic energy and the temperature would increase. The slope of the line in section "3" is related to the specific heat of liquid water. The temperature continues to rise as heat is added until the boiling point is reached. The temperature again remains constant through section "4" and the added heat becomes potential energy providing the heat of vaporization. During section "4," both liquid water and gaseous water are present. Once the entire sample has been converted to gas, the added heat again becomes kinetic energy and the temperature of the gas increases. Gaseous water also has its own specific heat.

Example 2

A 2,000. gram mass of water in a calorimeter has its temperature raised by 3.00°C while an exothermic chemical reaction is occurring. How much heat, in joules, is transferred to the water by the heat of reaction?

Solution

The heat is calculated by determining the heat absorbed by the water. This amount of heat is the product of three factors, 1) the mass of the water, 2) the specific heat of water, and 3) the change in temperature of the water.

heat = (mass of water)(C_{water})(Δt) heat = (2000. g)(4.18 J/g-°C)(3.00 °C) = 25,080 joules = 25,100 joules

Example 3

A 1,000. gram mass of water whose temperature was 50.°C lost 33,440 joules of heat over a 5-minute period. What was the temperature of the water after the heat loss?

Solution

heat = (mass)(C_w)(Δt)

$$\Delta t = \frac{\text{heat}}{\text{mass x } C_w} = \frac{-33{,}400 \text{ joules}}{(1000.\text{ g})(4.18 \text{ J/g}\cdot{}^{\circ}\text{C})} = -8.00^{\circ}\text{C}$$

If the original temperature was 50.°C and the temperature decreased by 8°C, then the final temperature would be 42°C.

Example 4

Use the thermodynamic data given to calculate the total amount of energy necessary to raise 25 grams of ice at -20°C to gaseous water at 120°C.

Melting point of ice = 0°C	Boiling point of water = 100°C
ΔH_{VAP} for water = 2260 J/g	ΔH_{FUSION} for water = 334 J/g

C_{ice} = 2.11 J/g.°C

C_{water} = 4.18 J/g.°C

$C_{water\ vapor}$ = 1.84 J/g.°C

Solution

There will be five steps in the solution process.

1) We must calculate the heat required to raise the temperature of the ice from -20°C to 0°C.

2) We must calculate the heat required to provide the heat of melting – to change ice at 0°C to water at 0°C.

3) We must calculate the heat required to raise the temperature of the liquid water from 0°C to 100°C.

4) We must calculate the heat required to provide the heat of vaporization – to change liquid water at 100°C to gaseous water at 100°C.

5) Finally, we must calculate the heat required to raise the temperature of the gaseous water from 100°C to 120°C.

Raising the temperature of ice, Q = mCΔt = (25 g)(2.11 J/g.°C)(20°C) = 1051 J

Melting ice to liquid, Q = (mass)(ΔH_{FUSION}) = (25 g)(334 J/g) = 8350 J

Raising the temperature of liquid, Q = mCΔt = (25 g)(4.18 J/g.°C)(100°C) = 10450 J

Vaporizing liquid to gas, Q = (mass)(ΔH_{VAP}) = (25 g)(2260 J/g) = 56500 J

Raising the temperature of gas, Q = mCΔt = (25 g)(1.84 J/g.°C)(20°C) = 920 J

The sum of all five steps is 77,000 J = 77 kJ

The cooling process would be exact reverse of the heating curve. If water in the gaseous phase is cooled, each 1.84 Joules of heat removed would lower the temperature of 1.00 g of gas by 1.00°C. When the gaseous water reaches the boiling point (also the condensation point), each gram of gaseous water that condenses to liquid will release 2260 Joules of heat. Once all the water is in the liquid form, the removal of each 4.18 Joules of heat by cooling will cause the temperature of 1.00 g of water to cool by 1.00°C. At the freezing point (also the melting point) 334 Joules of heat must be removed to convert each gram of liquid water to ice. When the entire sample of water is in the form of ice, 2.26 Joules of heat must be removed to cool each gram by 1.00°C. For all phase changes, going up in temperature or down in temperature, the entire sample will change phase before any temperature change will occur.

Since both melting points and heats of fusion are dependent on the strength of the attractive forces between molecules, a solid with a low melting point will usually also have a low heat of fusion and a solid with a high melting point will have a high heat of fusion.

Lesson Summary

- Solids melt when the vapor pressure of the solid equals the vapor pressure of the liquid.
- Heat must be absorbed by a solid to become a liquid even though the temperature remains the same. The quantity of heat absorbed per unit mass is called the heat of fusion.
- Stronger forces of attraction between particles in solids produce higher melting points and higher heats of fusion.
- During a phase change, all the added energy goes into the heat of fusion (potential energy) and none goes to kinetic energy (raising temperature).

Review Questions

Use the thermodynamic data given here to answer problems 1 - 5.

Thermodynamic Data of Various Substances

	Water	**Cesium, Cs**	**Silver, Ag**
Melting Point	0°C	29°C	962°C
Boiling Point	100.°C	690.°C	2162°C
ΔH_{fusion}	334 J/g	16.3 J/g	105 J/g
$\Delta H_{vaporization}$	2260 J/g	669 J/g	2362 J/g
Specific Heat, C, for Gas	2.01 J/g · °C	0.167 J/g · °C	0.159 J/g · °C
Specific Heat, C, for Liquid	4.18 J/g · °C	0.209 J/g · °C	0.294 J/g · °C
Specific Heat, C, for Solid	2.09 J/g · °C	0.251 J/g · °C	0.235 J/g · °C

1. How many Joules are required to melt 100. grams of silver at its normal melting point with no temperature change? **(Intermediate)**

2. How many Joules are required to boil 150. grams of cesium at its normal boiling point with no temperature change? **(Intermediate)**

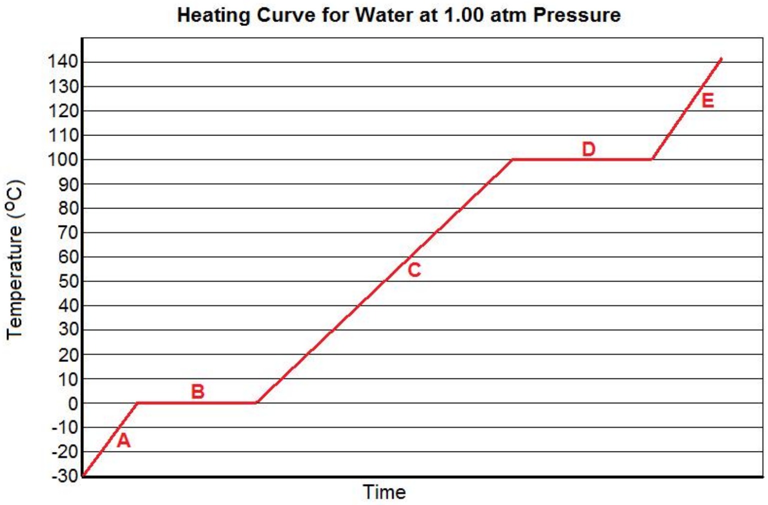
3. How many Joules are required to heat 200. g of liquid water from 25°C to steam at 125°C under normal pressure? **(Intermediate)**

4. How many Joules are required raise the temperature of 1.00 gram of water from -269°C (the current temperature of space) to 1.60 x 10^{15} °C (the estimated temperature of space immediately after the big bang)? **(Challenging)**

5. How many Joules are required to raise the temperature of 1000. g of cesium from -200.°C to +200.°C? **(Challenging)**

6. Why does the boiling point of water increase with increasing surrounding pressure? **(Beginning)**

7. Why must heat be absorbed to melt a solid even though both the solid and the liquid are at the same temperature? **(Intermediate)**



8. What is happening to the water in section B? **(Beginning)**

9. What is happening to the water in section A? **(Beginning)**

10. Why are the slopes of the lines in sections A, C, and E different? **(Challenging)**

Vocabulary

crystal	A solid consisting of plane faces and having definite shape with the atoms arranged in a repeating pattern.
freezing	The phase change from liquid to solid.
freezing point	The temperature at which a liquid changes to a solid.
fusion	1) The change of a liquid to a solid. 2) A nuclear reaction in which two or more smaller nuclei combine to form a single nucleus.
heat of condensation	The quantity of heat released when a unit mass of vapor condenses to a liquid at constant temperature.
heat of fusion	The quantity of heat released when a unit mass of liquid freezes to a solid at a constant temperature.

heat of vaporization	The quantity of heat absorbed when a unit mass of liquid vaporizes to a gas at constant temperature.
joule	A basic unit of energy in the SI system, equal to one Newton-meter.
melting	The phase change from solid to liquid.
melting point	The temperature at which a substance changes from the solid phase to the liquid phase.

Review Answers

1. How many Joules are required to melt 100. grams of silver at its normal melting point with no temperature change?

$Q = m \Delta H_{fus} = (100.\ g)(105\ J/g) = 10{,}500\ J = 10.5\ kJ$

2. How many Joules are required to boil 150. grams of cesium at its normal boiling point with no temperature change?

$Q = m \Delta H_{vap} = (150.\ g)(669\ J/g) = 100{,}350\ J = 100.\ kJ$

3. How many Joules are required to heat 200. g of liquid water from 25°C to steam at 125°C under normal pressure?

Heat the liquid water = $mC \Delta t = (200.\ g)(4.18\ J/g \cdot {}^{o}C)(75^{o}C) = 62{,}700\ J$

Boil to gas = $m \Delta H_{vap} = (200.\ g)(2260\ J/g) = 452{,}000\ J$

Heat the gas = $mC \Delta t = (200.\ g)(2.01\ J/g \cdot {}^{o}C)(25^{o}C) = 10{,}050\ J$

Total = 62,700 J + 452,000 J + 10,050 J = 524,750 J = 525 kJ

4. How many Joules are required raise the temperature of 1.00 gram of water from -269°C to 1.60×10^{15} °C?

Heat the solid = $mC \Delta t = (1.00\ g)(2.09\ J/g \cdot {}^{o}C)(269^{o}C) = 562\ J$

Melt the solid = $m \Delta H_{fus} = (1.00\ g)(334\ J/g) = 334\ J$

Heat the liquid = $mC \Delta t = (1.00\ g)(4.18\ J/g \cdot {}^{o}C)(100^{o}C) = 418\ J$

Boil to gas = $m \Delta H_{vap} = (1.00\ g)(2260\ J/g) = 2260\ J$

Heat the gas = $mC \Delta t = (1.00\ g)(2.01\ J/g \cdot {}^{o}C)(1.60 \times 10^{15}\ {}^{o}C) = 3.22 \times 10^{15}\ J$

The other numbers are not significant compared to the last one so the answer is 3.22×10^{15} J.

5. How many Joules are required to raise the temperature of 1000. g of cesium from -200.°C to +200.°C?

Heat the solid = $mC \Delta t = (1000.\ g)(0.251\ J/g \cdot {}^{o}C)(229^{o}C) = 57{,}479\ J$

Melt the solid = $m \Delta H_{fus} = (1000.\ g)(16.3\ J/g) = 16{,}300\ J$

Heat the liquid = $mC\Delta t = (1000.\ g)(0.209\ J/g \cdot {}^{\circ}C)(171^{\circ}C) = 35{,}739\ J$

Total = 57,479 J + 16,300 J + 35,739 J = 109,518 J = 110 kJ

6. Liquids boil when their vapor pressure equals the surrounding pressure. If the surrounding pressure is higher, a higher temperature will be necessary for the liquids vapor pressure to equal the higher surrounding pressure.

7. The molecules in a liquid are farther apart than those in a solid and therefore possess more potential energy. Work must be done to separate the molecules from solid form to liquid form and the work is stored in the liquid molecules as potential energy.

8. Solid water is melting to liquid water.

9. The temperature of solid water is being increased.

10. The slopes of the lines in A, C, and E are the specific heats of the solid, liquid, and gas, respectively. Since the specific heats of the three phases are not the same, the slopes will not be the same.

Types of Forces of Attraction for Solids.

Lesson Objectives

- The student describe the metallic bond and explain some of the solid characteristics that are due to metallic bonding.
- Given the characteristics of a solid such as conductivity of solid and liquid phase, solubility in water, malleability, and so on, the student will be able to identify the type of solid, i.e. the attractive forces holding the solid in the solid form.

Introduction

The range of melting points for the various types of solids is extremely wide. Substances with very weak London dispersion forces like helium, will melt at only a couple of degrees above absolute zero whereas solid substances like asbestos and diamond do not melt until the temperature is in excess of 3500°C.

Solids Held Together by Intermolecular Forces of Attraction

Each of the intermolecular forces of attraction discussed in the chapter on liquids (London dispersion forces, polar attractions, and hydrogen bonds) will also produce solids if the temperatures are low enough. Those intermolecular forces of attraction have the same causes in solids as they do in liquids but because of the lower temperatures and the closeness of the molecules in solids, the forces will be more effective in pulling the molecules together. The solids formed due to these intermolecular forces of attraction will be crystalline solids.

Solids held together by London dispersion forces are not soluble in water, nor are they good conductors of electricity or malleable. In terms of solubility, the general rule is “like dissolves like.” This means that polar solvents dissolve polar or ionic substances but not non-polar and non-polar solvents dissolve non-polar solutes but not polar. Since water is a strongly polar molecule, it will dissolve most polar solids. Polar solids are not good conductors and are not malleable.

Ionic Solids

Ionics solids are held together by the electrostatic attraction between oppositely charged ions. The ions are formed into various types of crystal lattice structures depending on the comparative sizes of the ions and the charges on each. These ionic charges are full 1+, 2+, 1-, 2-, and so on, charges and so they are considerably stronger than either polar attractions or the especially strong hydrogen bonds. This will cause the melting points for ionic substances to be quite high compared to the substances we have been considering. For example, the melting point of sodium chloride, NaCl, is 801°C and the melting point of calcium sulfate, $CaSO_4$, is 1460°C.

In solid state, the ions in ionic solids are held firmly in position and there are no spaces large enough for the ions to move through even if they could escape the forces of attraction. Since the ions cannot move, ionic solids are non-conductors of electricity. When the solid is melted to a liquid, however, the ions are free to migrate and therefore, ionic liquids are good conductors of electric current.

In ionic crystals, the positive and negative ions occupy positions so the ions will attract the maximum possible number of oppositely charged ions.

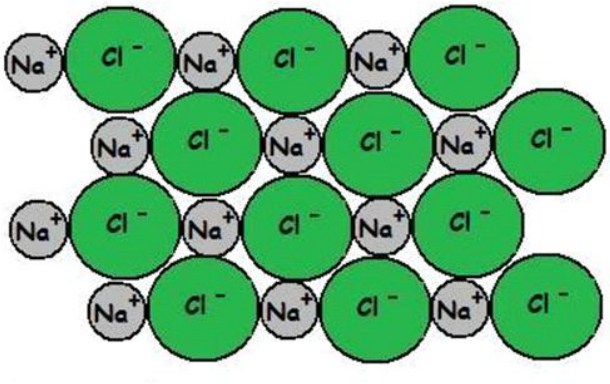


Figure 3: A NaCl crystal.

(*Created by:* Richard Parsons, *License:* CC-BY-SA)

In the NaCl lattice, each sodium ion is equally attracted to six chloride ions. In the sketch you can see each sodium surrounded by four chlorides, and in a three-dimensional structure, there would be another chloride above the sodium ions in the layer above and another one in the layer below, for a total of six.

The word malleable (in science) refers to a substance that can be pounded or beaten into another shape without breaking. Ionic solids are NOT malleable.

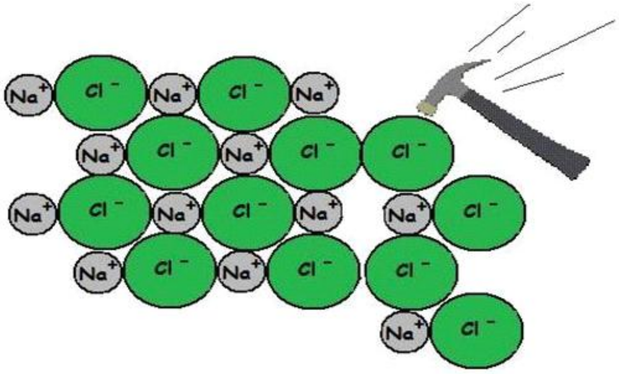


Figure 4: Ionic solids are not malleable.

(*Created by:* Richard Parsons, *License:* CC-BY-SA)

If an ionic crystal is struck, the ions are driven down a layer so that they will be next to like charges. These charges will repel and the crystal will shatter.

Ionic solids are usually quite soluble in water and the water solutions of ionic solids are good conductors of electricity because of the freedom of the ions to migrate through the solution.

Metallic Solids

Of the 81 elements which can be clearly classified as metals, all of them except mercury are solids at room temperature. Any model to explain the bonding in metallic solids must account for the properties of metals, some of which are quite unusual. The properties of metals include 1) excellent conductors of heat and electricity in both solid and liquid phase, 2) malleable, 3) most of them are white and shiny, 4) metallic solids are not soluble in any common solvent, polar or non-polar, and 5) they have a wide-range of melting points mostly higher than the melting points of polar solids.

The simplest bonding model that has been proposed to explain metallic behavior is the **metallic bond,** which envisions a regular pattern of cations surrounded by a “sea of electrons.” The metal ions (all of the metal atom except the valence electrons) occupy positions in a lattice structure while the mobile, free-moving, sea of valence electrons occupy all of the overlapping valence shell area.

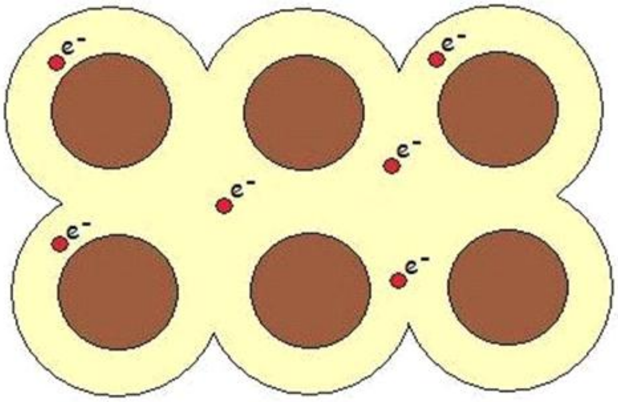


Figure 5: The metallic bond consists of non-directed bonds in which a “sea of electrons” surrounds all the bonded atoms.

(*Created by:* Richard Parsons, *License:* CC-BY-SA)

All the atoms are bonded in a single bond that includes the entire piece of metal. The bond is non-directional and does not hold adjacent ions in position relative to each other.

For purposes of comparison, consider the covalent bonding in a trigonal planar molecule (Figure 6). The central atom in this molecule contains three pairs of electrons. The electrons take positions as far away from each other as possible due to electrostatic repulsion. Therefore, the pairs of electrons maintain directed positions at angles of 120° from each other. The atoms that share these electron pairs in the covalent bond must be placed so that the shared electrons are in the overlapped orbitals of both atoms. Therefore, these bonded atoms may not move with respect to each other. The atoms hold their relative positions because of the **directional bonds**. Neither the bonding electrons nor the atoms are free to move with respect to each others.

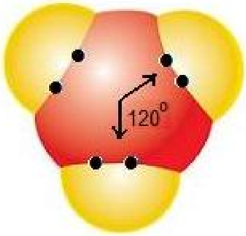


Figure 6: Directional bonding in trigonal planar molecule. (*Source:* CK-12, *License:* CC-BY-SA)

The model of the metallic bond, however, provides for mobile electrons that are free to move throughout the entire piece of metal and therefore, provides the means for the metal to be an excellent conductor of heat and electricity. Extra electrons pushed onto the metal on one side can easily move through the valence electron shells to the other side. The metal ions are not directionally bonded to their immediate neighbors and this allows them to be pushed to new positions without breaking the bond. As long as an atom or ion is not separated from the piece of metal, its position can be significantly changed while it remains bonded to the other atoms. This malleability allows metal cubes to be pounded into flat sheets without breaking the bond.

The freedom of the electrons on the surface of a piece of metal also allows the metal to absorb and emit many frequencies of light which accounts for the white, shiny appearance of many metals. The metals on the far left of the periodic table have the fewest valence electrons in the valence shells so the valence electrons in these metals would be least crowded, have the most freedom, and present the most complete metal character. The metals of families IA and IIA are excellent conductors, exceptionally malleable (soft enough to be cut with a spoon), and white and shiny in color.

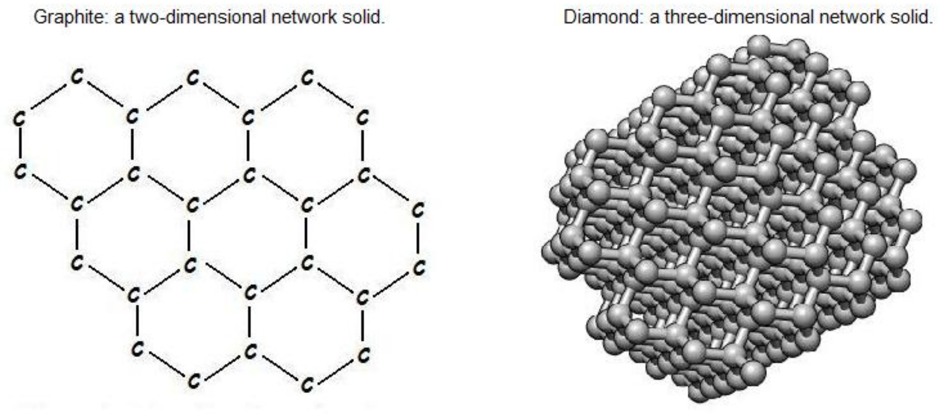
Other elements can be introduced into a metallic crystal relatively easily to produce substances known as **alloys.** An alloy is defined as a substance that contains a mixture of elements and has metallic properties. A fairly well-known alloy is brass which is an alloy composed of about two-thirds copper atoms and one-third zinc atoms. Sterling silver is an alloy composed of about 93% silver and 7% copper.

Iron is a metal that is commonly alloyed with carbon to produce **steel.** The carbon forms directional bonds with some of the iron atoms to make steel less malleable than pure iron. Steel with less than 0.2% carbon remains somewhat malleable and is used for nails and cables. Steel with around 0.6% carbon is harder and is used for railroad rails and structural steel beams. Steel with around 1.5% carbon is very hard and is used for tools and cutlery.

Network Solids

In some solids, all the atoms in the entire structure are bonded with covalent chemical bonds. These solids are a single giant molecule and are called **network solids.** When considering the strength of the bonds/attractions that hold various particles together in the solid state, the strongest of them all are covalent bonds. Therefore, network solids have the highest melting points of all solids. To melt a network solid requires enough molecular motion to disrupt covalent chemical bonds. Network solids are not soluble in any common solvent. Most network solids are non-conductors but graphite is an exception, it is a good conductor of electricity. Some examples of network solids are graphite, diamonds, mica, and asbestos.

The solid structure in graphite involves large two-dimensional molecules of covalently bonded carbon atoms. The carbon atoms form flat sheets (like a sheet of paper) bonded in the fashion shown in Figure 7.


Graphite: a two-dimensional network solid.

Diamond: a three-dimensional network solid.

Figure 7: One layer (sheet) of graphite, a 2-dimensional network solid, and diamond, a 3-dimensional network solid.

(*Source:* http://www.openchemistry.co.uk/images/diamond, *Modified by:* Richard Parsons, *License:* Creative Commons Attribution 3.0)

Then layers of these sheets are laid on top of each other and the sheets are held together by much weaker London dispersion forces. The sheets are extremely strong in the two dimensions involving covalent bonds but the forces holding the sheets together are weak and easily broken. The flat sheets slide over each other readily and this makes graphite a good lubricant for metal parts.

The mineral mica is also bonded in this two-dimensional network style. Mica is found in nature and appears as a rock but you can slide your fingernail between sheets and pull off large flats sheets of the rock. One type of mica, called muscovite mica, is transparent enough that you can see through several sheets. This material has been used to make small windows in furnaces so the operator can look in but the window is rock, not glass, so it won't melt.

Diamonds are giant molecules of carbon atoms bonded three-dimensionally in tetrahedral units. Every carbon atom in the structure is covalently bonded to four other carbon atoms. Diamonds are the hardest substance known and have one of the highest melting points of all substances.

Some forms of asbestos are a one-dimensional network solid in which atoms are bonded in a chain. The result is a fibrous molecule that can be woven into fabric.

Figure 8: Asbestos in the form of chrysotile. You can see fibers of asbestos in the upper left hand corner of the photo.

(*Source:* htt://wikipedia.org/File:Asbestos1USGOV, *Photo by:* This image is a cooperative effort between the United States Geological Survey and the Mineral Information Institute, *License:* Public Domain - USGov)

Due to the high melting point, asbestos fabric was used to make heat resistant materials (fireman's gloves, furnace padding, clutch plates, etc.) for many years until it was determined that asbestos fibers are hazardous if inhaled.

Amorphous Solids

Many important solids do not have the regular, repeating arrangement of atoms or molecules that is present in crystalline solids. Solids with irregular, unpredictable molecular organization are called **amorphous solids.** There are many solids that will form either crystalline or amorphous solids depending on how rapidly the liquid is cooled. Very rapid cooling of these substances frequently results in an amorphous solid whereas slow cooling produces crystalline solids. Amorphous solids have been described as appearing to have their molecules frozen in place before they had time to get into an organized pattern. Examples of amorphous solids are glass, paper, plastics, cement, and rubber.

Amorphous solids are called solids because they maintain their shape and volume. Some researchers insist that certain amorphous solids will flow under pressure, which is a characteristic of liquids. Antique windows have been found that are thicker at the bottom than at the top. Some chemists claim this is because the glass very slowly, over a hundred years, flowed downward under gravitational force. Other chemists claim the antique glass being of different thicknesses was caused by flaws in the glass making process of a hundred years ago. There was no mention in the opinion of why the thicker part of the glass was always at the bottom and never at the top.

Crystalline solids melt at sharply defined temperatures. Glass and some other amorphous solids, however, soften as they are heated. Some authors refer to amorphous solids as “not true solids”, others call them “supercooled liquids,” and still others insist that amorphous solids are absolutely solids. The importance of amorphous solids such as glass and plastics will insure that research on their structure continues.

Lesson Summary

- One type of solid is formed by ionic solids in which the inter-particle forces of attraction are electrostatic attractions due to the opposite charges of the ions.
- One type of solid is formed by metallic atoms where a sea of electrons exerts a force of attraction on the positive ions (metallic bond).
- Network solids have every atom in the structure attached to other atoms in the structure by covalent chemical bonds.
- Amorphous solids are solids that cooled so rapidly, the molecules did not get into the tight, organized solid pattern. Due to their disorganized structure, amorphous solids have some properties more like liquids.

Review Questions

1. Identify the most important type of inter-particle force present in the following solids that is responsible for binding the particles into a solid. **(Intermediate)**

A. He

B. NO

C. HF

D. $BaCl_2$

E. CH_4

F. $NaNO_3$

G. CO_2

H. $CHCl_3$

I. pure Mg

J. diamond

2. Predict which substance in the following pairs would have the stronger force of attraction between molecules and justify your answer. **(Intermediate)**

A. CO_2 or OCS

B. PF_3 or PF_5

C. NaI or I_2

D. H_2O or H_2S

E. solid argon or solid sodium

F. HF or HBr

3. In the following groups of substances, pick the one that has the requested property and justify your answer. **(Intermediate)**

A. highest boiling point: HCl, Ar, F_2

B. highest melting point: H_2O, NaCl, HF

C. lowest vapor pressure at 20° C: Cl_2 , Br_2, I_2

4. An unknown solid is not soluble in water or CCl_4. The solid conducts electricity and has a melting point of 800°C. Identify the most likely attractive forces holding the particles in the solid state. **(Intermediate)**

5. An unknown solid is soluble in water but not in CCl_4. The solid does not conduct electricity but its liquid does. The solid shatters when hammered and has a melting point of 1430°C. Identify the most likely attractive forces holding the particles in the solid state. *(Intermediate)*

6. Why would you expect ionic solids to have higher melting points that polar solids? **(Intermediate)**

7. Why does the melting point of water decrease with increasing surrounding pressure? **(Challenging)**

8. List the following substances in order of increasing boiling points: $BaCl_2$, H_2, CO, HF, Ne, CO_2. **(Intermediate)**

Select your answers for questions 9, 10, and 11 from these choices.

A. H_2 B. CH_3OH C. CH_2Cl_2 D. KCl E. CO

9. Which of these substance is most likely to be a solid at 25°C and 1.0 atm? **(Intermediate)**

10. Which of these substances is capable of hydrogen bonding? **(Intermediate)**

11. Which of the substances has its solid properties governed by London dispersion forces? **(Intermediate)**

12. Place these molecules, CF_4, $CaCl_2$, and ICl, in order of decreasing melting points (highest first). **(Intermediate)**

A. $CF_4 > CaCl_2 >$ ICl

B. $CaCl_2 >$ ICl $> CF_4$

C. $CaCl_2 > CF_4 >$ ICl

D. ICl $> CF_4 > CaCl_2$

E. $CF_4 >$ ICl $> CaCl_2$

Further Reading / Supplementary Links

http://learner.org/resources/series61.html'"

The ***learner.org*** website allows users to view streaming videos of the Annenberg series of chemistry videos. You are required to register before you can watch the videos but there is no charge. The website

has one video that relates to this lesson called ***Metals*** .

Website with lessons, worksheets, and quizzes on various high school chemistry topics.

- Lesson 4-6 is on Intermolecular Forces.
- Lesson 210 is on Heat Transfer Calculations.

http://www.fordhamprep.org/gcurran/sho/sho/lessons/lesson46.htm

http://dwb.unl.edu/teacher/nsf/c01links/www.ualberta.ca/!bderksen/florin.html

http://www.sciencedaily.com/releases/2008/07/080704153507.htm

http://www.bestcrystals.com/crystals2.html

Vocabulary

alloy	A substance composed of a mixture of two or more elements and having metallic properties.
conductivity	The property of being able to transmit heat and/or electricity.
conductor	A substance that can transmit heat and/or electricity.
ductility	The property of a substance that allows it to be drawn into a wire.
electrical conductivity	The ability of a substance to transmit an electric current.
malleable	The property of being able to be hammered or rolled into sheets.
metallic bond	The attractive force that binds metal atoms together. It is due to the attractive force that the mobile electrons exert on the positive ions.
specific heat	The amount of energy necessary to raise 1.00 gram of a substance by1.00^{o}C.

Review Answers

1.

A, E, and G are London dispersion force

B and H are polar attractions

C is hydrogen bonds

D and F are ionic bonds

I is metallic bond

J is covalent bond

2.

A. CO_2 would be London dispersion forces and OCS would be polar attractions. Since CO_2 has a smaller molecular weight than OCS, there is no reason for CO_2 to have unusually strong London dispersion forces. Therefore, OCS would most likely have the stronger attractions between particles.

B. PF_5 is non-polar and PF_3 is strongly polar. Since the molecular weights are not greatly different, PF_3 probably has the stronger attractive forces.

C. NaI is ionic and I_2 is London dispersion force. Ionic would have considerably stronger forces of attraction between particles.

D. H_2S is polar but water is hydrogen bonded. Water will have considerably stronger forces of attraction between particles.

E. Solid argon is London dispersion and solid sodium is metallic. Metallic is much more likely to be the stronger of the two.

F. HBr is polar but HF is hydrogen bonded. HF will have considerably stronger attractions between particles.

3.

A. Ar and F_2 are both held together in the solid state by London dispersion forces whereas HCl is strongly polar. HCl would be expected to have the highest boiling point of the three.

B. H_2O and HF are both hydrogen bonded but NaCl is ionic. Ionic charges are full charges while hydrogen bonds are only partial charges. NaCl will have the higher melting point.

C. All three of these molecules are London dispersion forces and the largest molecular weight is I_2. Therefore, I_2 will have the strongest forces of attraction and the lowest vapor pressure.

4. Since the solid conducts electricity, it is probably limited to metallic and a few network solids. The solubility doesn't help decide between these two but the melting point of 800°C is probably too low to be a network solid. This solid is most likely metallic.

5. Since the solid does not conduct electricity but the liquid does, it is almost sure to be an ionic solid. The solubility in water supports this conclusion as does the non-malleability. The melting point is much too high for London dispersion forces, polar, or hydrogen bonds.

6. Polar molecules carry partial charges due to their dipole while ions carry full charges due to the complete transfer of electrons. There will be stronger attraction between the full charges on ions than the partial charges on polar molecules.

7. Water in the solid form is held together by hydrogen bonds. Hydrogen bonding causes the solid water (ice) to expand. Extra surrounding pressure breaks some of the hydrogen bonds so that temperature isn't required to break them. The greater the pressure on ice, the lower the melting point becomes.

8. $H_2 < Ne < CO_2 < CO < HF < BaCl_2$

Hydrogen gas, neon, and CO_2 all have London dispersion force holding them in liquid form. The strength of London dispersion forces are related to the number of electrons in the particle. Since H_2 has the fewest electrons, it will have the weakest London dispersion forces and the lowest boiling point, followed in order by neon and carbon dioxide. Carbon monoxide and HF are polar molecules but HF is capable of forming hydrogen bonds and therefore, HF will have a higher boiling point than CO. $BaCl_2$ is an ionic solid and will have stronger intermolecular forces of attraction than either London dispersion forces or polar attractions.

9. D

10. B

11. A

12. B (ionic first, polar second, non-polar last)

Phase Diagrams

Lesson Objectives

- The student will be able to read specific requested information from a phase diagram.
- The student will be able to state the primary difference between a generic phase diagram and a phase diagram for water.

Introduction

A phase diagram is a convenient way of representing the phase of a substance as a function of temperature and pressure. Phase diagrams are produced by altering the temperature of a pure substance at constant pressure in a closed system. This process is repeated at many different pressures and the resultant phases charted.

Generic Phase Diagram

The phase diagram in Figure 8 is a generic phase diagram that would be produced by many pure substances. The differences in the diagram for different substances would be in the specific thermodynamic points like melting points, boiling points, and so on and differences in the slopes of the curved lines. The general shape of the phase diagram would be very similar for many substances.

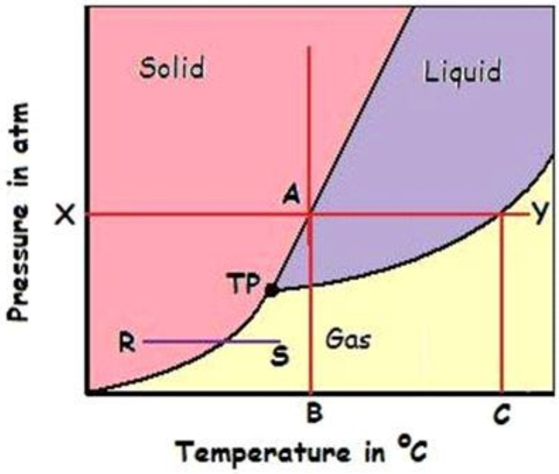


Figure 9: A generic phase diagram.

(*Created by:* Richard Parsons, *License:* CC-BY-SA)

In the pink area in the diagram, the substance would be in the solid state, the purple area represents liquid, and in the yellow area, the substance would be gaseous. Following a constant pressure line, such as XY, shows the phase of the substance at different temperatures for this pressure. Since line XY crosses from solid into liquid at point A, this temperature (B) would be the melting point of the substance. Continuing along the line, we see it crosses from liquid to gas and that point corresponds with temperature C. This is the boiling point of the substance at pressure X. The line between the pink and purple areas represent the various melting points at different pressures and the line separating the purple area from the yellow area represents the boiling point at various pressures. At the melting points, both solid and liquid can exist at the same time as the phase changes occurs but on either side of this temperature, the substance must be all in one phase. At the boiling points, the substance may exist in both liquid and gas phase at the same time but only exactly at the boiling point. There is one point on the diagram where all three phases may exist at one time. This point is called the **triple point**. The pressure at this point is called the triple point pressure and the temperature at this point is called the triple point temperature.

There is also a line separating the pink area from the yellow area. This line represents the phase change in which a solid changes directly to a gas without passing through the liquid phase. This phase change is known as **sublimation.** All substances undergo sublimation at the appropriate pressures. We do not see sublimation often because the pressures are frequently quite low and we do not encounter substances at low pressures in our daily lives. Some of us have seen carbon dioxide, CO_2, in the solid form which is called dry ice. If you have seen dry ice, you have noticed that the substance goes from the solid phase to the gaseous phase at room conditions without passing through a liquid phase. In the phase diagram for dry ice, we would see that the triple point is above normal atmospheric pressure and so at room conditions, carbon dioxide undergoes sublimation. Water also undergoes sublimation but the pressure where this would occur is below 4.58 torr or 0.0060 atm – a pressure we seldom witness.

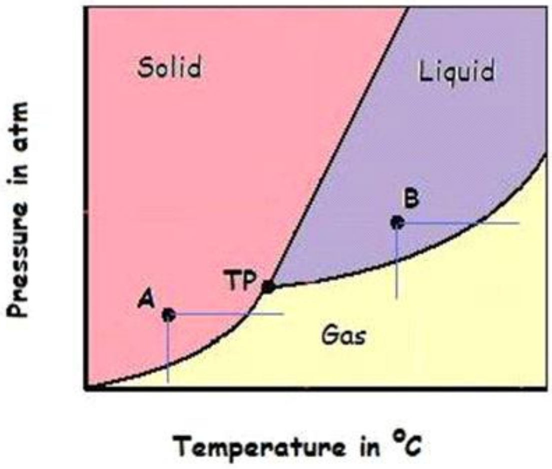


Figure 10: Another generic phase diagram.

(*Created by:* Richard Parsons, *License:* CC-BY-SA)

Figure 10 shows the same generic phase diagram we looked at before. Two points have been added to the diagram, labeled A and B. You should note that the substance at point A can be caused to go through a phase change from solid to gas (sublimation) in two different ways. The substance could be heated at constant pressure or the substance could undergo a lowering of pressure at constant temperature. Both of these procedures would cause the solid to undergo sublimation. Point B is a similar circumstance except that the substance begins as a liquid. The liquid at point B could be caused to under a phase change to gas either by heating it at constant pressure or by lowering the pressure at constant temperature. You might also note that the substance at the triple point will become a solid if pressure is increased and will become a gas if pressure is decreased.

Phase Diagram for Water

The phase diagram for water has one very interesting difference from the generic phase diagram. Please note that this diagram is not drawn to scale. If the distance between 1.0 atm and 218 atm was drawn to scale, the difference between 1.0 atm and 0.006 atm would be invisible. The diagram is drawn just to show specific points of interest.

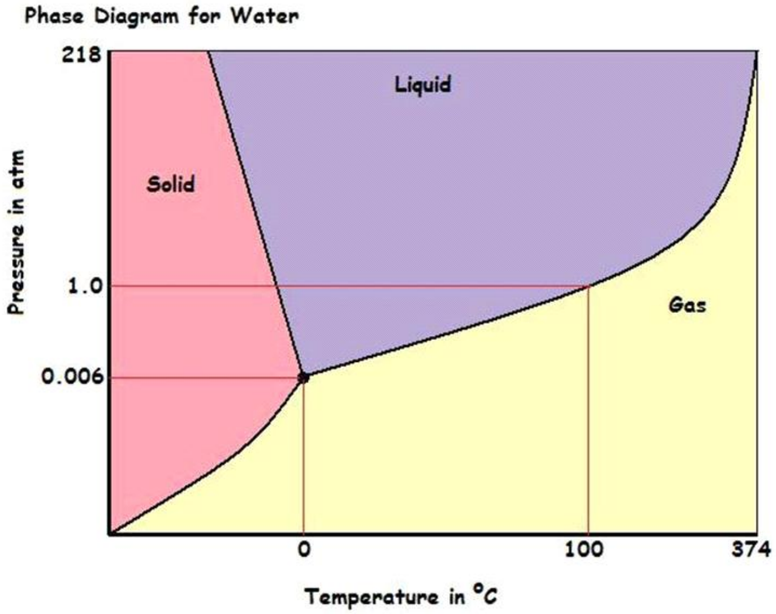


Figure 11: The phase diagram for water.

(*Created by:* Richard Parsons, *License:* CC-BY-SA)

The primary difference in the shape of this diagram and the generic diagram is that the solid-liquid equilibrium line (melting point) has a negative slope (tilts backwards). The positive slope of this line in the generic diagram indicates that as pressure increases, the melting point increases. That is reasonable because more pressure on the surface would require a higher temperature to overcome that extra pressure and melt the substance. The negative slope of this line in the water diagram indicates that as the pressure increases, the melting point of water decreases. The reason this occurs is because the increased pressure breaks some of the hydrogen bonds in the water and so LESS temperature is needed to melt ice at higher pressures. There is plenty of evidence of this in everyday life if you look for it. We all think of ice as being a very slippery substance but the surface of ice is no different from the surface of many other solids. The surface of ice is not smoother than the surface of copper or glass or most other solids. The reason that we slip on ice is that when you stand on ice or drive your car on ice, the pressure of your weight or the weight of your car causes the ice to melt. When you put pressure on ice, the surface between the ice and the weight is liquid and that makes it slippery. If you are an ice skater, you are aware that when you look closely at the track of the blade of an ice skate on ice, the track is filled with liquid, not solid.

If you follow the line at 1.0 atm pressure for water, you see that the melting points and boiling points are the temperatures noted as the normal melting point and the normal boiling point. The triple point for water is at 0.006 atm and 0.0098°C. Very expensive equipment is necessary if you wish to see water at its triple point. There are commercial processes that make use of the sublimation of water. Foods that are referred to as “freeze dried” have the surrounding pressure and temperature reduced to a point below the triple point and then they are heated while a vacuum pump removes vapor to keep the pressure below the triple point pressure. This causes the water in the food to sublimate (solid to gas) and it is drawn off by the pump. The end result is the food minus all the water that was in it. This process is supposed to damage the food less than getting rid of the water by heating the food. The idea is that you can just add water and the food will be like it was originally. The success or failure of that idea is for you to decide.

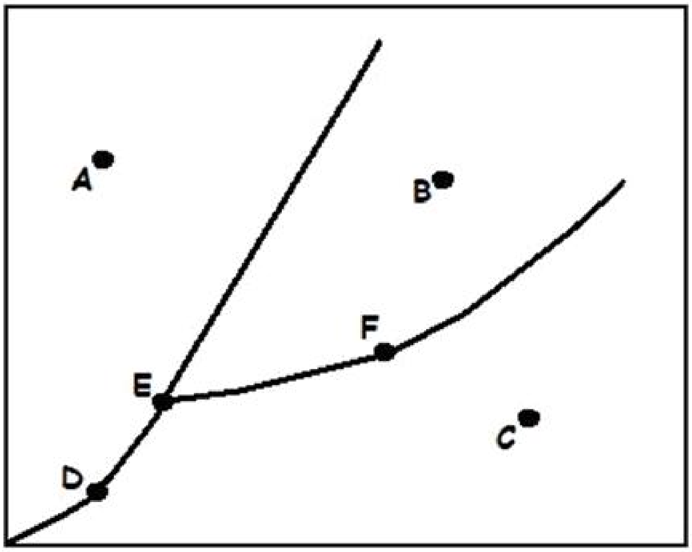
As the temperature of liquid is raised, the amount of pressure that is required to squeeze the substance and keep it in liquid form also increases. Liquids will eventually reach a temperature at which no amount of pressure will keep it in the liquid form. The substance at that temperature will vaporize regardless of the amount of pressure on it. The highest temperature a liquid reaches and can still be squeezed into a liquid is called the **critical temperature.** The pressure that is required at the critical temperature to force the liquid to stay in liquid form is called the **critical pressure.** The critical temperature and pressure for water is 374°C and 218 atm.

Lesson Summary

- Phase diagrams are graph showing the phase of a substance at various conditions of temperature and pressure.
- The phase diagram for water is different from most phase diagrams because unlike most substances, the melting point of water decreases as pressure increases.

Review Questions

1. Consider the phase diagram below. **(Beginning)**



Name the phases that may be present at each lettered point in the diagram.

Further Reading / Supplementary Links

Chemistry, Matter and Its Changes, 4th Edition, Chapter 12: Intermolecular Attractions and the Properties of Liquids and Solids, James E. Brady and Fred Senese, John Wiley & Sons, Inc., 2004.

http://dwb.unl.edu/teacher/nsf/c01links/www.ualberta.ca/!bderksen/florin.html

http://www.sciencedaily.com/releases/2008/07/080704153507.htm

Vocabulary

critical pressure	The pressure required to liquefy a gas at its critical temperature.
critical pressure	The pressure required to liquefy a gas at its critical temperature.

Review Answers

1.

A = solid only

B = liquid only

C = gas only

D = solid and gas

E = solid, liquid, and gas may be present

F = liquid and gas

21. The Solution Process

What Are Solutions?

Lesson Objectives

- Define solutions.
- Describe the composition of homogeneous solutions.
- Describe the different types of solutions that are possible within the three states of matter.
- Identify homogeneous solutions of different types.

Introduction

In this chapter we begin our study of solution chemistry. We have previously discussed a number of the concepts you will be learning in this chapter. But we will explore these ideas in greater detail in this chapter. Let's begin with a discussion of the definition of a solution. We all probably think we know what a solution is. We might be holding a can of soda or a cup of tea while reading this lesson and think … hey this is a solution. Well, you are right. But you might not realize that alloys, such as brass, are also classified as solutions, or that air is a solution. Why are these classified as solutions? Why wouldn't milk be classified as a true solution? To answer these questions, we have to learn some specific properties of solutions. Let's begin with the definition of a solution and view some of the different types of solutions.

Homogeneous Mixtures

A ***homogeneous mixture*** is a solution of the same appearance or composition throughout. Thinking of the prefix "homo" meaning "sameness", this definition makes perfectly good sense. Homogeneous solutions carry the same properties throughout the solution. Take, for example, vinegar that is used in cooking. Vinegar is approximately 5% acetic acid in water. This means that every teaspoon of vinegar that is removed from the container, contains 5% acetic acid and 95% water.

A point should be made here that when a solution is said to have uniform properties throughout, the definition is referring to properties at the particle level. Well, what does this mean? Let's consider brass as an example. The brass is an alloy made from copper and zinc. To the naked eye this brass coin seems like it is just one substance but at a particle level two substances are present (copper and zinc). An alloy is a homogeneous solution formed when one solid is dissolved in another. So the brass represents a homogeneous mixture. Now, consider a handful of zinc filings and copper pieces. Is this now a homogeneous solution? The properties of any scoop of the "mixture" you are holding would not be consistent with any other scoop you removed from the mixture. Thus the combination of zinc filings and copper pieces in a pile does not represent a homogeneous solution. Another example of a solution is margarine. Margarine is a combination of a number of substances at the molecular level but to the naked eye it is a homogeneous solution that looks like just one substance.

Varying Concentrations of Ingredients Produces Different Solutions

The point should be made that because solutions have the same composition throughout does not mean you cannot vary the composition. If you were to take one cup of water and dissolve ¼ teaspoon of table salt in it, a solution would form. The solution would have the same properties throughout, the particles of salt would be so small that they would not be seen and the composition of every milliliter of the solution would be the same. But you can vary the composition of this solution to a point. If you were to add another ½ teaspoon of salt to the cup of water, you would make another solution, but this time there would be a different composition than the last. You still have a solution where the salt particles are so small that they would not be seen and the solution has the same properties throughout, thus it is homogeneous. What would happen if you tried to dissolve ½ cup of salt in the water. Would the solution stay homogeneous? No, it would not. At this point, the solution has passed its limit as to the amount of salt it can dissolve and it would no longer be a homogeneous solution.

So solutions have constant composition but you can vary the composition up to a point. There are limits to the amount of substance that can be dissolved into another substance and still remain homogeneous.

Types of Solutions

There are three states of matter: solid, liquid, and gas. If we think about solutions and the possibilities of combining these states together to form solutions, we have nine possibilities. Look at the table below.

Table 1: Types of Solutions

	Solid	**Liquid**	**Gas**
Solid	Solid in a Solid	Solid in a Liquid	Solid in a Gas
Liquid	Liquid in a Solid	Liquid in a Liquid	Liquid in a Gas
Gas	Gas in a Solid	Gas in a Liquid	Gas in a Gas

In the table, there are really only four that are common types of solutions. These are shown in boldface. The others, although still solutions, are less common in everyday lives. For example, a solid in a liquid solution can be anything from salt or sugar solution, to seawater. Liquid in liquid solutions include the antifreeze/coolant we use for our cars and vinegar. For a gas in a liquid solution, the most common example is soda pop: carbon dioxide dissolved in water (with lots of sugar!) Another example is the ammonia solution you may use (or have seen used) to clean in the home. Finally, to understand the gas in a gas solution, take a deep breath. That's right, air is a solution made up of mostly oxygen gas and nitrogen gas.

A solid in a solid solution is less common but still we see a lot of steel and brass around in our everyday world. These are examples of solid – solid solutions. The other types of solutions are less common but do exist in the world of solution chemistry.

Lesson Summary

- A solution is a mixture that has the same properties throughout. Solutions have the same composition throughout but this composition can vary up to a point, or limit.
- With three states of matter, four types of solution can be classified as the most common as far as occurring in the everyday world. These include solid in a liquid, liquid in a liquid, gas in a liquid, and gas in a gas. The other types are less common.

Review Questions

1. What makes a solution homogeneous? **(Beginning)**

2. Which of the following are homogeneous? Explain. **(Intermediate)**

(a) gasoline

(b) chocolate

(c) blood

(d) brass

3. Which of the following is a solution? **(Intermediate)**

(a) milk

(b) blood

(c) gold

(d) air

(e) sugar

4. Which of the following is not a true solution? **(Intermediate)**

(a) vinegar

(b) sand and water

(c) hard water,$CaCO_{3(aq)}$

(d) mercury alloy

5. Give an example of a homogeneous solution that is made from the following combinations: **(Intermediate)**

a. a gas in a liquid

b. a solid in a solid

c. a solid in a liquid

d. a gas in a gas

6. Jack is practicing some household chemistry. He takes 1 tsp of sugar and dissolves it in 250 mL of water. He sees that the solution remains clear so continues his experiment by adding a second tsp of sugar. Stirring the solution makes this solution turn clear. After a few more attempts, Jack sees the solution turn murky then sugar crystals sinking to the bottom. What is Jack demonstrating? **(Intermediate)**

Further Reading / Supplemental Links

http://en.wikipedia.org

Vocabulary

solution	A homogenous mixture; composition can vary; but composition is the same throughout once the solution is made.

Review Answers

1. Answers will vary but students should indicate that a homogeneous solution has the same composition throughout.

2. (a) gasoline = solution because it has constant composition. (d) is also a solution for the same reason. (b) Chocolate is a heterogeneous mixture and (c) is also not a solution but a colloid.

3. (d) air

4. (b) sand and water

5.

(a) (soda pop)

(b) (brass)

(c) (salt water)

(d) (air)

6. Jack is demonstrating that solutions can have varying compositions but only up until a point. Then, they reach a limit for the amount of particles that can be dissolved and the rest precipitate out.

Why Solutions Occur

Lesson Objectives

- Describe why solutions occur; the "like dissolves like" generalization.
- Determine if solutions will occur by studying the molecular structure.
- State the importance of water as the "universal solvent."

Introduction

We have learned that solutions can be formed in a variety of combinations using solids, liquids and gases. We also know that solutions have constant composition and we can also vary this composition up to a point to maintain the homogeneous nature of the solution. But how exactly do solutions form? Why is it that when you mix oil and water together a solution does not form even though it is a liquid in a liquid and yet vinegar and water will? Why could we dissolve table salt in water but not in vegetable oil? The reasons why solutions form will be explored in this lesson, along with a discussion of why water is used most frequently to dissolve substances of various types.

Here is some new vocabulary you will meet in this chapter.

Solution: a homogeneous mixture of substances

Solute: the substance dissolved in a solution, usually determined by being the smaller quantity

Solvent: the substance the solute is dissolved in, usually determined by being the larger quantity

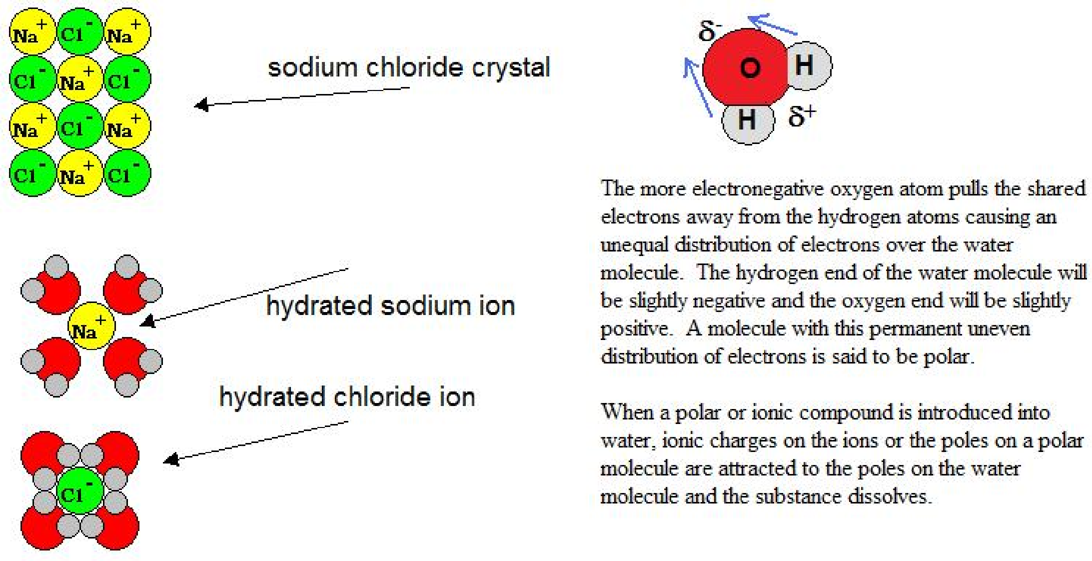
Similar Structures Allow Solutions to Occur

Over the course of your study in chemistry you have learned the terms polar and non-polar. Recall that in chemistry, a polar molecule is one that has a positive end and a negative end while nonpolar molecules have charges that are evenly distributed throughout the molecule. In fact, during the study of Valence Shell Electron Pair Repulsion Theory (VSEPR), you learned that the chemical structures themselves have built in molecular polarity.

In solution chemistry, we can predict when solutions will form and others won't using a little saying … "like dissolves like". The "like dissolves like' saying helps us to predict solubility based on the two parts of a solution having similar intermolecular forces. For example, suppose you are dissolving methanol in water. Both methanol and water are polar molecules and form a solution because they both have permanent dipoles (positive and negative parts of the molecules) that allow the molecules of each of the substances to be attracted to the other. When this occurs, a solution is made.

A way to understand this is to think about why Velcro is used to hold two different pieces of fabric together. The two sides of Velcro allow the pieces of fabric to be fastened together because the Velcro has similar structure that “attract” each other. However, one side of Velcro would not stay together with a piece of silk since the silk doesn’t have any part of its structure with which the Velcro can connect.

Let’s look at the individual structure of the water and methanol molecules. Notice in the representation of the individual molecules of methanol and water how the methanol has a permanent dipole due to the C – O – H bonds and is a polar molecule. In the representation of the water molecule, you can see that there are also permanent dipoles making it a polar molecule. The intermolecular forces for both of these molecules are dipole-dipole attractions. Since these molecules are both polar, they will form a solution when mixed together. We say they are **miscible**, which means these two liquids will make a solution.



The more electronegative oxygen atom pulls the shared electrons away from the hydrogen atoms causing an unequal distribution of electrons over the water molecule. The hydrogen end of the water molecule will be slightly negative and the oxygen end will be slightly positive. A molecule with this permanent uneven distribution of electrons is said to be polar.

When a polar or ionic compound is introduced into water, ionic charges on the ions or the poles on a polar molecule are attracted to the poles on the water molecule and the substance dissolves.

Figure 1: The hydration of ions in a polar solvent.

(*Created by:* Richard Parsons, *License:* CC-BY-SA)

The same is true for the case of a non-polar substance such as carbon tetrachloride being dissolved in another nonpolar substance such as pentane. London-dispersion forces are the intermolecular bonds that hold the carbon tetrachloride together as a liquid. London-dispersion forces are also the forces that allow pentane to be a liquid at room temperature. Since both of these substances have the same intermolecular forces, when they are mixed together, a solution will be formed.

Unlike the polar molecules, the non-polar molecules have, at any given time, no permanent dipole. If we were to add table salt, NaCl, to either carbon tetrachloride or pentane, we would find that the salt would not dissolve. The reason for this is again explained with the structures of the substances. Since carbon tetrachloride (or pentane) has no permanent dipoles in its molecules, there would be place for the charges particles in a crystal of NaCl to be attracted.

In a polar solvent, the molecules of solvent are attracted to each other by the partial charges on the ends of the molecules. When a polar solute is added, the positive polar ends of the solute molecules attract the negative polar ends of the solvent molecules and vice versa. This attraction allows the two different types of molecules to form a solution. If a non-polar solute was added to a polar solvent, the non-polar solute particles cannot attract the solvent molecules away from each other - so a solution does not form.

Polar solvents will dissolve polar and ionic solutes because of the attraction of the opposite charges on the solvent and solute particles. Non-polar solvents will only dissolve non-polar solutes because they cannot attract the dipoles or the ions.

Water: The Universal Solvent

Think of the title of this section, water: the ***universal solvent*** . The term solvent is used to represent the medium that is used to produce the solution. The term *universal* is used to describe the fact that water, along with many of its other unique aspects, can dissolve many types and kinds of substances. For instance, table salt, NaCl, is an ionic compound but easily makes a solution with water. This is true for many ionic compounds. And from your own experience you know that table sugar, a polar covalent compound, also dissolves in water. And this is also true for other polar compounds such as vinegar and corn syrup.

Even some nonpolar substances dissolve is water but only to a limited degree. Have you ever wondered why fish are able to breathe? Oxygen gas, a nonpolar molecule, does dissolve in water and it is this oxygen that the fish take in through their gills. Or, one more example of a nonpolar compound that dissolves in water is the reason we can enjoy carbonated sodas. Pepsi-cola and all the other sodas have carbon dioxide gas, CO_2, a nonpolar compound, dissolved in a sugar-water solution. In this case, to keep as much gas in solution as possible, the sodas are kept under pressure. But that's another part of the story!

Lesson Summary

- Whether or not solutions are formed depends on the similarity of polarity or the "like dissolves like" rule. Polar molecules dissolve in polar solvents, non-polar molecules dissolve in non-polar solvents, and ionic molecules in polar solvents. Polarity is determined from molecular geometry.
- Water is considered as the universal solvent since it can dissolve both ionic and polar solutes, as well as some non-polar solutes (in very limited amounts).

Combinations to form solutions with polar, ionic, and non-polar substances:

Combination	Solution formed
Polar substance in a polar substance	yes
Non-polar substance in a non-polar substance	yes
Polar substance in a non-polar substance	no
Ionic substance in a polar substance (i.e. water)	yes
Ionic substance in a non-polar substance	no

Review Questions

1. What is the "like dissolves like" generalization and provide an example to illustrate your answer. **(Intermediate)**

2. Why will LiCl not dissolve in CCl_4? **(Intermediate)**

3. Will acetic acid dissolve in water? Why? **(Intermediate)**

4. What is the difference between intermolecular and intramolecular bonds? **(Intermediate)**

5. In which compound will benzene (C_6H_6) dissolve? **(Intermediate)**

(a) Carbon tetrachloride

(b) water

(c) vinegar

(d) none of the above

6. In which compound will sodium chloride dissolve? **(Intermediate)**

(a) Carbon tetrachloride

(b) methanol

(c) vinegar

(d) none of the above

7. In which compound will ammonium phosphate dissolve? **(Intermediate)**

(a) Carbon tetrachloride

(b) water

(c) methanol

(d) None of the above

8. Thomas is making a salad dressing for supper using balsamic vinegar and oil. He shakes and shakes the mixture but cannot seem to get the two to dissolve. Explain to Thomas why they will not dissolve. **(Intermediate)**

Further Reading / Supplemental Links

http://en.wikipedia.org

Vocabulary

intermolecular bonds	Forces of attraction between molecules.
intramolecular bonds	Forces of attraction between atoms in a molecule.
universal solvent	A solvent able to dissolve practically anything (water).

Review Answers

1. The “like dissolves like” generalization revolves around substances that are dissolving having the same type of bonding as the substance that they are being dissolved in. For example dissolving acetic acid (a polar compound) in water (another polar compound) is an example of a solution formed based on the “like dissolves like” generalization.

2. Lithium chloride (LiCl) is ionic and CCl_4 is non-polar and ionic compounds do not dissolve in non-polar compounds.

3. Yes because both acetic acid and water are polar molecules.

4. Intramolecular bonds are forces between atoms in molecules; intermolecular bonds are forces of attraction between molecules.

5. (a) carbon tetrachloride

6. (c) vinegar

7. (b) water

8. The vinegar is an aqueous solution so therefore is polar and the oil is non-polar so the two solutions will not mix.

Solution Terminology

Lesson Objectives

- Define solute, solvent, soluble, insoluble, miscible, immiscible, saturated, unsaturated, concentrated, and dilute.

Introduction

Like any discipline that you would study or learn in our world, there are terms that are a part of the normal day- to- day conversation that takes place. The same is true when people get together to talk about solutions. You cannot talk about skateboarding without knowing about grinds and slides; you can't talk about bowling without knowing about spares and strikes; and, you can't talk about solutions without knowing terms such as solute, dilute, and saturated, just to name a few. In this section, you will learn the terms of solution chemistry.

Solvent and Solute

The solvent and solute are the two basic parts of a solution. The term ***solvent*** is the substance present in the greatest amount. The ***solute*** , then, is the substance present in the least amount. Let's think for a minute that you are making a cup of hot chocolate. You take a teaspoon of chocolate and dissolve it in one cup of hot water. Since the chocolate is in the lesser amount it is said to be the solute; and the water is the solvent since it is in the greater amount.

Sample question: Name the solute and solvent in each of the following mixtures

(a) Kool-aid

(b) iced tea

(c) soft drinks

Solutions:

(a) solute = Kool-aid crystals (and sugar); solvent = water

(b) solute = ice tea mix (and sugar); solvent = water

(c) solute = carbonic acid (and sugar or sweetener, chemicals, etc..); solvent = water

Soluble and Insoluble

Did you ever try to make a solution and yet it did not matter how much shaking and stirring that you did, the solid just kept falling to the bottom of the container. Try it for yourself. Take some sand and try to dissolve it in a cup of water. What happens? The sand will not dissolve. It is insoluble. Now if you were to take a teaspoon of table salt or sugar and do the same experiment, what a different result. There's no problem dissolving these substances. Salt and sugar are both soluble in water. When a ***substance*** is soluble, it means that the substance has the ability to dissolve in another substance. And being **insoluble** means that the substance does not dissolve.

Miscible and Immiscible

When referring to liquid solutes in liquid solvents, we can use the terms ***miscible*** and ***immiscible***. Liquids are said to be miscible when they can dissolve in each other. Therefore if they are immiscible, they are insoluble. When making a cake using a cake mix, you often use 1+ cups of water and 1/3 cup of oil and then you add this to the mix. If you first mix this together you would see that the mixture is an immiscible solution. The oil does not dissolve in the water. Since cooking oil is non-polar and the water is polar, they have different types of intermolecular bonds and they will not make a solution. When making biscuits, on the other hand, the recipe may call for you to add a little vinegar to the water before adding the liquid to the dry ingredients. The vinegar will be miscible in water because both vinegar and water are polar compounds and therefore have the same type of intermolecular bonds and can make a solution.

Saturated and Unsaturated

A ***saturated*** solution is one in which a given amount of solvent has dissolved the absolute maximum solute at that temperature. Let's go back to our table salt and water example from before: now try to dissolve 2 teaspoons of table salt in one cup of water. This is probably the maximum amount of salt that could dissolve. Try now to dissolve 3 teaspoons, some of the table salt would probably sit on the bottom of the glass; but at 2 teaspoons, all of the salt is in solution. The solution becomes saturated. If more solute is added to a saturated solution, the excess solute remains undissolved and simply sits on the bottom of the cup. If only one (1) teaspoon was placed in the glass, the solution would be said to be ***unsaturated***. This is because the solvent is holding less than the maximum amount of solute at that temperature. An unsaturated solution is one that contains less than the maximum amount of solute that is possible in a given amount of solvent.

Concentrated and Dilute

Solutions can also be said to be dilute or concentrated. A dilute solution is a concentrated solution that has been, in essence, watered down. Think of the frozen juice containers you buy in the grocery store. What you have to do is take the frozen juice from inside these containers and usually empty 3 or 4 times the container size full of water to mix with the juice concentrate and make your container of juice. Therefore, you are *diluting* the *concentrated* juice. When we talk about solute and solvent, the concentrated solution has a lot of solute verses the dilute solution that would have a smaller amount of solute. A ***concentrated*** solution is one in which there is a large amount of solute in a given amount of solvent. A ***dilute*** solution is one in which there is a small amount of solute in a given amount of solvent.

Lesson Summary

- Generally speaking, in a solution, a solute is present in the least amount (less than 50% of the solution) whereas the solvent is present in the greater amount (more than 50% of the solution).
- When a substance can dissolve in another it is said to be soluble; when it cannot, it is said to be insoluble. For two liquids, when they are soluble in each other the liquids are said to be miscible; when they are insoluble the liquids are considered immiscible.
- A saturated solution holds the maximum amount of solid at a specific temperature. An unsaturated solution does not have the maximum amount of solute dissolved at that temperature in a given amount of solvent. A concentrated solution has a large amount of solute in a given amount of solvent. A dilute solution has a lesser amount of solute.

Review Questions

1. Distinguish between soluble, insoluble and miscible, immiscible. Use an example in your answer. **(Intermediate)**

2. How can a solution that is concentrated be made more dilute and a dilute be made more concentrated? **(Intermediate)**

3. Vinegar and water will mix together. Therefore two liquids are said to be: **(Beginning)**

(a) saturated

(b) miscible

(c) unsaturated

(d) immiscible

4. A solution is analyzed and found to contain 90 g of solute in 100 mL of solution. What can be concluded about this solution? **(Intermediate)**

(a) The solution is concentrated.

(b) The concentration of the solution is 90 g/100 mL of water.

(c) The solution is saturated.

(d) The solution is holding the maximum amount of solute.

5. A solute is defined as: **(Beginning)**

(a) The substance in a solution present in the least amount.

(b) The substance in a solution that represents less than 50% of the solution.

(c) The substance that is dissolved in the solvent.

(d) All of the above.

(e) None of the above.

6. Match the following words with the examples that describe them. **(Intermediate)**

a) solute	Adding only one can of water to a frozen concentrated juice mix will form this type of solution.
b) solvent	Adding eight cans of water to a frozen concentrated juice mix will form this type of solution.
c) soluble	Alcohol and water will have this property.
d) insoluble	Gasoline and water will have this property.
e) miscible	The water of a NaOH(aq) solution.
f) immiscible	When salt is added to water it is said to have this property.
g) saturated	The copper(II) sulfate crystals in a solution of $CuSO_4$(aq)
h) unsaturated	The maximum amount of silver nitrate that can dissolve in 100mL of water is 220g. What term is given to this solution?
i) concentrated	If 220g of $AgNO_3$ can dissolve in 100 g of water and only 50 g are added, what type solution is formed?
j) dilute	Adding calcium hydroxide to water forms a milky white precipitate. What term is given to calcium hydroxide?

7. Nisi is given two bottles of copper (II) sulfate solutions in her senior high chemistry lab. She is told that one bottle contains a saturated solution and the other one contains an unsaturated solution. What can Nisi do to identify the two solutions? **(Intermediate)**

8. Can you have a solution that is saturated and dilute at the same time? Explain. **(Challenging)**

Vocabulary

solute	The substance in a solution present in the least amount.
solvent	The substance in a solution present in the greatest amount.
soluble	The ability to dissolve in solution.
insoluble	The inability to dissolve in solution.
miscible	Two liquids having the ability to be soluble in each other.
immiscible	Two liquids not having the ability to be soluble in each other.
saturated	A solution holding the maximum amount of solution in a given amount of solvent.
unsaturated	A solution holding less than the maximum amount of solution in a given amount of solvent.
concentrated	A solution where there is a large amount of solute in a given amount of solvent.
dilute	A solution where there is a small amount of solute in a given amount of solvent.

Review Answers

1. Answers will vary but students should first define the terms and then specify that the terms miscible and immiscible only refer to liquid solutions. Soluble means that the two substances have the ability to dissolve. Miscible means the two liquids have the ability to be soluble in each other. Insoluble means the two substances cannot dissolve in each other. Immiscible means the two liquids do not have the ability to be soluble in each other. Salt is soluble in water as is vinegar. Vinegar and water are also miscible. Oil is not soluble in water and is also immiscible in water.

2. A solution that is concentrated is made dilute by adding more solvent such as water. A solution that is dilute would have to be made more concentrated only by adding more of the solute.

3. b miscible

4. a The solution is concentrated.

5. d

6. j, i, e, f, b, c, a, g, h, d

7. Nisi could add a few crystals of copper (II) sulfate to each of the bottles. If a precipitate forms (or the crystals sink to the bottom of the container) it is a saturated solution and if no precipitate forms, it is unsaturated.

8. A solution can be saturated and dilute if the solute does not dissolve very well in the solvent. Take, for example, calcium hydroxide. Calcium hydroxide is only slightly soluble in water. Therefore if we dissolve only a small amount of $Ca(OH)_2$ in water then the solution is dilute. Yet if this amount is the maximum amount of $Ca(OH)_2$ that the given amount of water will hold, the solution is also saturated.

Measuring Concentration

Lesson Objectives

- Define molarity, mass percent, ppm, and molality.
- Calculate molarity, mass percent, ppm, and molality.

- Explain the importance of quantitative measurement in concentration.

Introduction

Although qualitative observations are necessary and have their place in every part of science, including chemistry, we have seen throughout our study of science that there is a definite need for quantitative measurements in science. This is particularly true in solution chemistry. We might read in the headlines that the amount of mercury found in the fish is up by 0.5 ppm and say to ourselves, what does that mean? Is it important? We read labels in the grocery store that are in weight percent. What does this mean? So being able to deal with the quantitative side of solutions helps us to move toward a deeper understanding of solutions, one that involves not only a numerical analysis but a critical analysis as well. Let's explore some of the different quantitative applications of solution chemistry.

Molarity

Of all the quantitative measures of concentration, molarity is the one used most frequently by chemists. Molarity is defined as the moles of solute per liter of solution. The symbol given for molarity is ***M***. You will see molarity units of both ***moles/liter*** and ***M***. Chemists also used square brackets **[ ]** to indicate a reference to the molarity of a substance. For example, the expression $[Ag^+]$ refers to the molarity of the silver ion.

It should be noted that when making solutions to a certain molarity, the amount of solvent to be used cannot be measured. The amount of solvent used will be whatever is necessary to bring the total solution to the required volume. This amount of solvent cannot be calculated beforehand either by volume or by mass because it is not known what volume will be required to reach the total volume of solution. Solution concentrations expressed in molarity are the easiest to calculate with but the most difficult to make in the lab.

molarity = mols/L =

$$\frac{\text{moles of solute}}{\text{liters of solution}}$$

Sample question 1: What is the concentration, in mol/L, where 2.34 mol of NaCl has been dissolved in 500 mL of H_2O.

Solution:

$$[\text{NaCl}] = \frac{2.34 \text{ mols}}{0.500 \text{ liters}} = 4.68 \text{ M}$$

The concentration of the NaCl solution is 4.68 mol/L

Sample question 2: What would be the mass of 500 mL of a 1.25 mol/L potassium sulfate solution?

Solution:

$$M = \frac{\text{mol}}{\text{L}} \quad \text{so} \quad \text{mols M x L}$$

mols = (1.25 mol/L(0.500 L) = 0.625 mol

$$\text{mols} = \frac{\text{mass}}{\text{molar mass}} \quad \text{so} \quad \text{mass = (mols)(molar mass)}$$

mass = (0.625 mol)(174.3 g/mol) = 109 g

Therefore the mass of K_2SO_4 that dissolves in 500 mL of H_2O to make this solution is 109 g.

Mass Percent

Mass percent, is the number of grams of the solute in the number of grams of solution. Mass percent is a term frequently used when referring to solid solutions. It has the formula:

$$\text{percent by mass} = \frac{\text{mass of solute}}{\text{solute mass} + \text{solvent mass}} \times 100$$

or

$$\text{percent by mass} = \frac{\text{mass solute}}{\text{mass solution}} \times 100$$

Sample question: An alloy is prepared by adding 15g of zinc to 65g of copper. What is the mass percent of zinc?

Solution:

$$\text{percent by mass} = \frac{\text{mass of solute}}{\text{solute mass} + \text{solvent mass}} \times 100$$

$$\text{percent by mass} = \frac{\text{mass Zn}}{\text{mass Zn} + \text{mass Cu}} \times 100 = \frac{15\text{ g}}{15\text{ g} + 65\text{ g}} \times 100 = \frac{15\text{ g}}{80\text{ g}} \times 100 = 19\%$$

Parts Per Million

Parts per million is another unit for concentration. Obscure in the sense that it is used less frequently than the others that will be dealt with in this unit. This does not mean that it is any less important than the others, it just means that for the normal “day to day” conversations that folks have around the solution chemistry lab, parts per million might not come up all that often. Parts per million denotes that there is 1 milligram of solute for every kilogram of solvent. Usually you hear about parts per million when governments are talking to us about drinking water or poisons in fish and other food products. It is used most frequently when dealing with environmental issues when you pick up the newspaper or common news magazines around the house. To calculate parts per million, the following formula is used.

$$\text{ppm} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^6$$

Sample question: Mercury levels in fish have often been at the forefront of the news for people who love to eat fresh fish. Salmon, for instance, contains 0.01 ppm compared to shark which contains 0.99 ppm. In the United States, canned tuna is the most popular selling fish and has a mercury level of 0.12 ppm according to the FDA statistics. If one were to consume 1.00 kg of canned tuna over a certain time period, how much mercury would be consumed?

Solution

$$\text{ppm} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^6$$

so

$$\text{mass of solute} = \frac{(\text{mass of solution})(\text{ppm})}{1 \times 10^6}$$

$$\text{mass of solute} = \frac{(1000.\text{ g})(0.12)}{1 \times 10^6} = 1.2 \times 10^{-4}\text{ g}$$

Molality

Molality is one further way to measure concentration of a solution. It is calculated by dividing the moles of solute by the kilograms of solvent. Molality has the symbol, ***m*** .

$$\textbf{molality (m)} = \frac{\text{moles solute}}{\text{kg of solvent}}$$

An interesting sidebar: molality is used for specific topics in solution chemistry as molarity as a method for measuring concentration. So why learn both? Well, oddly enough it all boils down to temperature … pardon the pun! Molarity, if you recall, is moles of solute per volume of solution and the volume is temperature dependent. As the temperature rises, the molarity of the solution will actually decrease slightly because the volume will increase slightly. Molality does not involve volume and mass is not temperature dependent. Thus, there is a slight advantage to using molality over molarity when temperatures move away from standard conditions. Yet, still, the choice of majority falls to using molarity.

Sample question: Calculate the molality of a solution of hydrochloric acid where 12.5 g of hydrochloric acid has been dissolved in 115 g of water.

Solution:

$$\text{mol HCl} = \frac{12.5\text{ g}}{36.46\text{ g/mol}} = 0.343\text{ mol}$$

$$\text{molality HCl} = \frac{\text{moles solute}}{\text{kg solvent}} = \frac{0.343\text{ mol}}{0.115\text{ kg}} = 2.98\text{ m}$$

Lesson Summary

- Molarity is the moles of solute per liter of solution. Molarity normally uses the symbol ***M*** . Mass percent is the number of grams of the solute in the number of grams of solution, of course multiplied by 100.
- Parts per million means that there is 1 milligram of solute for every kilogram of solvent. Therefore it is the mass of solute per mass of solution multiplied by 1 million.
- Molality is calculated by dividing the moles of solute by the kilograms of solvent. It is less common than molarity but more accurate because of its lack of dependence on temperature.

Review Questions

1. Calculate the mass percent of silver when a silver/nickel solution is made with 34.5 g of silver and 72.3 g of nickel. **(Intermediate)**

2. What would be the ppm of silver for the data presented in question 1? **(Intermediate)**

3. Why is it a good idea to learn mass percent when molarity and molality are the most commonly used concentration measures? **(Intermediate)**

4. Most times when news reports indicate the amount of lead or mercury found in foods, they use the concentration measures of ppb (parts per billion) or ppm (parts per million). Why use these over the others we have learned? **(Intermediate)**

5. What is the molarity of a solution prepared by dissolving 2.5 g of $LiNO_3$ in sufficient water to make 60 mL of solution? **(Intermediate)**

(a) 0.036 mol/L

(b) 0.041 mol/L

(c) 0.60 mol/L

(d) 0.060 mol/L

6. A solution is known to have a concentration of 325 ppm. What is the mass of the solute dissolved in 1.50 kg of solvent? **(Intermediate)**

(a) 0.32 mg

(b) 0.49 mg

(c) 325 mg

(d) 488 mg

7. Calculate the molality of a solution of copper(II) sulfate where 11.25 g of the crystals has been dissolved in 325 g of water. **(Intermediate)**

(a) 0.0346 m

(b) 0.0705 m

(c) 0.216 m

(d) None of the above

8. What is the mass of magnesium chloride present in a 250 g solution found to be 21.4% $MgCl_2$? **(Intermediate)**

(a) 21.4 g

(b) 53.5g

(c) 196.5 g

(d) 250 g

9. What is the concentration of each of the following solutions in mol/L. **(Intermediate)**

a. 3.50 g of potassium chromate dissolved in 100 mL of water

b. 50.0 g of magnesium nitrate dissolved in 250 mL of water.

10. Find the mass of aluminum nitrate required to produce 750 g of a 1.5 molal solution.

11. The Dead Sea contains approximately 332 grams of salt per kilogram of seawater. Assume this salt is all NaCl. Given that the density of the Dead Sea water is approximately 1.20 g/mL, calculate:

A. the mass percent of NaCl. **(Intermediate)**

B. the mole fraction of NaCl. **(Intermediate)**

C. the molarity of NaCl. **(Challenging)**

Further Reading / Supplemental Links

Website with lessons, worksheets, and quizzes on various high school chemistry topics.

- Lesson 6-4 is on Molarity.

http://www.fordhamprep.org/gcurran/sho/sho/lessons/lesson31.htm

Vocabulary

molarity	A concentration unit measuring the moles of solute per liter of solution.
mass percent	A concentration unit measuring the mass of solute per mass of solution. This unit is presented as a percent.
weight percent	Another name for mass percent.
parts per million (ppm)	A concentration unit measuring the mass of solute per mass of solution multiplied by 1 million.
molality	A concentration unit measuring the moles of solute per kilograms of solutions.

Review Answers

1. 32.3%

2. 323,000 ppm

3. Answers will vary but students may talk about the fact that weigh percent is often used when describing solid – solid solutions. The weight percent of zinc in common brass is 37% meaning that 37 g of every 100 g of brass is zinc. Also, the weight percent is like a ppm calculation but it provides the solute amount as a percent. 10.5% NaCl solution is 10.5 g NaCl in 100 g H_2O, for example.

4. Answers may vary. The amounts of lead and mercury (and other hazardous chemicals) found in foods are very small. Having said this, these amounts do not have to be large to be dangerous. But since they are so small, the units of ppm or ppb are the best units to provide us with a number that is reasonable for the majority of the population to comprehend.

5. (c) 0.60 mol/L

6. (d) 488 mg

7. c

8. (b) 53.5g

9.

(a) The concentration of the K_2CrO_4 solution is 0.180 mol/L

(b) The concentration of the $MgNO_3$ solution is 2.32 mol/L

10.

mol $Al(NO_3)_3$ = (1.5 m) × (0.750 kg)
mol $Al(NO_3)_3$ = 1.125 mol
mass $Al(NO_3)_3$ = (1.125 mol) × (213.0/mol)
mass $AL(NO_3)_3$ = 239.6 g

Therefore to produce a 1.5 molal solution of $Al(NO_3)_3$, you would need to dissolved 240 g of Al(NO3)3 in the 750 mL of water.

11. If we choose a sample of 1.00 kg of seawater, the mass of NaCl is 332 g and the mass of water is 668 g.

moles of NaCl = $\frac{332\text{ g}}{58.44\text{ g/mol}}$ = 5.68 moles

moles of water = $\frac{668\text{ g}}{18.02\text{ g/mol}}$ = 37.1 moles

A. mass percent of NaCl = $\frac{332\text{ g}}{1000.\text{ g}}$ x 100 = 33.2%

B. mole fraction of NaCl = $\frac{5.68\text{ mols}}{42.78\text{ mols}}$ = 0.133

C. The volume of 1.00 kg of seawater = $\frac{1000.\text{ g}}{1.20\text{ g/mL}}$ = 833 mL

molarity of NaCl = $\frac{5.68\text{ mols}}{0.833\text{ L}}$ = 6.82 M

Solubility Graphs

Lesson Objectives

- Define solubility.
- Read and report data from solubility graphs.
- Read and report saturation points from a solubility graph.

Introduction

In an earlier chapter we have discussed solubility as it applied to data analysis. Solubility graphs are an excellent way of organizing and displaying data for interpretation. In this lesson, we will explore this concept in learning how to read and analyze a solubility graph in order to extract the relevant data. In the everyday world, solutions play a key role in our lives from the foods we eat (through proper mixing), the solutions we prepare to clean homes, and also are essential in the laboratory.

Reading Solubility From a Graph

Solubility , as we already know, is the amount of solute that will dissolve in a given amount of solvent at a particular temperature. The latter part of this statement is significant since, for many solutes, the solubility will increase as the temperature is increased. There are exceptions, of course, just as there are exceptions to every rule. Sodium chloride (table salt), for example, will dissolve to the extent of about 36 g in 100 g of water at 25 °C and there is little change as the temperature increases. The solubility of cesium sulfate actually decreases as temperature increases. But a vast majority of ionic solids that are solutes do increase their solubility with temperature.

Think of the solutes you would be dissolving in your own environment. If you make a cup of instant coffee you most likely boil the water first to dissolve more of the coffee crystals. If you are making hot chocolate, you would also use boiling water; hot tap water would not do the trick quite so well. Making a bowl of “Cup of Noodles” simply does not taste quite as good when you do not have the noodles heated in the boiling water because the noodles cannot dissolve all of the spices to the flavor that is expected. Think also of a can of cola. This is a solution of a gas, CO_2, in a liquid. When you have a can of soda at room temperature there is more gas above the surface of the liquid in the can than if you have a can of soda cooled to an icy cold temperature. This is because the solubility of the gas in solution decreases as the temperature is increased and the gas moves up to the air space in the can above the liquid. Think of this before you open up the next warm pop.

To display the different solubilities at different temperatures, a solubility graph is drawn to show the data in a more coherent manner. Having a solubility graph allows us to read the data about a particular solute or to compare solutes at a particular temperature quickly and easily. Let's look at a typical solubility graph and see how it works.

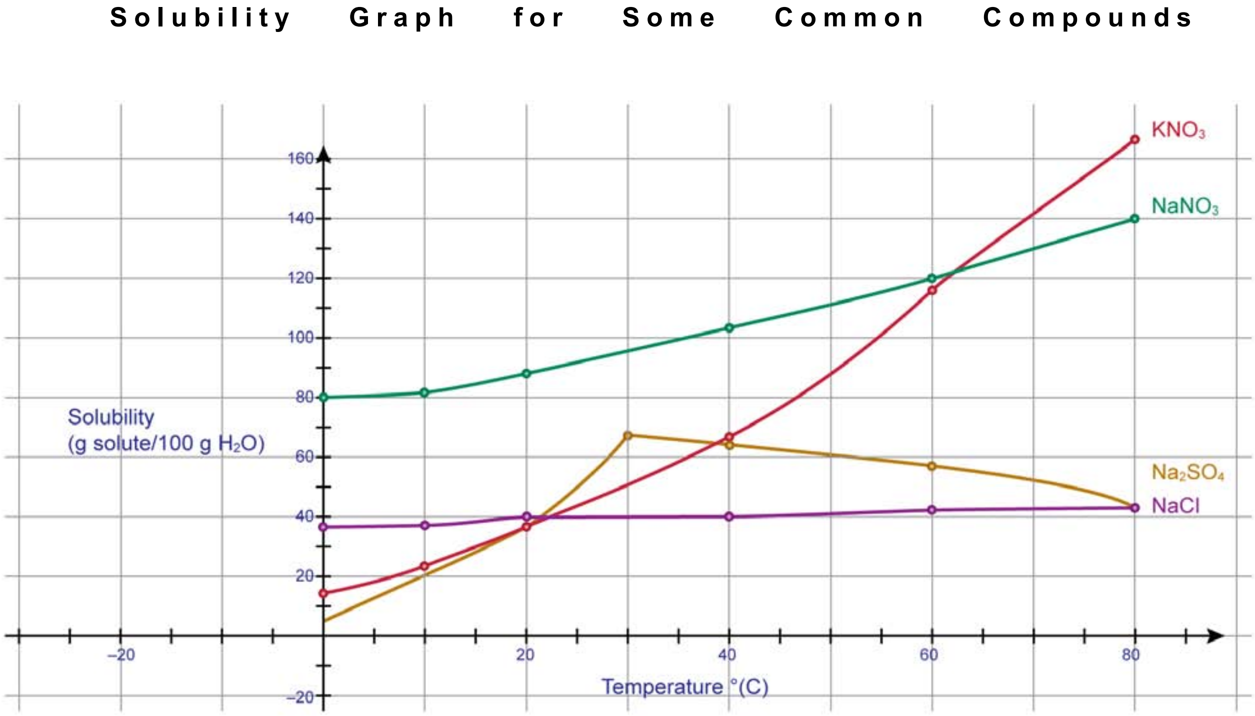


Figure 2: A solubility graph for some common compounds.

(*Source:* CK-12 Foundation, *License:* CC-BY-SA)

What kind of information does this graph tell us? You can see that three of the four solids increase solubility with increasing temperature, NaCl only slightly, and KNO_3 solid increases substantially with increasing temperature. In addition to general trends in the solubility of a substance, you can also get detailed facts from a solubility graph. For example, we can see that at 30 ºC, 95 g of sodium nitrate, $NaNO_3$, will dissolve but at 60 ºC, 120 g will dissolve in 100 g of H_2O. At these same two temperatures, only 50 g of Na_2SO_4 and 113 g, of potassium nitrate, KNO_3, will dissolve in 100 g of H_2O.

Sample question 1: Answer the following questions using Figure 21.5.1.

(a) How much sodium nitrate will dissolve at 30 ºC?

(b) What solid is more soluble at 60 ºC?

(c) What solid is least soluble at 40 ºC?

(d) At what temperature will 60 g of sodium sulfate dissolve in 100 g of water?

Solution:

(a) Looking at the solubility graph below, you draw a line up (vertically) from 30 ºC until it hits the $NaNO_3$ line. Following this, carry the line over (horizontally) to find the amount of NaNO3 that dissolves.

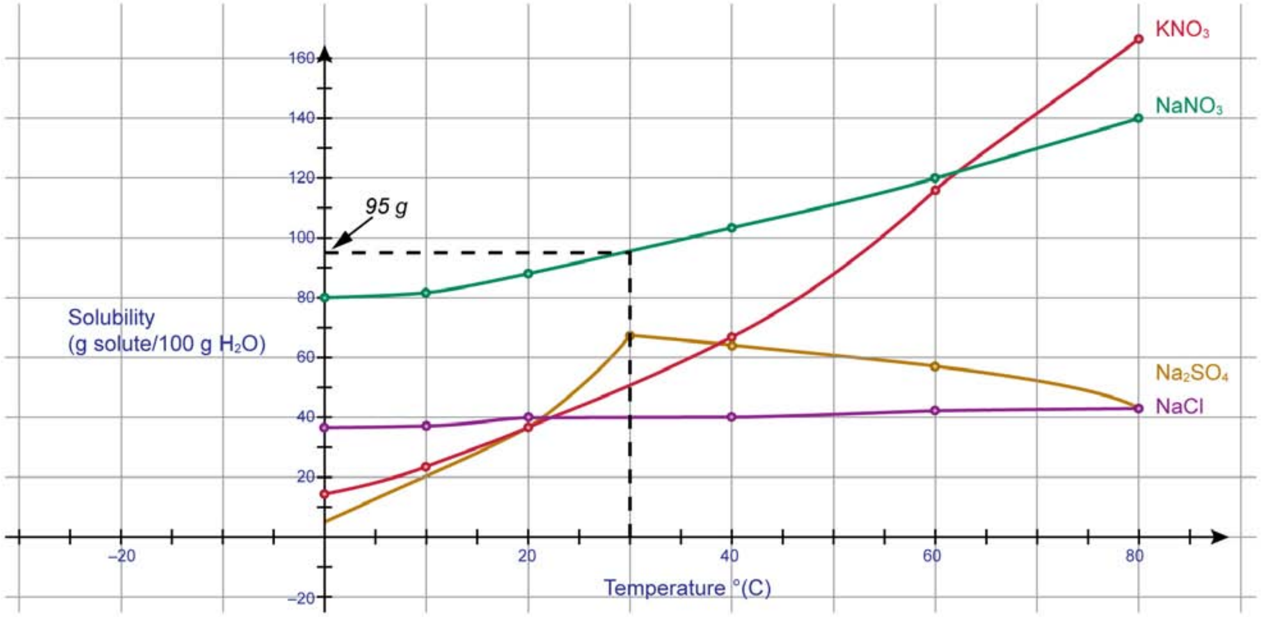


Figure 3: Reading a solubility graph.

(*Source:* CK-12 Foundation, *License:* CC-BY-SA)

Therefore approximately 95 g of $NaNO_3$ will dissolve in 100 g of water at 30 ºC.

(b) The highest line at 60 ºC is the green line ($NaNO_3$), therefore it is the most soluble at 60 ºC.

(c) The lowest line at 40 ºC is the purple line (NaCl), therefore NaCl is the least soluble at 40 ºC.

(d) Looking at the solubility graph below, you draw a line over (horizontally) from 60 g until it hits the Na_2SO_4 line. Following this, carry the line down (vertically) to find the temperature at which 60 g of Na_2SO_4 will dissolve.

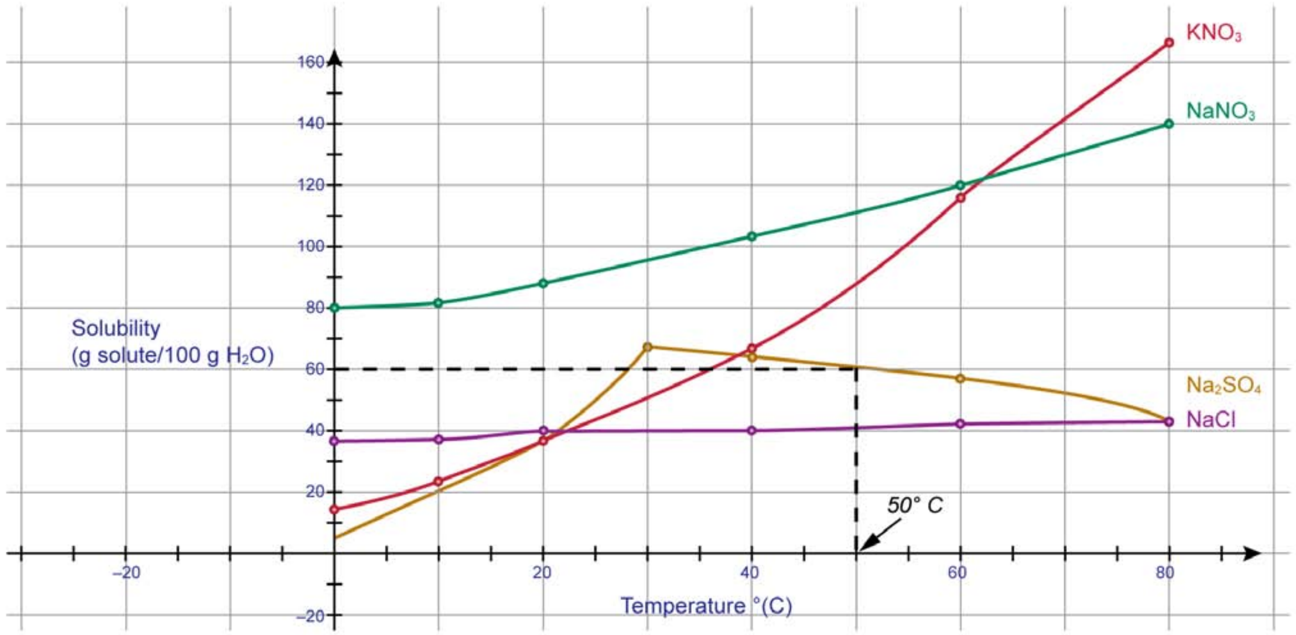


Figure 4: Reading a solubility graph.

(*Source:* CK-12 Foundation, *License:* CC-BY-SA)

Therefore 60 g of Na_2SO_4 will dissolve in 100 g of water at 50 ºC.

Reading Saturated Solutions From a Graph

Look at the solubility graph that shows more common ionic compounds. The lines on the solubility curves represent the amounts that dissolve in the given amount of solvent at a specific temperature. Look at the line for NH_3. According to the graph that NH_3 is the only substance of this group that decreases in solubility as the temperature is increased. We can also see that the most soluble substance at room temperature (25°C) is NH_3 because it is the line highest up on the graph at 25 °C. The highest point on the solubility curve is at approximately y = 92. We can say then that the most soluble substance at 0°C is ammonia with a solubility of approximately 92 g in 100 g of water.

Solubility Graph for More Common Ionic Compounds and Ammonia

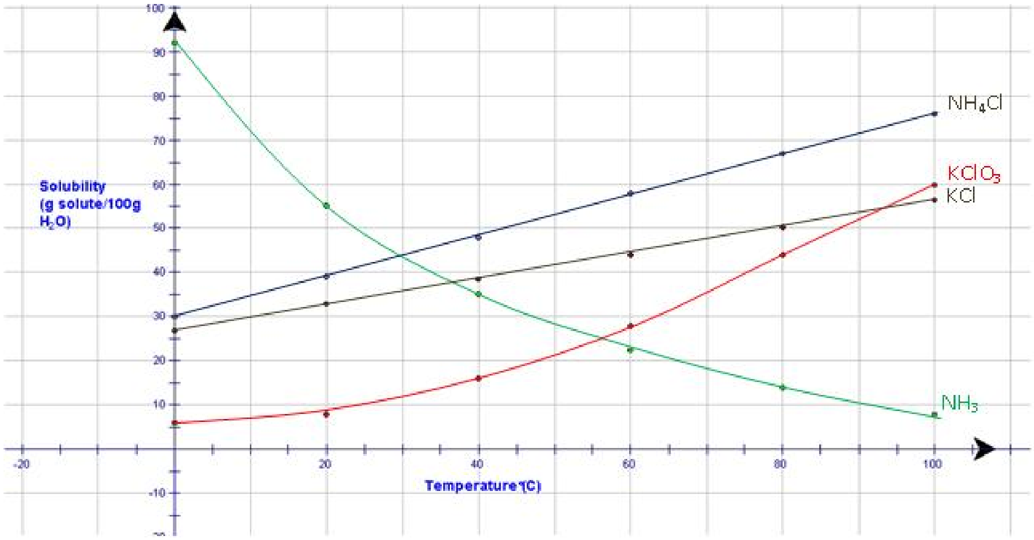


Figure 5: A solubility graph for common ions and ammonia.

(*Created by:* Therese Forsythe, *License:* CC-BY-SA)

All of this information can be obtained from reading the solubility graph. What other information can you obtain from a solubility graph? You could do a number of different types of calculations. For example, what if you were doing an experiment in the lab (at room temperature) and needed a saturated solution of potassium chloride dissolved in 35 g of water. How much KCl would you need?

At 25°C (room temperature), approximately 35 g of KCl will dissolve in 100. g of water. For 35 g of water:

Proportion

$$\frac{x\ \text{g KCl}}{35\ \text{g}\ H_2O} = \frac{35\ \text{g KCl}}{100.\ \text{g}\ H_2O}$$

x = 12 g KCl

Another type of problem that can be answered using a solubility graph is to determine if you have saturated solutions or not. For example, you have a solution of potassium chlorate that you know is 76g dissolved in 250 g of water. You want to know if this solution is saturated or unsaturated when your solution is being heated at 80 °C.

Looking at the solubility graph, at 80 °C, 44 g of $KClO_3$ will dissolve in 100 g of H_2O. Therefore we can use the same type of equation as used previously to determine how much would dissolve in 250 g of H_2O.

Proportion

$$\frac{x\ \text{g}\ KClO_3}{250.\ \text{g}\ H_2O} = \frac{44\ \text{g}\ KClO_3}{100.\ \text{g}\ H_2O}$$

x = 110. g $KClO_3$

Since it is possible to dissolve 110 g of $KClO_3$ in 250 g of H_2O and our solution only has 76 g dissolved in 250 g of H_2O, the solution is unsaturated.

Lesson Summary

- Solubility is the amount of solute that will dissolve in a given amount of solvent at a specific temperature. A solubility graph is drawn to display the solubility at different temperatures. It is the mass of the solute/100g of H_2O versus temperature in °C.

- From reading a solubility graph, one can determine the mass of solute that can dissolve at specific temperatures and also compare solubility's of different substances at specific temperatures.

Review Questions

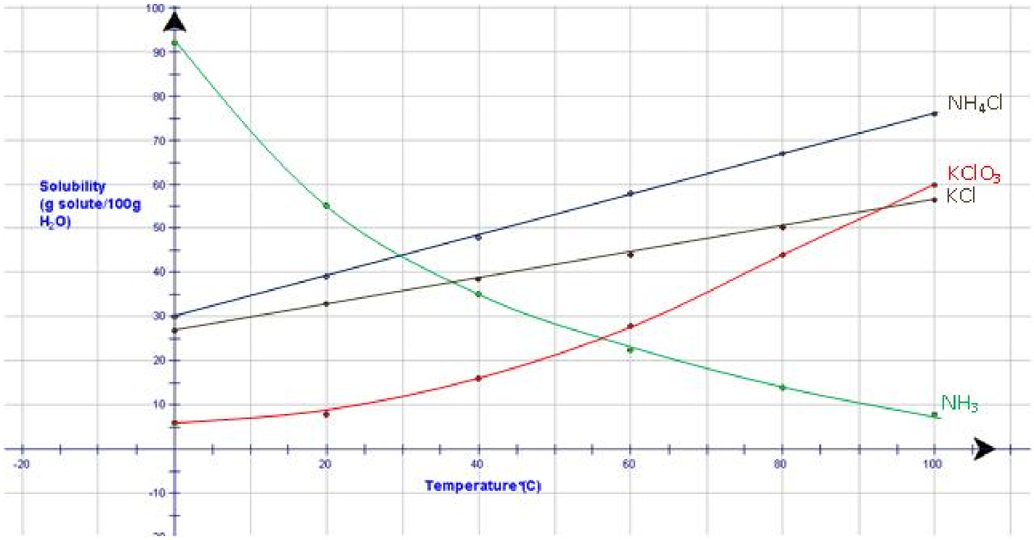
1. Using the graph below, determine: **(Beginning)**

(a) How much ammonia will dissolve at 30 ºC?

(b) What solid is more soluble at 50 ºC?

(c) What solid is least soluble at 60 ºC?

(d) At what temperature will 50 g of ammonium chloride dissolve in 100 g of water?



2. Why are solubility graphs useful? **(Intermediate)**

3. Define solubility and solubility graph. **(Beginning)**

4. How many grams of NaCl are in 450 g of water at $30^{o}C$ if the solubility is 39.8 g per 100 g of water? **(Intermediate)**

(a) 8.84 g

(b) 39.8 g

(c) 100 g

(d) 179 g

5. How many moles of ammonium chloride are in 225 g of water at 40°C if the solubility is 45.8 g per 100 g of water? **(Intermediate)**

(a) 0.86 mol

(b) 1.92 mol

(c) 20.3 mol

(d) 103 mol

6. How many moles of potassium chloride are in 500 g of water at 80°C if the solubility is 51.3 g per 100 g of water? **(Intermediate)**

(a) 0.140 mol

(b) 0.688 mol

(c) 3.44 mol

(d) 10.3 mol

7. Plot the following data on a solubility graph and then answer the questions below. **(Intermediate)**

Temp (°C)	g NH_4Br /100 g H_2O	g NH_4ClO_4 /100 g H_2O	g $NaClO_3$ /100 g H_2O
0	60.0	13.0	80.0
20	75.5	23.5	98.0
40	92.0	36.8	118.0
60	107.8	51.5	143.0
80	126.0	67.9	172.0
100	146.0	87.0	207.0

a. Which substance is the most soluble at 50°C?

b. Which substance is the least soluble at 90°C?

c. What is the solubility of NH_4ClO_4 at 30°C?

d. How many grams of NH_4ClO_4 would dissolve in 250 mL at 30°C?

e. At what temperature will 20 g potassium sulfate dissolve in 100 g of water?

8. Plot the following data on a solubility graph and then answer the questions below. **(Intermediate)**

Temp (°C)	g NaCl /100 g H_2O g	K_2SO_4 /100 g H_2O	g $CuSO_4$ /100 g H_2O
0	35.7	7.4	14.3
20	36.0	11.1	20.7
40	36.5	14.8	28.7

60	37.3	18.2	40.0
80	38.1	21.4	56.0
100	39.2	24.1	80.0

a. Which substance is the most soluble at 50°C?

b. Which substance is the least soluble at 90°C?

c. What is the solubility of $CuSO_4$ at 30°C?

d. At what temperature will 20 g potassium sulfate dissolve in 100 g of water?

Vocabulary

solubility	The amount of solute that will dissolve in a given amount of solvent at a particular temperature.
solubility graph	A solubility graph is drawn to display the solubility at different temperatures. It is the mass of the solute/100g of H_2O versus temperature in °C.

Review Answers

1. (a) 45 g/100 g H_2O (b) NH_4Cl (c) NH_3 (d) 42°C

2. Answers will vary but students may describe the visual nature of the graphs and how they can be easily read to interpret how the amounts of the substance that can dissolve change with temperature or how different substances vary in solubility at a given temperature.

3. Solubility is the amount of solute that will dissolve in a given amount of solvent at a particular temperature. A solubility graph is a pictorial representation of substances solubility at specific temperatures. The solubility graph represents the data in a coherent manner.

4. (d) 179 g

5. (b) 1.92 mol

6. (c) 3.44 mol

7. Answers will vary.

8. Answers will vary.

Factors Affecting Solubility

Lesson Objectives

- Describe the factors that affect solid solubility.
- Describe the factors that affect gas solubility.

- Describe how pressure can affect solubility.

Introduction

Solubility, as we have learned, is the maximum amount of a substance that will dissolve in a given amount of solvent at a specific temperature. There are two direct factors that affect solubility, temperature and pressure. The effects of temperature on solubility can be found for both solids and gases but pressure effects are only related to the solubility of gases. Surface area, while not affecting how much of a solute will be dissolved, is a factor in how quickly or slowly the saturation point will be reached. In this section, we will explore all three of these factors and how they affect the solubility of solids and gases.

The Effect of Temperature on Solubility

As we learned in the solubility graphs from the previous section, temperature has a direct effect on solubility. For the majority of ionic solids, increasing the temperature increases how quickly that solution can be made. As the temperature increases, the particles of the solid move faster which increases the chances that they will interact with more of the solvent particles. This results in increasing the rate at which a solution occurs.

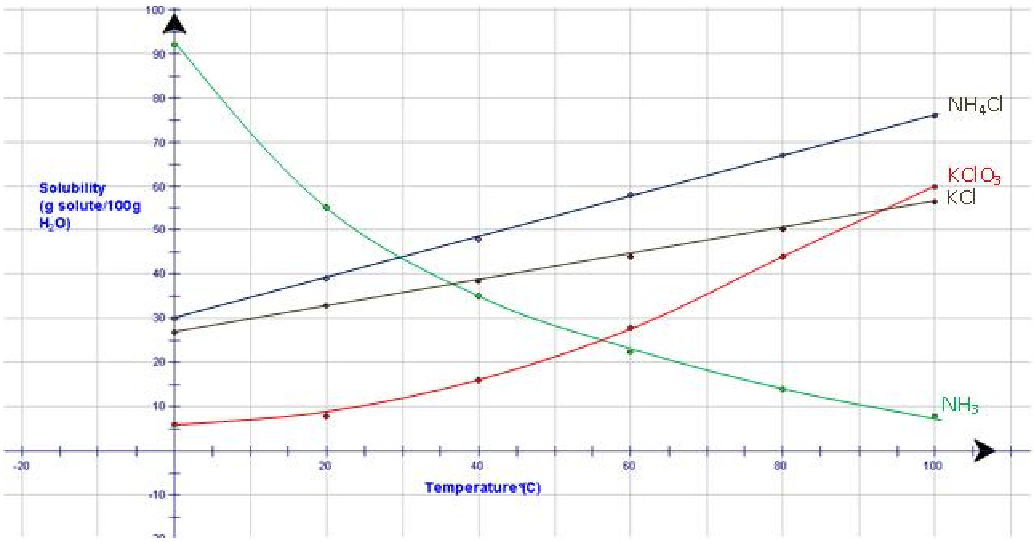
However, temperature can also increase the amount of solute that can be dissolved in a solvent. Generally speaking, as the temperature is increased, more solute particles will be dissolved. Do take note that this is a generalization but one with which you might already be familiar. For instance, when you add table sugar to water, a solution is quite easily made. When you heat that solution and keep adding sugar, you find that large amounts of sugar can be added as the temperature keeps rising. This is how candy is made. The reason this occurs is that as the temperature increases, the intermolecular bonds can be more easily broken which allows more of the solute particles to be attracted to the solvent particles.

There are other examples, though, when increasing the temperature has very little effect on how much solute can be dissolved. Table salt is a good example: you can dissolve just about the same amount of table salt in ice water as you can in boiling water.

Chemistry often has exceptions to the rules. For all gases, as the temperature increases, the solubility decreases. Using the kinetic molecular theory to explain this phenomenon, as the temperature increases, the gas molecules move faster and are then able to escape from the liquid. Their solubility then decreases.

Look at the graph below, ammonia gas, NH_3,shows a sharp decline in solubility as the temperature increases whereas all of the ionic solids show an increase in solubility as the temperature increases.

Solubility graph for ionic solids and NH_3.



Remember from earlier chapters, that endothermic changes absorb energy and exothermic changes release energy. When gases dissolve in water, it is usually with an exothermic change. Notice that in Figure 1, the

NH_3(g) solubility decreases with temperature and as we look at the equation for the dissolution of NH_3(g), we see that it is exothermic.

$NH_{3(g)} \rightarrow NH_{3(aq)}$ + energy

A graph for the solubility of oxygen gas, O_2, would be very similar to the one for NH_3(g); in other words, oxygen gas would decrease in solubility as the temperature rises. Or, conversely, the colder the temperature, the greater amount of O_2(g) would be dissolved. This is an important environmental concept in understanding the effect of the increase in the temperature in the world's oceans and its effect on the oceanic life.

The Effect of Pressure

The second factor, pressure, affects the solubility of a gas in a liquid but never a solid dissolving in a liquid. When pressure is applied to a gas that is above the surface of a solvent, the gas will move into the solvent and occupy some of the spaces between the particles of the solvent. A good example is carbonated soda. Pressure is applied to force the CO_2 molecules into the soda. The opposite is also true. When the gas pressure is decreased, the solubility of that gas is decreased. One example you can think about is when you open a can of soda pop, or any carbonated beverage, for that matter. When you hear the "pop" as a can or bottle of soda pop is opened, the pressure in the soda is lowered and the gas immediately starts leaving the solution. The carbon dioxide stored in the soda is released and you see the fizzing on the surface of the liquid.

This gas pressure factor is expressed in Henry's Law. ***Henry's Law*** states that at a given temperature the solubility of a gas in a liquid is proportional to the pressure of the gas above the liquid. An example of Henry's Law occurs in SCUBA diving. As a person dives into deep water, the pressure increases and more gases are dissolved into the blood. While ascending from a deep water dive, the diver needs to return to the surface of the water at a very slow rate since all of the dissolved gases have to come out of the blood very slowly. If for some reason a person ascends too quickly, a medical emergency may occur since the gases will come out of the blood too quickly. This is called having the "bends".

Increased Surface Area Increases Rate of Dissolving

Another factor that affects the rate of solubility is the surface area of a solid. If we were to increase the surface area of a solid then it would have been broken into smaller pieces. We would do this to increase how quickly the solute would dissolve in solution. If you were to dissolve sugar in water, a sugar cube will dissolve slower than an equal amount of tiny pieces of sugar crystals. The combined surface area of all of the sugar crystals have a much greater surface area than the one sugar cube and therefore will have more contact with the water molecules. This allows the sugar crystals to dissolve much more quickly. Try it on your own and see! What other examples can you think of?

If you were working in a lab, you might be asked to make a solution of copper(II) sulfate. Copper(II) sulfate comes in several forms: one being a large beautiful blue crystal and the other ground-up blue crystals. When you set equal amounts of each of these is test tubes filled with 10 mL of water, you will notice after 5 minutes that more of the ground-up crystal will have dissolved (and the solution will be a darker blue) than the test tube with the large crystal. Or, you can take two samples of the ground-up crystal and put into separate test tubes. This time stopper one of the test tubes and carefully shake it while you let the other test tube simple sit still. Again you are increasing the surface area by increasing the how much of the ground-up crystal will come in contact with the water. The result will still be the same as before: the test tube with the greater surface area will go into solution at a faster rate. Even though maximum solubility is achieved more quickly with greater surface area, the concentration of the solute at maximum solubility will be exactly the same.

Figure 1: Crystalline copper (II) sulfate. (*Source:* http://commons.wikimedia.org/wiki/File:CuSO4.5H2O.jpg, *License:* Public Domain)

Figure 2: Powdered copper (II) sulfate. (*Source:* http://commons.wikimedia.org/wiki/File:Cupper(II)-sulfate-pentahydrate-sample.jpg, *License:* Public Domain)

Lesson Summary

- Temperature affects the solubility of both gases and solids. With solids, generally the solubility increases with increasing temperature. With gases, the solubility tends to decrease with increasing temperature.
- Pressure only affects the solubility of gases. Henry's Law states that at a given temperature the solubility of a gas in a liquid is proportional to the pressure of that gas.
- Increasing the surface area increases the rate of solubility of a solid because a larger number of molecules of the greater surface area have contact with the solvent.

Review Questions

1. What are the factors that affect solubility? **(Intermediate)**

2. What is Henry's Law? **(Beginning)**

3. Is it ever possible to have ionic solids decrease solubility with increasing temperature? **(Intermediate)**

4. What factor would affect the solubility of sodium sulfate? **(Intermediate)**

I: temperature

II: pressure

III: surface area

(a) I, II, and III

(b) I and II

(c) I and III

(d) II and III

5. What factor would affect the solubility of methane? **(Intermediate)**

I: temperature

II: pressure

III: surface area

(a) I, II, and III

(b) I and II

(c) I and III

(d) II and III

6. If you crush a cube a sugar before putting it in your cup of coffee, how have you affected its solubility? **(Intermediate)**

(a) Crushing it has really no affect on solubility because we have not heated it at all.

(b) Crushing it has increased the surface area so it speeds up the dissolving process but doesn't change maximum solubility.

(c) Crushing it has really no affect on solubility because we have not stirred it at all.

(d) Crushing it has increased the surface area so it increases the maximum solubility.

7. Why do people add chlorine to their swimming pools on a hot day? **(Intermediate)**

8. Explain why crushed table salt at room temperature dissolves faster than rock salt. **(Intermediate)**

9. Under which of the following sets of conditions would the solubility of $CO_{2(g)}$ be lowest? The pressure given is the pressure of $CO_{2(g)}$ above the solution. **(Intermediate)**

A. 5.0 atm and 75°C

B. 1.0 atm and 75°C

C. 5.0 atm and 25°C

D. 1.0 atm and 25°C

E. 3.0 atm and 25°C

10. An aqueous solution of KCl is heat from 15°C to 85°C. Which of the following properties of the solution remain the same? **(Challenging)**

I. molality

II. molarity

III. density

A. I only B. III only C. I and II only D. II and III only E. I, II, and III

Vocabulary

Henry's Law	At a given temperature the solubility of a gas in a liquid is proportional to the pressure of that gas.

Review Answers

1. The factors that affect solubility are temperature, pressure, and surface area. The solubility of ionic solids is affected by temperature. In most cases, it increases with increasing temperature. The solubility of gases is affected by pressure. In most cases it increases with increasing pressure. Surface area is an indirect factor on solubility in that by increasing the surface area, you are decreasing particle size and therefore increasing the ability to dissolve.

2. Henry's Law is a law that states that a given temperature the solubility of a gas in a liquid is proportional to the pressure of that gas. It is important for calculating the change in concentration of the gas at different pressures. It is also the law that is used to explain the "bends" experienced by divers.

3. Yes it is. With any general rule, there are always exceptions. Na_2SO_4 is one example of an ionic solid that decreases solubility with increasing temperature.

4. (c) I and III

5. (b) I and II

6. (b)

7. Chlorine decreases solubility with increasing temperature and chlorine is added to pools to kill bacteria. If the temperature of the water increases because of a really hot day, the chlorine will come out of solution and result in an increase in bacteria in the pool.

8. Crushed table salt has a greater surface area than rock salt.

9. C (high pressure and low temperature favor gas solubility)

10. A (changing temperature changes volume; of these three properties, only molality has no volume measurement)

Colligative Properties

Lesson Objectives

- Describe vapor pressure lowering.
- Define boiling point elevation and freezing point depression.
- Describe what happens to the boiling points and freezing points when a solute is added to a solvent.
- Describe the importance of the van't Hoff factor.
- Calculate the boiling point elevation for electrolyte and non-electrolyte solutions.

- Calculate the freezing point depression for electrolyte and non-electrolyte solutions.

Introduction

Pure solvents and solutions of solutes in solvents vary in their boiling points and freezing points. People who live in colder climates have seen the trucks put salt on the roads when snow or ice is forecast. Why do they do that? When planes fly in cold weather, the planes need to be de-iced before liftoff. Why is that done? In this lesson you will learn why these events occur. You will also learn to calculate exactly how much of an effect a specific solute can have on the boiling point or freezing point of a solution.

Vapor Pressure Lowering

In the chapter on liquids, you studied the concept of vapor pressure for liquids. An enclosed liquid will reach a vapor pressure equilibrium with its vapor in the space above the liquid and this vapor pressure depends on the temperature of the liquid. This vapor pressure equilibrium is reached when the rate of evaporation and the rate of condensation become equal. Raising the temperature increases the rate of evaporation and therefore, increases the vapor pressure of the liquid. When the temperature of the liquid becomes high enough for the vapor pressure to equal the surrounding pressure, the liquid will boil. When the surrounding pressure is 1.00 atm, the boiling point is called the "normal" boiling point.

A pure liquid solvent, at normal atmospheric pressure, cannot have its temperature raised above the normal boiling point because at the normal boiling point, all of the liquid will vaporize before the temperature will increase.

Adding a solute to a solvent lowers the vapor pressure of the solvent. There are two suggested explanations for why the addition of a solute lowers the vapor pressure of a solution. Since they seem equally valid, both will be presented here.

Remember that only the molecules on the surface of a liquid are able to evaporate.

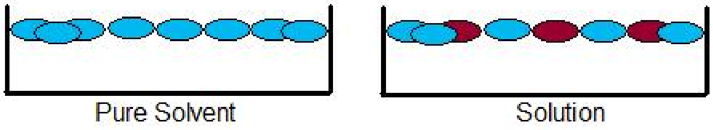


Figure 1: Pure solvent particles versus intermixed solute particles.

(*Created by:* Richard Parsons, *License:* CC-BY-SA)

In a pure solvent, all the molecules at the surface are solvent molecules. Therefore, the entire surface area is available for evaporation and the forces to be overcome are the attractive forces between the solvent molecules. One of the explanations says that in a solution, some of the surface molecules are solute molecules and since these solute molecules take up some of the surface area, less surface area is available for evaporation. Therefore, the rate of evaporation of the solvent will be lower and so the vapor pressure will be lower at the same temperature. The other explanation says that the attractive forces between the solvent molecules and the solute molecules are greater than the attractive forces between solvent molecules and therefore, the solvent molecules will not evaporate at as high a rate. Once again vapor pressure will be lowered. Both explanations start with the same premises and end with the same result so there doesn't seem to be a reason to choose between them.

The amount of vapor pressure lowering is related to the molal concentration of the solute. Suppose a pure solvent has a vapor pressure of 20. mm of Hg at a given temperature. Suppose further that sufficient non-electrolyte solvent is dissolved in the solvent to make a 0.20 m solution and that the vapor pressure of the solution at the same temperature is 18 mm of Hg. Then, if enough solute is dissolved to make the solution 0.40 m, the vapor pressure of the more concentration solution will be 16 mm of Hg. There is a direct mathematical relationship between the molality of the solution and the vapor pressure lowering.

Experiments with this phenomenon demonstrate that as long as the solute is a non-electrolyte, the effect is the same regardless of what solute is used. The effect is related only to the number of particles of solute, not the chemical composition of the solute. That is the definition of the term ***colligative properties*** ; properties that are due only to the number of particles in solution and not related to the chemical properties of the solute. Any polar, non-ionic solid used to make a 0.20 m solution would cause the exact same vapor pressure lowering.

Boiling Point Elevation

The boiling point of a liquid occurs when the vapor pressure above the surface of the liquid equals the surrounding pressure. We know that water boils at 100°C at 1 atm but a solution of salt water does not. When table salt is added to water the resulting solution has a higher boiling point because the salt causes the vapor pressure of the solvent to lower. The ions form an attraction with the solvent particles which then prevent the water molecules from going into the vapor phase. Pure water at 100°C has a vapor pressure of 1.00 atm and since the surrounding pressure is 1.00 atm, the pure water boils at this temperature. If some quantity of table salt is added to the water, the vapor pressure of the solution at 100°C might be only 0.98 atm. Therefore, the salt water solution will not boil at 100°C. In order to cause the salt water solution to boil, the temperature must be raised above 100°C in order to get the vapor pressure up to 1.00 atm and allow the solution to boil. This is true for any solute added to a solvent; the boiling point of the solution will be higher than the boiling point of the pure solvent (without the solute). The ***boiling point elevation*** is the difference in the boiling points of the pure solvent and the solution.

The boiling point elevation due to the presence of a solute is also a colligative property. That is, the amount of change in the boiling point is related to number of particles of solute in a solution and is not related to chemical composition of the solute. A 0.20 m solution of table salt and a 0.20 m solution of hydrochloric acid would have the same effect on the boiling point.

Freezing Point Depression

The effect of adding a solute to a solvent has the opposite effect on the freezing points of a solution as it does on the boiling point. A solution will have a **lower** freezing point than a pure solvent. The freezing point is the temperature at which the liquid changes to a solid. At a given temperature, if a substance is added to a solvent (such as water), the solute-solvent interactions prevent the solvent from going into the solid phase. The solute-solvent interactions require the temperature to decrease further in order to solidify the solution. A common example is found when salt is used on icy roadways. Here the salt is put on the roads so that the water on the roads will not freeze at the normal 0°C but at a lower temperature, under ideal conditions to as low as -9°C. The de-icing of planes is another common example of freezing point depression in action. A number of solutions are used but commonly a solution such as ethylene glycol, or a less toxic monopropylene glycol, is used to de-ice an aircraft. The aircrafts are sprayed with the solution in weather conditions suspected of dropping below the freezing point. The ***freezing point depression*** is the difference in the freezing points of the solution from the pure solvent.

Mathematics of Boiling Point and Freezing Point Changes

The boiling point of a solution is higher than the boiling point of a pure solvent and the freezing point of a solution is lower than the freezing point of a pure solvent. However, the amount to which the boiling point increases or the freezing point decreases depends on the amount solute that is added to the solvent. A mathematical equation is used to calculate the difference in difference of the boiling point elevation or the freezing point depression. The boiling point elevation is the difference between the boiling points of the pure solvent and the solution. Remember the solution has a higher boiling point so to find the boiling point elevation you would subtract the boiling point of the solvent from the boiling point of the solution. For example, the boiling point of pure water at 1.0 atm is 100.°C while the boiling point of a 2% salt water solution is about 102°C. Therefore, the boiling point elevation would be 2°C. The freezing point depression is the difference in the freezing points of the solution from the pure solvent. Remember that the solution has a lower freezing point so the freezing point depression is found by subtracting the freezing point of the solution from the freezing point of the pure solvent.

Both the boiling point elevation and the freezing point depression are related to the molality of the solutions. Looking at the formulas for the boiling point elevation and freezing point depression, we can see similarities between the two.

$\Delta T_b = K_b m$	$\Delta T_f = K_f m$
where: ΔT_b = T (pure solution) – T (pure solvent)	ΔT_f = T (pure solvent) – T (pure solution)
K_b = boiling point elevation constant	K_f = freezing point depression constant
m = molality of the solution	m = molality of the solution

The boiling point constants and freezing point constants are different for every solvent and are determined experimentally in the lab. You can find these constants for hundreds of solvents listed in data reference publications for chemistry and physics.

Sample question 1: Antifreeze is used in automobile radiators to keep the coolant from freezing. In geographical areas where winter temperatures go below the freezing point of water, using pure water as the coolant could allow the water to freeze. Since water expands when it freezes, freezing coolant could crack engine blocks, radiators, and coolant lines. The main component in antifreeze is ethylene glycol, $C_2H_4(OH)_2$. If the addition of an unknown amount of ethylene glycol to 150 g of water dropped the freezing point of the solution by -1.86°C, what mass of ethylene glycol was used? The freezing point constant, K_f for water is -1.86°C/m.

Solution:

$$\Delta T_f = K_f m$$

$$m = \frac{\Delta t_f}{K_f} = \frac{-1.86^\circ C}{-1.86^\circ C/m} = 1.00\ m$$

$$m = \frac{\text{mols solute}}{\text{kg solvent}}$$

moles solute = (molality)(kg solvent) = (1.00 mol/kg)(0.150 kg) = 0.150 mol

mass $C_2H_4(OH)_2$ = (mols)(molar mass) = (0.150 mol)(62.1 g/mol)

mass $C_2H_4(OH)_2$ = 9.3 g

Therefore 9.3 g of ethylene glycol would have been added to the 150. g of water to lower the freezing point by 1.86°C.

One factor that must be considered when using these formulas is to first determine whether or not the solution is an electrolyte or a non-electrolyte.

Recall that an electrolyte solution is one where the solute will separate into ions and is thus able to conduct electricity (hence the term electrolyte). If, for example, you have a solution of sodium chloride, the sodium chloride separates into sodium ions and chloride ions. A non-electrolyte solution does not separate into ions and therefore does not conduct electricity. For example a sugar/water solution stays as sugar + water with the sugar molecules staying as molecules.

Remember that colligative properties are due to the number of solute particles in the solution. Adding 10 molecules of sugar to a solvent will produce 10 solute particles in the solution. When the solute is an electrolyte, such as NaCl however, adding 10 molecules of solute to the solution will produce 20 ions (solute particles) in the solution. Therefore, adding enough NaCl solute to a solvent to produce a 0.20 m solution **will have twice the effect** of adding enough sugar to a solvent to produce a 0.20 m solution. It is the number of solute particles in the solution that control the colligative properties.

To add this “electrolyte” factor into the formulas above, we use a concept called the **van't Hoff factor**, symbolized by the letter *i*. The van't Hoff factor is the number of particles that the solute will dissociate into upon mixing with the solvent. For example, sodium chloride, NaCl, will dissociate into two ions so the van't Hoff factor for NaCl is *i* = 2, for lithium nitrate, $LiNO_3$, *i* = 2, and for calcium chloride, $CaCl_2$, *i* = 3.

We can now rewrite our colligative properties formulas and include the van’t Hoff factor.

$\Delta T_b = iK_bm$	$\Delta T_f = iK_fm$
where: ΔT_b = T (pure solution) – T (pure solvent)	ΔT_f = T (pure solvent) – T (pure solution)
i = van’t Hoff factor	*i* = van’t Hoff factor
K_b = boiling point elevation constant	K_f = freezing point depression constant
m = molality of the solution	m = molality of the solution

Why can we use this formula for both electrolyte and non-electrolyte solutions? Since the van’t Hoff factor for non-electrolytes is always 1 (because they do not dissociate), *i* is always equal to 1.

Sample question 2: A solution of 10.0 g of sodium chloride is added to 100.0 g of water in an attempt to elevate the boiling point. What is the boiling point of the solution?

Solution:

$\Delta T_b = iK_bm$

$$\text{mols NaCl} = \frac{\text{grams}}{\text{molar mass}} = \frac{10.0\ \text{g}}{58.5\ \text{g/mol}} = 0.171\ \text{mols}$$

$$\text{molality} = \frac{\text{mols solute}}{\text{kg solvent}} = \frac{0.171\ \text{mol}}{0.100\ \text{kg}} = 1.71\ \text{m}$$

For NaCl, *i* = 2 $(NaCl \rightarrow Na^+ + Cl^-)$

K_b (water) = 0.52°C/m

$\Delta T_b = iK_bm$

$\Delta T_b = (2)(0.52^\circ C/m)(1.71m)$

$\Delta T_b = 1.78^\circ C$

T_b (solution) = T_b (pure solvent) + ΔT_b

T_b (solution) = 100°C + 1.78°C = 101.78°C.

Therefore the boiling point of the solution of 10 g of NaCl in 100 g of water is 102°C.

Lesson Summary

- Boiling points of solutions are higher that the boiling points of the pure solvents. Freezing points of solutions are lower than the freezing points of the pure solvents. Boiling point elevation is the difference between the boiling points of the pure solvent and the solution. The boiling point elevation can be calculated using the formula $\Delta T_b = K_b m$, where ΔT_b is the boiling point elevation, K_b is the boiling point elevation constant, and m is molality.
- Freezing point depression is the difference between the freezing points of the solution and the pure solvent. The freezing point depression can be calculated using the formula $\Delta T_f = K_f m$, where ΔT_f is the freezing point depression, K_f is the freezing point depression constant, and m is molality.
- For electrolyte solutions, the van't Hoff factor is added to account for the number of ions that the solute will dissociate into in solution. For non-electrolyte solutions, the van't Hoff factor = 1. The equations change to account for this factor ($\Delta T_b = K_b m$ becomes $\Delta T_b = iK_b m$ and $\Delta T_f = K_f m$ becomes $\Delta T_f = iK_f m$, where *i* is the number of particles each solute molecule produces in solution.

Review Questions

1. What must be measured in order to determine the freezing point depression? **(Intermediate)**

2. From a list of solutions with similar molalities, how could you quickly determine which would have the highest boiling point? **(Intermediate)**

3. Why would table salt not be a good solution to use when deicing a plane? **(Intermediate)**

4. When a solute is added to a solution: **(Intermediate)**

I: the boiling point increases.

II: the boiling point decreases.

III: the freezing point increases.

IV: the freezing point decreases.

(a) I and III are true

(b) I and IV are true

(c) II and III are true

(d) II and IV are true

5. If 25.0 g of sucrose ($C_{12}H_{22}O_{11}$) is added to 500 g of water, the boiling point is increased by what amount? (K_b (water) = 0.52°C/m) **(Intermediate)**

(a) 0.076°

(b) 0.025°

(c) 26°

(d) None of these

6. The solubility of seawater (an aqueous solution of NaCl) is approximately 0.50 m. Calculate the freezing point of seawater. (K_f (water) = 1.86°C/m) **(Intermediate)**

(a) -0.93°

(b) 0.93°

(c) 1.86°

(d) -1.86°

7. Determine which of the following solutions would have the lowest freezing point. **(Intermediate)**

a. 15 g of ammonium nitrate in 100 g of water.

b. 50 g of glucose in 100 g of water.

c. 35 g of calcium chloride in 150 g of water.

8. A 135.0 g sample of an unknown nonelectrolyte compound is dissolved in 725 g of water. The boiling point of the resulting solution was found to be 106.02°C. What is the molecular weight of the unknown compound? **(Challenging)**

9. What is the van't Hoff factor for each of the following: **(Intermediate)**

a. $MgCl_2$

b. Ammonium sulfate

c. CH_3OH

d. Potassium chloride

e. KCH_3COO

10. Calcium chloride is known to melt ice faster than sodium chloride but is not used on roads because the salt itself attracts water. If 15 g of $CaCl_2$ was added to 250 g of water, what would be the effect on the freezing point of the solution? (K_f (water) = -1.86°C/m) **(Intermediate)**

Vocabulary

boiling point elevation	The difference in the boiling points of the pure solvent from the solution.
freezing point depression	The difference in the freezing points of the solution from the pure solvent.
Van't Hoff factor	The number of particles that the solute will dissociate into upon mixing with the solvent

Review Answers

1. The freezing point depression is found using the formula: $\Delta T_b = iK_b m$ K_b is a constant so it is not "measured" but is known. *i* is found by knowing first if the solute is an electrolyte or a non-electrolyte and then if an electrolyte, how many particles it forms in solution.

What is left is m. In order to calculate m, we need the **moles** of solute and the **kilograms** of solvent. The moles of solute are equivalent to the **grams** of solute divided by the molar mass. Since molar mass is another constant, what needs to be measured is the number of grams of solute and the number of kilograms of solvent.

2. Adding a solute to a pure solution increases the boiling point. This is calculated using the formula $\Delta T_b = iK_b m$. With similar molalities, and since K_b is a constant for the solvent, the determining factor for the difference in the boiling point elevation would be the van't Hoff Factor. Thus the greater the number for *i*, the higher the boiling point.

3. Salt causes corrosion of metal. Since many of the planes landing pieces etc. are made of metal, a solution of salt would cause damage to the planes structural integrity. Therefore they use an alternative solution that does the same job of lowering the freezing point.

4. (b) I and IV are true

5. (a) 0.076°

6. (d) -1.86°

7.

a)

mols $NH_4NO_3 = \frac{15\ \text{g}}{80.0\ \text{g/mol}} = 0.187$ mol

molality $= \frac{0.187\ \text{mol}}{0.100\ \text{kg}} = 1.87$ m

$\Delta t_f = iK_f m = (2)(-1.86^\circ\text{C/m})(1.87\ \text{m}) = -6.96^\circ\text{C}$

Solution freezing point $= 0^\circ\text{C} - 6.3^\circ\text{C} = -6.96^\circ\text{C}$

(b) -5.15°C

(c) -11.7°C

Therefore the calcium chloride (solution c) would have the lowest freezing point.

8.

$\Delta t_b = 106.02^\circ\text{C} - 100.00^\circ\text{C} = 6.02^\circ\text{C}$

$\Delta t_b = iK_b m$ so

$m = \frac{\Delta t_b}{iK_b} = \frac{6.02^\circ\text{C}}{(1)(0.52^\circ\text{C/m}} = 11.6$ m

mols solute = (molality)(kg solvent) = (11.6 m)(0.725 kg) = 8.41 mols

molar mass $= \frac{\text{grams}}{\text{mols}} = \frac{135\ \text{g}}{8.41\ \text{mols}} = 16.1$ g/mol

9. (a) 3 (b) 3 (c) 1 (d) 2 (e) 2

10.

mols $CaCl_2 = \frac{15 \text{ g}}{111 \text{ g/mol}} = 0.135$ mol

molality $= \frac{0.135 \text{ mol}}{0.250 \text{ kg}} = 0.540$ m

$\Delta T_f = iK_fm = (3)(-1.86^\circ C/m)(0.540 \text{ m}) = -3^\circ C$

Solution freezing point $= 0^\circ C - 3^\circ C = -3^\circ C$

Colloids

Lesson Objectives

- Define colloids and suspensions.
- Compare solutions, colloids, and suspensions.
- Characterize solutions as suspensions, colloids, or solutions.
- Name some common examples of colloids.

Introduction

In this final section regarding solution chemistry, we will take a look at colloids and suspensions; two different types of mixtures that are not classified as true solutions. Following this, a look at the different types of colloids in terms of the solute/solvent combinations will be examined to see how we have many examples in our everyday lives. Do you know that the majority of our encounters with mixtures are actually colloids? Think of that the next time you drink a glass of milk, put whipping cream on your dessert, look up at the clouds, or add some butter to your toast!

Comparison of Suspensions, Colloids and Solutions

We learned early in the chapter that a solution is a mixture of substances in such a way that the final product has the same composition throughout. Remember the example of vinegar that is 5%, by mass, acetic acid in water. This clear liquid is a solution since light easily passes through it and it never separates.

On the other hand, ***colloids*** are mixtures in which the size of the particles is between 1×10^3 pm and 1×10^6 pm. In meters, these sizes translate to 1×10^{-9} m to 1×10^{-6} m; a small grain of sand has a diameter of 2×10^{-5} m. A common example for a colloid is milk. One way to tell that milk is a colloid is to test it using the Tyndall Effect. The ***Tyndall effect*** involves shining a light through the mixture: when the light is not allowed to pass through the mixture, that is, the light is scattered, the mixture is considered a colloid. This is why milk appears “cloudy” – or what we think of as “milky”. In contrast, when light is passed through a true solution, the particles in solution are so small [atoms, ions, small molecules] that they do not obstruct the light. However, when light is passed through a colloid, since the particles are larger, they will act as an obstruction to the light and the light is scattered. However, these particles, while able to scatter light, are still small enough so that they do not settle out of solution.

In contrast, ***suspensions*** are mixtures where the particles settle to the bottom of the container which means that the particles in a suspension are large enough so that gravity pulls them out of solution. With suspensions, filtration is usually able to be used to separate the excess particles from the solution. A common example of a suspension is muddy water. If you had a beaker of water and added a handful of fine dirt, even if you stirred it (making a colloid type solution), letting it stand, dirt would settle to the bottom.

Many Common Products Are Colloids

It is amazing just how common colloids are to us in our everyday lives. In our earlier lessons we discussed solutes and solvents and what types of solutions formed as a result. In this final section of this final lesson, let's do the same process. Let's look at a table of some common colloid products that are formed when different phase solutes and solvents are mixed.

	Solid Solvent	Liquid Solvent	Gas Solvent
Solid Solute	Ruby, brass, steel	Butter, cheese, mustard, Jell-O	Marshmallow
Liquid Solute	Paint, milk of magnesia	Milk, Mayonnaise, Creams (i.e. face creams)	Whipping Cream, Shaving Cream
Gas Solute	Airborne viruses, car exhaust, smoke	Fog, Smoke, Clouds,	Aerosol Sprays

Lesson Summary

Colloids are mixtures in which the size of the particles is between 1×10^3 pm and 1×10^6 pm. Suspensions are mixtures in which the particles are large enough so that they settle to the bottom of the container and can be filtered using filter paper. The Tyndall effect involves shining a light through the mixture, if the light scatters, the mixture is a colloid or a suspension. Common examples of colloids include milk, butter, Jell-O, and clouds.

Review Questions

1. Distinguish between a solution, a colloid, and a suspension. **(Beginning)**

2. What is one true way to tell you have a colloid solution? **(Intermediate)**

3. Why do you think there is no example of a gas - gas colloid? **(Intermediate)**

4. Which is an example of a colloid? **(Intermediate)**

(a) air

(b) brass

(c) milk

(d) none of these

5. Which is not an example of a colloid? **(Intermediate)**

(a) human body

(b) mayonnaise

(c) mustard

(d) cloud

6. The biggest difference between a colloid and a suspension is that: **(Intermediate)**

(a) In colloids, the solute is permanently dissolved in the solvent.

(b) In colloids the particles eventually settle to the bottom.

(c) In suspensions the particles eventually settle to the bottom.

(d) None of these are correct

7. Karen was working in the lab with an unknown solution. She noticed that there was no precipitate in the bottom of the beaker even after it had been on the lab bench for several days. She tested it with a light and saw that light scattered as it passed through the solution. Karen concluded that the liquid was what type of a mixture? **(Intermediate)**

a. colloid

b. suspension

c. homogeneous

d. heterogeneous

8. What are two good common examples of colloids? **(Intermediate)**

Vocabulary

colloid	Mixtures where the size of the particles is between 1 x 10^3 pm and 1 x 10^6 pm (i.e., milk).
suspension	Mixtures where the particles settles to the bottom of the container and can be separated by filtration.
Tyndall Effect	Involves shining a light through the mixture, if the light scatters, the mixture is a colloid.

Review Answers

1. A solution is a mixture where there is constant composition throughout. A colloid is a mixture where the particle size is larger (between 1 x 10^3 pm and 1 x 10^6 pm) and the Tyndall effect scatters light when shown through it. A suspension is a solution where the particle size is so large that it can be filtered using filter paper and the particles settle to the bottom of the container.

2. Use a flashlight and test with the Tyndall effect. If the light scatters, the solution is a colloid, if not it is a pure solution.

3. Because all gas solutes are soluble in gas solvents (they would not form colloids with larger particle sizes)

4. (c) milk

5. (a) human body

6. (c) In suspensions the particles eventually settle to the bottom.

7. (a) colloid

8. (Answers will vary but Jell-O and blood are acceptable).

Separating Mixtures

Lesson Objectives

- The student will describe differences between the physical properties of pure substances and solutions.
- The student will list and describe methods of separation for mixtures.
- The student will explain the principles involved in chromatographic separation.
- The student will identify the mobile and stationary phases in a chromatography design.
- Given appropriate data, the student will calculate R_f values.

Introduction

Mixtures occur very commonly in chemistry. When a new substance is synthesized, for example, the new substance usually must be separated from various side-products, catalysts, and any excess reagent still present. When a substance must be isolated from a natural biological source, the substance of interest is generally found in a very complex mixture with many other substances, all of which must be removed. Chemists have developed a series of standard methods for the separation of mixtures. (The separation of mixtures into their constituent substances defines an entire sub-field of chemistry referred to as *separation science*.

Differing Solubilities

Mixtures of solids may often be separated on the basis of **differing solubilities** of the solids. If one of the components of the mixture is soluble in water while the other components are insoluble in water, the water-soluble component can be removed from the mixture by dissolving the mixture in water and filtering the mixture through filter paper. The component dissolved in water will pass through the filter while the undissolved solids will be caught in the filter. The solubility of substances is greatly influenced by temperature. By controlling the temperature at which solution occurs or at which the filtration is performed, it may be possible to separate the components. Most commonly, a sample is added to water and heated to boiling. The hot sample is then filtered to remove completely insoluble substances. The sample is then cooled to room temperature or below which causes crystallization of those substances whose solubilities are very temperature dependent. These crystals can then be separated by another filtration and the filtrate (the stuff that went through the filter) will then contain only those substances whose solubilities are not as temperature dependent.

Distillation

Homogeneous solutions are most commonly separated by ***distillation*** . In general, distillation involves heating a liquid to its boiling point, then collecting, cooling, and condensing the vapor produced into a separate container. For example, salt water can be desalinated by boiling off and condensing the water. *In solutions of nonvolatile solid solutes in liquid solvent, when the solution is boiled, only the solvent boils off, all the solid remains in the solution. The vapor passing off is pure solvent. As the solvent passes off and the all the solute remains behind, the same amount of solute is now dissolved in less solvent and so the concentration increases. This results in the boiling point of the solution increasing. As a solution boils, increased temperature is necessary to keep the solution boiling because its boiling point has increased. This is a quick method of determining if a liquid is a pure substance or a solution; start it boiling and if it continues to boil at the same temperature, it is a pure substance whereas if its boiling point increases, it is a solution.* For a mixture of liquids in which several components of the mixture are likely to be volatile (easily vaporized), the separation is not easy. If the components of the mixture differ reasonably in their boiling points, it may be possible to separate the mixture simply by monitoring the temperature of the vapor produced as the mixture is heated. Liquid components of a mixture will each boil in turn as the temperature is gradually increased, with a sharp rise in the temperature of the vapor being distilled indicating when a new component of the mixture has begun to boil. By changing the receiving flask at the correct moment, a separation can be accomplished. This process is known as **fractional distillation**.

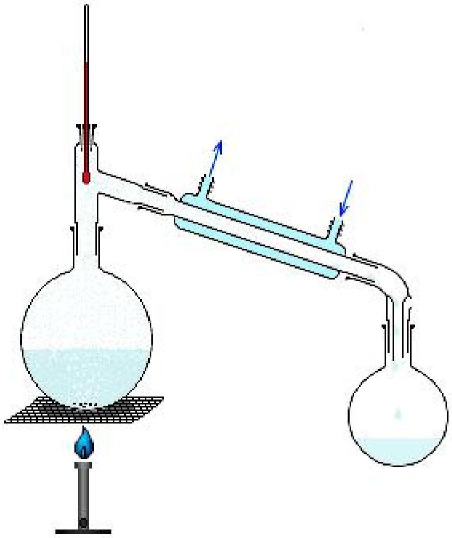


Figure 1: Distillation Apparatus (*Source:* http://wikimedia.org/wiki/File:Simple_chem_distallation, *Created by:* H Padleckas, *License:* GNU Free Documentation License.)

Chromatography

The word ***chromatography*** means *color-writing*. The name was chosen around 1900 when the method was first used to separate colored components from plant leaves. Chromatography in its various forms is perhaps the most important known method of chemical analysis of mixtures. Paper and thin-layer chromatography are simple techniques that can be used to separate mixtures into the individual components. The methods are very similar in operation and principle and differ primarily in the medium used.

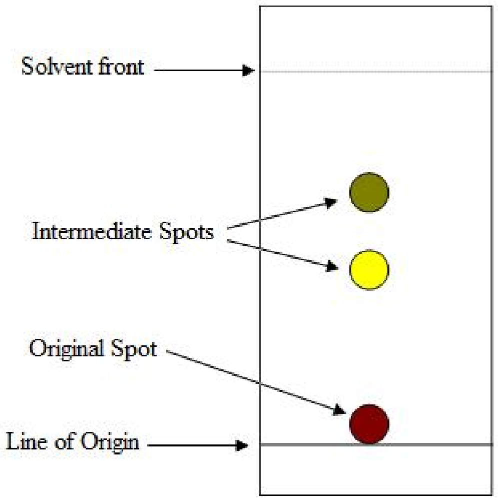


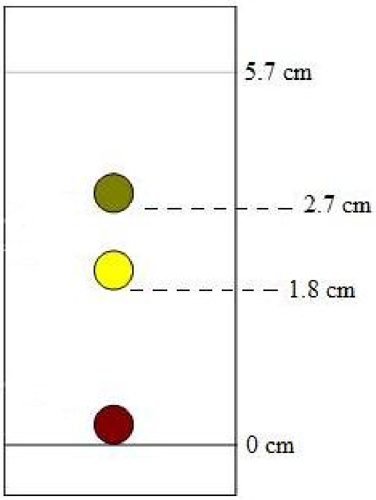
Figure 2: Paper chromatography strip (*Created by:* Richard Parsons, *License:* CC-BY-SA.)

Paper chromatography uses ordinary filter paper as the medium upon which the mixture to be separated is applied. Thin-layer chromatography (abbreviated TLC) uses a thin coating of aluminum oxide or silicagel on a glass microscope slide or plastic sheet to which the mixture is applied. A single drop of the unknown mixture to be separated is applied about half an inch from the end of a strip of filter paper or TCL slide. The filter paper or TLC slide is then placed in a shallow layer of solvent in a jar or beaker. Since filter paper or the TLC slide coating is permeable to liquids, the solvent begins rising up the paper by capillary action. As the solvent rises to the level of the mixture spot, various effects can occur, depending on the constituents of the spot. Those components of the spot that are completely soluble in the solvent will be swept along with the solvent front as it continues to rise. Those components that are not at all soluble will be left behind at the original location of the spot. Most components of the mixture will move up the paper or slide at an intermediate speed somewhat less than the solvent front speed but not remaining at the original spot either. In this way, the original spot of mixture is spread out into a series of spots or bands, with each spot representing one single component of the mixture. The separation of a mixture by chromatography is not only a function of the solubility in the solvent used. The filter paper or TLC coating consists of molecules that may interact with the molecules of mixture as they are carried up the medium. The primary interaction between the mixture components and the medium is due to the polarity of the components and that of the medium. Each component of the mixture is likely to interact with the medium to a different extent thus slowing the components of the mixture differentially depending on the level of interaction.

A quantitative basis is added to the chromatography analysis using a mathematical function call the ***retention factor*** . The retention factor, Rf, is defined as

$$\mathbf{R_f} = \frac{\textbf{distance travelled by spot}}{\textbf{distance travelled by solvent front}}$$

R_f is the ratio of the distance a substance moves up the stationary phase to the distance the solvent have moved. The retention factor depends on what solvent is used and on the specific composition of the filter paper or slide coating used. The R_f value is characteristic of a substance when the same solvent and the same type of stationary phase is used. Therefore, a set of known substances can be analyzed at the same time under the same conditions and if the same R_f value is produced for a known and unknown, it is a step toward identifying the unknown. In the case shown at right, the R_f for the green spot is



$R_f = \frac{2.7\ \text{cm}}{5.7\ \text{cm}} = 0.47$ and for the yellow spot

$$R_f = \frac{1.8\ \text{cm}}{5.7\ \text{cm}} = 0.32$$

Paper chromatography and TLC are only two examples of many different chromatographic methods. Mixtures of gases are commonly separated by ***gas chromatography***. In this method, a mixture of liquids are vaporized and passed through a long tube of solid absorbent material. A carrier gas, usually helium, is used to carry the mixture of gases through the tube. As with paper chromatography, the components of the mixture will have different solubilities and different attractions for the solid absorbent. Separation of the components occurs as the mixture moves through the tube. The individual components exit the tube one by one and can be collected.

Another form of chromatography is ***column chromatography***. In this form, a vertical column is filled with solid absorbent, the mixture is poured in at the top, and a carrier solvent is added. As the mixture flows down the column, the components are separated, again, by differing solubilities in the carrier solvent and different absorbencies to the solid packing. As the liquid drips out the bottom of the column, components of the solution will exit at different times and can be collected.

Lesson Summary

- Mixtures of solids may be separated by differing solubilities of the solids.
- Components of a solution composed of a non-volatile solid solute and a liquid solvent can be separated by distillation.
- Mixtures of liquids with reasonably different boiling points can also be separated by distillation.
- Solutions with several components can be separated by paper or thin-layer chromatography.
- Gas chromatography and column chromatography are also used to separate the components of a solution.

Review Questions

1. In a paper chromatography experiment to separate the various pigments in chlorophyll, a mixture of water and ethanol was used as the solvent. What is the stationary phase in this separation? **(Beginning)**

2. Do you think that paper chromatography or TLC would be useful for separating a very large quantity of a mixture? Explain why or why not. **(Beginning)**

3. If the mobile phase in a chromatographic experiment moved 15.0 cm and one of the compounds in the mixture moved 12.7 cm, what is the R_f value for this compound? **(Intermediate)**

4. If the stationary phase in a paper chromatography experiment was very polar and the solvent was moderately polar, would the polar components in the mixture be closer to the bottom of the paper or toward the top of the paper? **(Intermediate)**

Vocabulary

distillation	The evaporation and subsequent collection of a liquid by condensation as a means of purification.
fractional distillation	This is a special type of distillation used to separate a mixture of liquids using their differences in boiling points.
chromatography	Any of various techniques for the separation of complex mixtures that rely on the differential affinities of substances for a mobile solvent and a stationary medium

through which they pass.

Review Answers

1. the filter paper

2. Paper chromatography and TLC use small spots or single drops of mixture for separation. The process would not be functional for large quantities of material.

3. 0.847

4. Using a very polar stationary phase would tend to cause polar solutes to stay toward the bottom because they would be more attracted to the stationary phase than to the mobile phase. If the stationary phase is less polar, polar solutes will tend to move greater distances.

22. Ions in Solution

Ionic Solutions

Lesson Objectives

- Describe electrostatic attraction.
- Explain how ionic solids attract water molecules when they dissolve in water.
- Explain the difference between physical changes and chemical changes.
- Define electrolyte solutions and be able to identify electrolytes.

Introduction

Ionic solids are a particular type of substance. They form when metal ions combine with nonmetal ions, which come about through the transfer of electrons. Because of this transfer and the distinct charges that result when the metals and nonmetal ions form, ionic solids have properties that are unique to themselves. In this lesson we will begin to look at the forces that exist within the ionic solids and what happens when these solids dissolve in water. There are some new terms in this unit and a few reviewed terms that you have seen in previous units that will become clearer in this chapter.

Ions in Solids are Held With Electrostatic Attraction

In an earlier chapter you learned that metals form positive ions by losing electrons and nonmetals form negative ions by gaining electrons. When solids form from a metal atom donating an electron (thus forming a positive cation) to a nonmetal atom (thus forming a negative anion), the ions in the solid are held together by the attraction of these oppositely charges particles. The attraction of oppositely charged particles is called ***electrostatic attraction.*** For example:

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

$\text{I} + \text{e}^- \rightarrow \text{I}^- + \text{energy of electron affinity}$

$\text{Na}^+ + \text{I}^- \rightarrow \text{NaI} + \text{energy}$ (NaI is held together by electrostatic attraction)

In the world of chemical bonding, electrostatic attraction is quite strong and therefore compounds with this type of bonding have high melting points and boiling points. Take a look at the table and see how the melting points and boiling points change for ionic solids.

Compound	**Melting Point (°C)**	**Boiling Point (°C)**
$LiCl$	613	1360
$NaCl$	801	1413
KCl	772	1500
$MgCl_2$	714	1412
$CaCl_2$	772	1935

All of the compounds in the table are bonded due to the attraction of the oppositely charged ions. Look at the next examples to see lithium, sodium, and potassium chlorides.

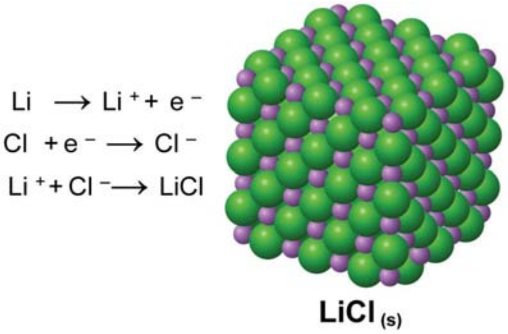


Figure 1: An example of Lithium Chloride.

(*Source:* CK-12 Foundation, *License:* CC-BY-SA)

Figure 2: An example of Sodium Chloride.

(*Source:* CK-12 Foundation, *License:* CC-BY-SA)

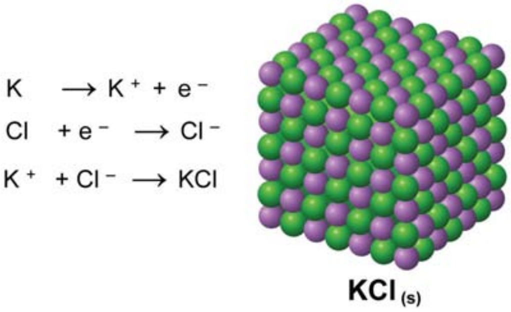


Figure 3: An example of Potassium Chloride.

(*Source:* CK-12 Foundation, *License:* CC-BY-SA)

To review from a previous chapter, ionic compounds do not form molecules. The empirical formula represents the lowest whole number ratio of the ions involved in the compound. When we interact with these substance in our environment, we detect that they are crystalline structures. As shown in the diagrams, ionic compounds are crystals that are held together by electrostatic attraction.

Sample question 1: Which compounds would contain an electrostatic attraction as bonds between ions?

(a) $MgCl_2$

(b) Al_2O_3

(c) CH_4

Solution:

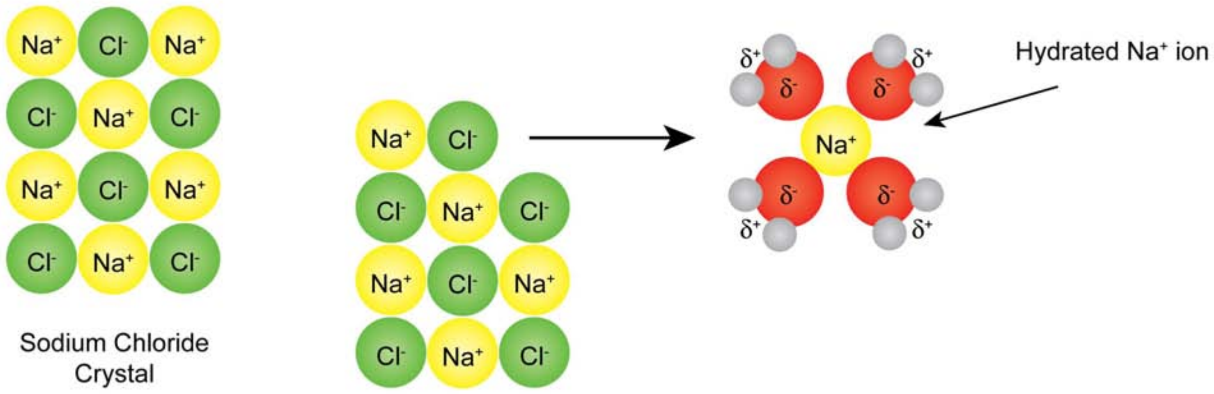
(a) and (b) would contain electrostatic attraction because they are both ionic but (c) is not. It does not form bonds by the transfer of electrons but rather by sharing electrons and therefore does not have ions for electrostatic attraction.

Ions Are Attracted to the Polar Water Molecule

Since ionic compounds can dissolve in polar solutions, specifically water, we can extend this concept to say that ions themselves are attracted to the water molecules because the ions of the ionic solid are attracted to the polar water molecule. When you dissolve table salt in a cup of water, the table salt dissociates into sodium ions and chloride ions (Equation 1).

$$NaCl(s) \rightarrow Na^{+}_{(aq)} + Cl^{-}_{(aq)}$$ (Equation 1)

The sodium ions then get attracted to the negative ends of the water molecule and the chloride ions get attracted to the positive end of the water molecule. The process of water molecules attaching to ions is called **hydration**. Look at the figure below.



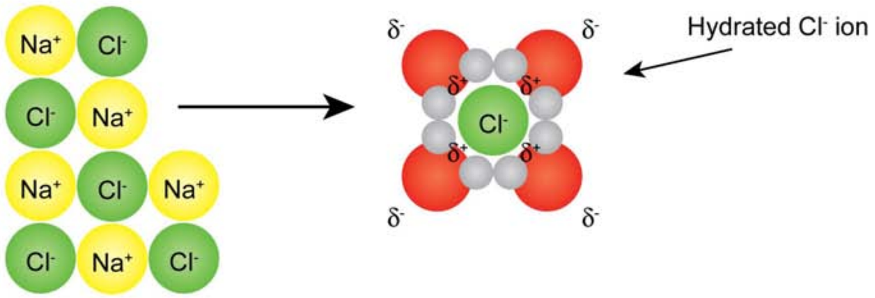


Figure 4: The dissociation and hydration of Na^+ and Cl^- in water.

(*Source*: CK-12 Foundation, *License:* CC-BY-SA)

The same is true for any ionic compound dissolving in water. The ionic compound will separate into the positive and negative ions and the positive ion will be attracted to the negative end of the water molecules (oxygen) while the negative ion will be attracted to the positive end of the water molecules (hydrogen).

Dissociation is a Physical Change

Matter can go through both chemical changes and physical changes. ***Chemical changes*** are ones that occur with the chemical bonding and a new substance or substances are formed. For example, if you add a piece of lead to a solution of silver nitrate, silver precipitates out and lead nitrate is formed (Equation 2).

$$Pb_{(s)} + 2\ AgNO_{3(aq)} \rightarrow 2\ Ag_{(s)} + Pb(NO_3)_{2(aq)} \qquad \text{(Equation 2)}$$

Of importance to us in this unit are physical changes. ***Physical changes*** are those that occur in the physical state of the substance but do not affect the identity of the substance. For example, grinding a sugar cube is a physical change or dissolving table salt in water; the sugar is still sugar and the table salt is still table salt. Look at the reaction for the dissolving of copper(II) sulfate in water (Equation 4).

$$CuSO_{4(s)} \rightarrow Cu^{2+}{}_{(aq)} + SO_4{}^{2-}{}_{(aq)} \qquad \text{(Equation 4)}$$

We begin with copper(II) sulfate as a solid that contains Cu^{2+} ions and $SO_4{}^{2-}$ ions and it produces Cu^{2+} ions and $SO_4{}^{2-}$ ions in solution. We dissolved a sample of $CuSO_4$ in a beaker of water. If we look at this change, we may first think it is a chemical change because we might think that we have new substances being formed. But realistically, if we boiled off the water containing the dissolved copper (II) sulfate ions, the $CuSO_4$(s) would remain in the beaker. In other words, we can regain our original starting material by a simple physical change, that is, evaporation. Think of the crystal of copper(II) sulfate as a combination of the Cu^{2+} ions and $SO_4{}^{2-}$ ions that have taken position and then when dissolved in water, lose their position. When the water is evaporated, they regain their position. Then the dissolving of an ionic solid seems more like a physical change.

Sample question: Which of the following are physical changes?

(a) burning paper

(b) melting wax

(c) evaporating water

Solution:

(a) burning paper is a chemical change (new substances are produced)

(b) melting wax and (c) evaporating water are physical changes as no new substances are produced. (both involve a change in state)

Solutions of Electrolytes Can Conduct Electricity

When we started this lesson we said that ionic compounds are held together by electrostatic attraction. Arrhenius in the late 1800s first thought that when these ionic compounds dissolved in water, they separated from each other into ions and classified them as ***electrolytes.*** Since they could conduct electricity in water solution, they are considered electrolytes. According to Arrhenius (and current theory – pardon the pun!), the ions in solution provided the charged particles needed to conduct electricity. Look at the equation below for the dissociation of NaCl.

$NaCl_{(s)} \rightarrow Na^{+}_{(aq)} + Cl^{-}_{(aq)}$

The sodium and chlorine ions are present in the crystal. But once the solid NaCl is added to the water, it dissolves, which means that the ions move away from their crystalline structure and are now dispersed throughout the water molecules. If two electrodes were to be immersed into a solution of NaCl(aq), the Na^{+}(aq) ions would move toward one electrode and the Cl^{-}(aq) ions would move toward the second electrode. This movement of the ions allows the electric current to flow through the solution. Therefore, NaCl(aq) will behave as an electrolyte and conduct electricity because of the presence of Na^{+}(aq) and Cl^{-}(aq) ions. The more ions that are present in solution when the salt dissolves, the stronger the electrolyte solution is.

Sample question: Which of the following will form electrolyte solutions and conduct electricity?

(a) CaF_2 (aq)

(b) $C_6H_{12}O_6$ (aq)

(c) KOH (aq)

Solution:

(a) and (c) are solutions that contain positive cations and negative anions that would separate when dissolved in water. Since ions are separated in solution, they are electrolytes and will conduct electricity.

$CaF_2(s) \rightarrow Ca^{2+}(aq) + 2F^{-}(aq)$

Calcium fluoride

$KOH(s) \rightarrow K^{+}(aq) + OH^{-}(aq)$

Potassium hydroxide

(b) Is not an ionic compound but a covalent compound. This means that when it dissolves in water it stays together as a molecule and is a non-electrolyte

$C_6H_{12}O_6(s) \rightarrow C_6H_{12}O_6(aq)$

Glucose separate glucose molecules

Lesson Summary

- Electrostatic attraction describes the bonding that occurs between the ions of ionic solids. Because of the strong electrostatic attraction in ionic solids, ionic compounds tend to have high melting points and boiling points.

- Ionic compounds dissolve in polar solvents, especially water. This occurs when the positive cation from the ionic solid is attracted to the negative end of the water molecule (oxygen) and the negative anion of the ionic solid is attracted to the positive end of the water molecule (hydrogen).
- Electrolyte solutions are ones in which free-moving charged particles can conduct an electrical current.

Review Questions

1. Write the reactions for the dissolving of the following. **(Intermediate)**

(a) $NaOH_{(s)}$

(b) $LiOH_{(s)}$

(c) $C_5H_{10}O_{4\ (s)}$

(d) $NH_4Cl_{(s)}$

(e) $MgCl_{2\ (s)}$

2. Which of the following represent physical changes? Explain. **(Intermediate)**

(a) explosion of TNT

(b) dissolving KCl

(c) sharpening a pencil

(d) souring milk

3. Which compound contains electrostatic forces? **(Intermediate)**

(a) natural gas

(b) table salt

(c) air

(d) sugar

4. Which of the following is a physical change? **(Intermediate)**

a. rotting wood

b. rising of bread dough

c. rusting iron

d. molding cheese

5. Which of the following is not a physical change? **(Intermediate)**

a. melting iron

b. pumping gas

c. reaction of chlorine with sodium

d. reaction of magnesium chloride with water

6. Which compound is considered to be an electrolyte when dissolved in water? **(Intermediate)**

a. HNO_3

b. $C_{12}H_{22}O_{11}$

c. N_2O

d. CH_4

7. Which compound is not considered to be an electrolyte? **(Intermediate)**

a. AgCl

b. $PbSO_4$

c. C_2H_6

d. $HClO_3$

8. Janet is given three solutions. She is to determine if the solutions are electrolytes or not but is not told what the solutions are. She makes the following observations. What can you conclude from her observations and what help can you offer Janet to determine if the solutions are indeed electrolytes? **(Intermediate)**

Solution 1: Clear

Solution 2: Blue but transparent

Solution 3: Clear

Further Reading / Supplemental Links

http://en.wikipedia.org/wiki

Vocabulary

electrostatic attraction	When solids form from a metal atom donating an electron (thus forming a positive cation) to a non-metal (thus forming a negative anion) the two ions in the solid are held together by the attraction of oppositely charged particles.
chemical changes	Changes that occur with the chemical bonding where a new substance is formed.
physical changes	Changes that occur in the physical structure but do not occur at the molecular level.
electrolyte solutions	Solutions that contain ions that are able to conduct electricity.

Review Answers

1.

(a) $NaOH_{(s)} \longrightarrow Na^{+}{}_{(aq)} + OH^{-}{}_{(aq)}$

(b) $LiOH_{(s)} \longrightarrow Li^{+}{}_{(aq)} + OH^{-}{}_{(aq)}$

(c) $C_5H_{10}O_{4(s)} \rightarrow C_5H_{10}O_{4(aq)}$

(d) $NH_4Cl_{(s)} \rightarrow NH_4^{+}{}_{(aq)} + Cl^{-}{}_{(aq)}$

(e) $MgCl_{2(s)} \rightarrow Mg^{2+}{}_{(aq)} + 2\ Cl^{-}{}_{(aq)}$

2. Only (b) and (c) are physical changes because they do not result in a change in the bonding structure but just a change in the state of the original material. Dissolving KCl has KCl(s) going to KCl(aq), sharpening a pencil is like grinding a solid, it takes a larger piece and shaves off the outer edges to get the pointed lead pencil to work with. (a) and (c) are both chemical changes.

3. (b) table salt

4. (b) rising of bread dough

5. (c) reaction of chlorine with sodium

6. (a) HNO_3

7. (c) C_2H_6

8. Her observations are completely useless in determining if any of these solutions are electrolytes. To test to see if any of the solutions are electrolytes, you have to see if these conduct electricity. To do this, you could use a conductivity meter.

Covalent Compounds in Solution

Lesson Objectives

- Understand and describe intermolecular bonds.
- Understand why molecules stay together when dissolving in solvents.
- Understand and define non-electrolytes.

Introduction

Unlike their ionic counterparts, covalent compounds have a different type of attraction occurring between the solute and solvent molecules. As we work through this lesson, think about the periodic table and remember that covalent compounds are made up of only nonmetals. This is the foundation for the reasoning behind the way covalent compounds dissolve.

Molecules Held Together by Intermolecular Forces of Attraction

Unlike ionic bonds that transfer electrons, covalent compounds share electrons to complete an outer electron configuration. As a result there are no distinct charges associated with the atoms in covalent compounds. Look at the formula for CO_2. Carbon has 4 valence electrons and oxygen has 6 valence electrons.

C: $1s^2\ 2s^2\ 2p^2$

O: $1s^2\ 2s^2\ 2p^4$

Carbon will share four electrons with other atoms and oxygen will share two electrons with other atoms. In CO_2, each oxygen atom shares two of its electrons with carbon and the carbon shares two of its electrons with each oxygen atom. Look at the figure below.

This sharing of valence electrons represents covalent bonding. However, this sharing of electrons may not be equal sharing and in the case of carbon and oxygen, it is not equal sharing. An electronegativity table lists the electronegativities for elements in the periodic table. Elements with a greater electronegativity have a stronger attraction for shared electrons. Therefore they can pull the electrons closer to themselves and away from the element that has the more positive electronegativity. For carbon, the electronegativity value is 2.5, and for oxygen it is 3.5.

The reason that oxygen has a higher electronegativity is due to its larger nuclear charge and smaller diameter. While both carbon and oxygen have the same shielding of their nuclei, that is, $1s^2$, oxygen has eight protons in its nucleus while carbon only has six. As a result oxygen will pull any shared electrons closer to it. This pulling of electrons is what is being measured in electronegativity. The result in this molecule is that the electrons are pulled closer to oxygen than carbon and the resultant structure is represented below.

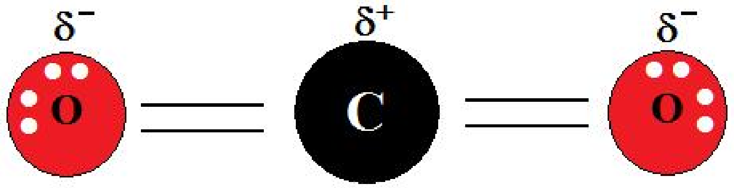


Figure 1: Polar bonds in a carbon dioxide molecule (but not a polar molecule).

(*Created by:* Richard Parsons, *License:* CC-BY-SA)

The bonding that occurs within the molecule, as we know, involves intramolecular forces. In this molecule, while the sharing of electrons inside the molecule is unequal and therefore polar, the overall result produces a non-polar molecule because the shifting of the shared electrons toward the oxygen atoms are in equal but opposite directions and there is no dipole moment on the molecule.

When we dissolve a nonpolar covalent compound, such as CO_2, in a non-polar solvent, such as benzene, the attraction between the molecules of CO_2 and C_6H_6 would be ***intermolecular forces of attraction.*** The intermolecular attractions that occur between all non-polar substances are London-dispersion forces. This similarity of intermolecular forces is what allows these two substances to form a solution.

Molecules Separate When Dissolved in Solution

When we studied how ionic solids dissolve, we said that as they dissolve in solution, these solids separate into ions. More specifically, ionic solids separate into their positive ions and negative ions in solution. The same is not true for molecular compounds. Molecular compounds are held together with covalent bonds meaning they share electrons. When they share electrons, their intramolecular bonds do not easily break apart, thus the molecules stay together even in solution. For example, when you dissolve a spoonful of sugar into a glass of water, the **intermolecular** bonds are broken but not the **intramolecular** bonds. You can write the following equation for the dissolution of sugar in water.

$C_{12}H_{22}O_{11(s)} \rightarrow C_{12}H_{22}O_{11(aq)}$ (Equation 1)

Notice how the molecules of sugar are now separated by water molecules. In other words, sugar's **intermolecular** bonds are broken but since the molecule has not broken apart, this tells us that the **intramolecular** bonds have not broken. Since sugar is a polar compound, its intermolecular bonds are dipole-dipole including some hydrogen bonding. The same is true for water and it is this similarity of intermolecular bonding that allows the sugar and water to form a solution. Also be sure to take note that the sugar did not separate into carbon ions, hydrogen ions and oxygen ions but stayed together as a sugar molecule when dissolved in water. This is characteristic of covalent compounds or compounds formed between non-metals.

Sample question: Which compounds will dissolve in solution to separate into ions?

(a) LiF

(b) P_2F_5

(c) C_2H_5OH

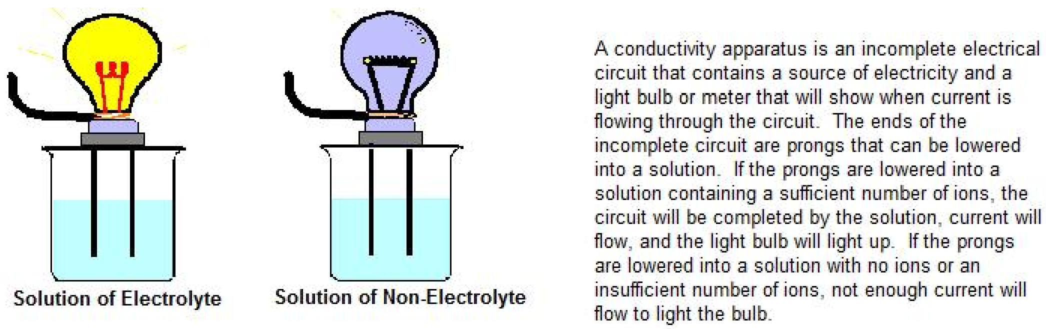
Solution:

LiF will separate into ions when dissolved in solution: $LiF(aq) \rightarrow Li^+(aq) + F^-(aq)$

P_2F_5 and C_2H_5OH are both covalent and will stay as molecules in a solution.

Non-Electrolytes

Remember that solutions of electrolytes conduct electricity and the conduction is the result of ions moving through a solution. With covalent compounds, there are no ions moving around in solution, therefore they are classified as non-electrolytes. ***Non-electrolytes*** are solutions that do not conduct electricity. If you were to connect a conductivity meter to these solutions, there would be no reading or a light would not turn on if the wires were placed in a solution containing a non-electrolyte.



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 2: Electrical conduction by an electrolyte.

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Lesson Summary

- Covalent compounds share electrons to obtain a completed outer energy level.
- Covalent compounds do not form ions in solution; they stay together as molecules. For example: $C_{12}H_{22}O_{11(s)} \rightarrow C_{12}H_{22}O_{11(aq)}$

- Non-electrolytes are solutions that do not conduct electricity.

Review Questions

1. Describe the intermolecular bonding that would occur between glucose, $C_6H_{12}O_6$, and water. **(Intermediate)**

2. Define non-electrolyte and give at least one example. **(Intermediate)**

3. How can you tell by looking at a formula that it is most likely a covalent compound? What does this tell you about the bonding? **(Intermediate)**

4. Describe how you could tell the difference between an electrolyte and a non-electrolyte solution. **(Intermediate)**

5. Looking at the periodic table, which pair of elements will form a compound that is covalent? **(Intermediate)**

a. Ca and Br

b. Fe and O

c. Si and F

d. Co and Cl

6. Which of the following compounds will conduct the least amount of electricity if dissolved in water? **(Intermediate)**

a. KNO_3

b. $BaCl_2$

c. CsF

d. CO_2

7. Steve is given five solutions in the lab to identify. He performs a conductivity test, a solubility (in water) test, crudely measures the hardness of each substance, and determines the melting point using a melting point apparatus. Some of the melting points, the teacher tells him are too high or low to measure using the laboratory melting point apparatus so she gives him the melting point. For the liquids, he determined the boiling points. He gathers all of his data and puts it into a table. His teacher gives him the names of the five solutions to match his five unknowns to. Can you help Steve match the properties of the unknowns (from the table below) to the solution names (found under the table)? **(Challenging)**

Unknown Substance	**Conductivity**	**Solubility (in water)**	**Hardness**	**Melting Point (°C)**	**Boiling Point (°C)**
1	no (aq)	soluble	semi- brittle	164	
2	yes (aq)	soluble	NA(liquid)		100
3	yes (aq)	soluble	brittle	≈ 800	
4	no (s)	insoluble	soft	82	
5	yes (s)	soluble	NA(liquid)		118

List of Unknown names: Sodium chloride

Naphthalene
Sucrose
Hydrochloric acid (dilute)
Acetic acid

8. Predict the type of bonding that will form between the elements sulfur and bromine. Will this molecule conduct electricity in water solution? **(Intermediate)**

Further Reading / Supplemental Links

http://en.wikipedia.org/wiki

Vocabulary

intermolecular bonding	The bonding that occurs between molecules.
non-electrolytes	Solutions that do not conduct electricity.

Review Answers

1. Intermolecular bonds are forces of attraction between molecules. For sugar and water, these intermolecular bonds are dipole-dipole and hydrogen bonding.

2. A non-electrolyte dissolves in a solvent and does not conduct electricity since there are no ions in solution. An example would be the glucose from question 1, or sugar and water.

3. Covalent compounds are formed between non-metals. In terms of bonding, this means that the electrons are shared rather than transferred as seen with ionic compounds.

4. Use a conductivity apparatus.

5. (c) Si and F

6. (d) CO_2

Solution 1 = Sucrose, soluble in water, it is somewhat brittle, does not conduct electricity in solution and the melting point is between 160 and 186°C.

Solution 2 = Hydrochloric acid, soluble in water, it's brittleness is undetermined since it was a liquid, conducts electricity in solution and the boiling point is 100°C (same as water since it is dilute).

Solution 3 = Sodium chloride, soluble in water, it is brittle, conducts electricity in solution and the melting point is 801°C.

Solution 4 = Naphthalene (moth balls), insoluble in water, it is brittle (flakey almost), does not conduct electricity in solution and the melting point is 80°C.

7. Solution 5 = Acetic acid, soluble in water, it's brittleness is undetermined since it was a liquid, conducts electricity in solution and the boiling point is 117°C.

8. Sulfur is in Group 6A and bromine is in group 7A, both in the non-metal side of the periodic table. Therefore the most likely compound formed would be a covalent compound. If we look at the electronegativities for sulfur and bromine we see that sulfur has an electronegativity of 2.58 and bromine has an electronegativity of 2.96. This means that the electrons are not shared equally but the electrons are held closer to bromine and bromine has a slightly negative charge. When dissolved in water, since the molecule is covalent, it will not separate into ions and will not conduct electricity.

Reactions Between Ions in Solutions

Lesson Objectives

- Use the solubility chart and/or solubility rules to determine if substances are soluble in water.
- Use the solubility chart and/or the solubility rules to determine if precipitates will form.
- Write molecular, ionic, and net ionic equations.
- Understand the use of ionic and net ionic equations.
- Identify spectator ions in ionic equations.

Introduction

Many ionic compounds are said to be soluble in water while others are said to be insoluble. However, no ionic compound is completely insoluble in water. Every ionic compound dissociates into its ions to some extent when placed in water. In fact, the solubility of ionic compounds ranges across a full spectrum from as little solubility as 1×10^{-100} moles/liter to 20 moles/liter. Most chemistry textbooks contain, somewhere in them, a chart or table of the solubility of ionic compounds. Most tables divide the ionic compounds into two groups, "soluble" or "insoluble". Some books add a third category of "slightly soluble", but this term often becomes synonymous with insoluble. It is clear that in order to take a large spectrum of solubilities and put them into two categories, a decision must be made on a dividing line. A particular solubility is chosen as the dividing line and those compounds whole solubility is below that line are called insoluble and those above the line are called soluble. It is possible to find, in different textbooks, solubility tables that disagree as to whether or not a particular substance is soluble. If one table had a dividing line of 0.10 M, silver acetate would be called insoluble whereas a slightly lower dividing line of 0.075 M would list silver acetate as soluble. So, keep in mind that sometimes, it is important to determine the actual numerical solubility of a substance instead of to rely on a chart of soluble and insoluble compounds.

When solutes are dissolved in a solution, the solution is transparent so the dissolved solute particles cannot be visually detected. If undissolved particles are present in a liquid, they form a cloudy barrier to light passing through the liquid and hence their presence can be detected visually. Eventually, the un-dissolved particles will settle to the bottom of the container and then it becomes more apparent that an undissolved solid is present.

When ionic solutions are mixed together, it is often possible to form an insoluble ionic compound even though both original compounds were soluble. For example, both silver nitrate and sodium chloride are soluble compounds. In 1.0 M solution of these substances, the compounds would be completely dissociated. One solution would contain Ag^+ and NO_3^- ions and the other solution would contain Na^+ and Cl^- ions. When these two solutions are poured together, all of these ions move around in the solution and come into contact with each other. If a sodium ion temporarily attaches to either a chloride ion or a nitrate ion, nothing happens because sodium ions are soluble with both these ions and the ions would simply re-dissociate. If a silver ion temporarily joins a nitrate ion, nothing happens because silver nitrate is soluble. But, when a silver ion comes into contact with a chloride ion, the two ions join together permanently because silver chloride is not soluble. When a silver ion combines with a chloride ion, they form an insoluble solid particle that will not dissolve. Therefore, when two solutions are mixed, a cloudy, non-transparent substance forms and eventually this substance will settle to the bottom of the container. When a non-soluble substance is formed in a solution, it is called a **precipitate**, and the process is called **precipitation**.

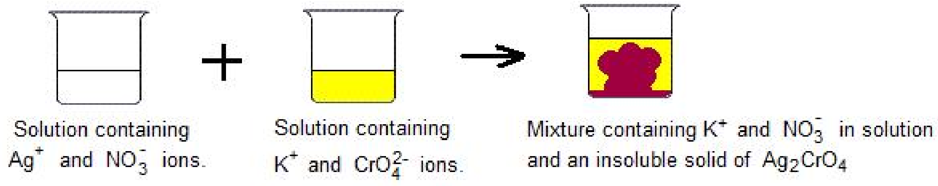

Figure 1: Formation of a precipitate.

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Ions in Solution Can React and Produce Precipitates

Once a solid substance has been separated into its ions, the ions are then available for reactions. When a compound is in the solid state, the ions are held with electrostatic attractions. It must first be dissolved in solution to allow ions to move freely. Take for example the reaction between sodium chloride and silver nitrate. Both of these compounds are available commonly in the solid form. First, you would take both solids and dissolve them in solution, in this case water. (Equation 1 and Equation 2)

$AgNO_{3(s)} \rightarrow Ag^+_{(aq)} + NO_3{}^-_{(aq)}$ (Equation 1)

$NaCl_{(s)} \rightarrow Na^+_{(aq)} + Cl^-_{(aq)}$ (Equation 2)

Once the solid dissolves to separate into its ions in solution, these ions are available to react together in the chemical reaction (Equation 3).

$AgNO_{3(aq)} + NaCl_{(aq)} \rightarrow AgCl_{(s)} + NaNO_{3(aq)}$ (Equation 3)

Make note that the $AgNO_{3(aq)}$ and $NaCl_{(aq)}$ reactants show the ions are in solution. In other words $AgNO_{3(aq)}$ is equivalent to $Ag^+_{(aq)} + NO_3{}^-_{(aq)}$, and $NaCl_{(aq)}$ is equivalent to $Na^+_{(aq)} + Cl^-_{(aq)}$. The equation represented in Equation 3 is a double displacement reaction which means the cations exchange anions in the reactants to form the products. In the laboratory, a precipitate is formed that we determine is silver chloride.

The same reactions can be seen when substances undergo ionization. Remember that ionization forms ions in solution. For example, look at Equation 4 for the ionization of sulfuric acid (chemical change) and Equation 5 for the dissolving of sodium hydroxide (physical change). Notice how they both end up with ions in solution.

$H_2SO_{4(aq)} \rightarrow 2H^+_{(aq)} + SO_4{}^{2-}_{(aq)}$ (Equation 4)

$NaOH_{(aq)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$ (Equation 5)

When sulfuric acid reacts with sodium hydroxide we have a double displacement reaction where the cations exchange anions. Equation 6 shows this reaction.

$H_2SO_{4(aq)} + 2NaOH_{(aq)} \rightarrow 2H_2O_{(L)} + Na_2SO_{4(aq)}$ (Equation 6)

Notice in Equation 6, that liquid water is produced, not a solid. As well, the second product is an aqueous ionic solution containing the ions $Na^+_{(aq)}$ and $SO_4{}^{2-}_{(aq)}$. What is essential to these equations and equations like these is to visualize the ionic aqueous solutions as ions in solution.

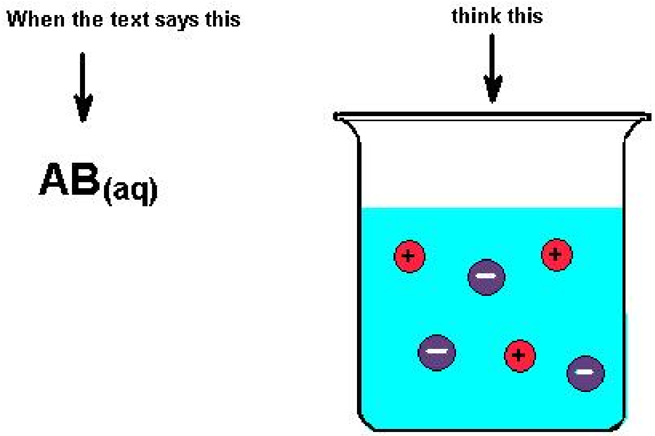

Figure 2: Most ionic compounds dissociate in water.

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Using Solubility Charts and/or Solubility Rules

How do you know if a precipitate is produced in a double replacement reaction? Not all reactions of this type will produce a precipitate. Take for example, if you were to mix a solution of table salt, $NaCl_{(s)}$, and Epsom salts, $MgSO_{4(s)}$, in water, you would not get a precipitate. The reaction is seen below.

$2\ NaCl_{(aq)} + MgSO_{4(aq)} \rightarrow Na_2SO_{4(aq)} + MgCl_{2(aq)}$ (Equation 7)

So, how would you know when you would get a precipitate and when not? What scientists use is a set of solubility rules or, even better, a solubility chart. Table 1 represents the solubility chart for the most common cations and anions found in ionic solids.

Table 1: Solubility Chart

	$C_2H_3O_2^-$	Br^-	CO_3^{2-}	Cl^-	ClO_3^-	CrO_4^{2-}	I^-	NO_3^-	OH^-	O^{2-}	PO_4^{3-}	SO_4^{2-}	S^{2-}
Ag^+	ii	I	I	I	S	ii	I	S	*	ii	I	ii	I
Al^{3+}	S	S	*	S	S	*	S	S	I	I	I	S	*
Ba^{2+}	S	S	ii	S	S	I	S	S	S	S	I	I	*
Ca^{2+}	S	S	ii	S	S	ii	S	S	ii	ii	ii	ii	ii
Cu^{2+}	S	S	*	S	S	*	*	S	I	I	I	S	I
Fe^{2+}	S	S	ii	S	S	*	S	S	I	I	I	S	I
Fe^{3+}	S	S	*	S	S	I	S	S	I	I	ii	ii	*
Hg_2^{2+}	S	S	*	S	S	ii	ii	S	I	ii	i	I	I
K^+	S	S	S	s	S	S	s	S	S	S	S	S	S
Mg^{2+}	S	S	ii	S	S	ii	S	S	I	I	ii	S	*
Mn^{2+}	S	S	ii	S	S	*	S	S	I	I	ii	S	I

Na^+	S	S	S	S	S	S	S	S	S	S	S	S	S
NH_4^+	S	S	S	S	S	S	S	S	S	S	S	S	S
Pb^{2+}	S	I	I	I	S	I	I	S	ii	ii	I	ii	I
Sn^{2+}	*	S	*	S	S	I	S	S	I	I	I	S	I
Sn^{4+}	S	S	*	*	S	ii	*	S	ii	I	*	S	I
Sr^{2+}	S	S	ii	S	S	ii	S	S	S	S	I	ii	S
Zn^{2+}	S	S	ii	S	S	ii	S	S	I	ii	I	S	I

S = soluble in water, I = insoluble in water, ii = partially soluble in water, * = unknown or does not exist.

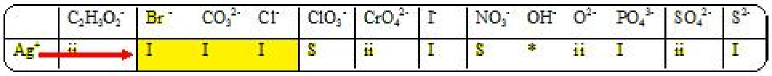
Let's now see how we use the ***solubility chart*** to determine if two compounds will form a precipitate when they react. If we had a reaction between sodium bromide and silver nitrate, we know that this is a reaction between two compounds and therefore is a double replacement reaction. How do we know the states of the products formed? The reaction is seen below.

$NaBr_{(aq)} + AgNO_{3(aq)} \rightarrow NaNO_{3(?)} + AgBr_{(?)}$ (Equation 8)

Look at the solubility chart and see if you can predict if the reaction will produce any precipitates. If you look across the row for sodium ion, all sodium compounds are soluble (S), therefore you can fill in this part of the equation (See Equation 9)

$NaBr_{(aq)} + AgNO_{3(aq)} \rightarrow NaNO_{3(aq)} + AgBr_{(?)}$ (Equation 9)

If you look across the row for silver, under bromide ion, you find an I for insoluble. Figure 22.4.1 shows this row of the solubility chart.



	$C_2H_3O_2^-$	Br^-	CO_3^{2-}	Cl^-	ClO_3^-	CrO_4^{2-}	I^-	NO_3^-	OH^-	O^{2-}	PO_4^{3-}	SO_4^{2-}	S^{2-}
Ag^+	ii	I	I	I	S	ii	I	S	*	ii	I	ii	I

Figure 2: Solubility chart being used to determine whether the bromide anion and silver cation combination will produce a precipitate.

Therefore we can complete the equation (Equation 10).

$NaBr_{(aq)} + AgNO_{3(aq)} \rightarrow NaNO_{3(aq)} + AgBr_{(s)}$ (Equation 10)

Let's try another one. Take a reaction between ammonium phosphate and lead acetate.

$2\ (NH_4)_3PO_{4(aq)} + 3\ Pb(C_2H_3O_2)_{2(aq)} \rightarrow 6\ NH_4C_2H_3O_{2(aq)} + Pb_3(PO_4)_{2(s)}$ (Equation 11)

How did we know that the lead(II) phosphate would precipitate from solution? Why did the ammonium acetate not precipitate? If we follow the ammonium row in the solubility table across to the acetate column, we find an "S" at the intersection which indicates this compound is soluble. If we follow the lead row across to the phosphate column, we find an "I" at the intersection, which indicates insolubility and therefore a precipitate of this compound will form.

As we said at the beginning, rather than using a solubility chart, some scientists simply use a set of ***solubility rules.*** The rules are as follows:

1. All group 1 metals and ammonium compounds are soluble.
2. All nitrates, chlorates, and bicarbonates are soluble.
3. Halides are soluble except for Ag^+, $Hg_2{}^{2+}$, and Pb^{2+}
4. Sulfates are soluble except for Ag^+, Ba^{2+}, Ca^{2+}, $Hg_2{}^{2+}$, Sr^{2+}, and Pb^{2+}
5. Carbonates, chromates, phosphates, and sulfides are insoluble except those from rule #1.
6. Hydroxides are insoluble except for those in rule #1, and Ba^{2+}.

It is important to remember that this is a priority set of rules. What this means is that Rule #1 is first. All group 1 metals and ammonium compounds are always soluble. For example, even though sulfide compounds are rarely soluble for any cation (rule #5), they will be soluble with group 1 metal ions or with ammonium ions (rule #1). It also does not matter whether you use the set of rules or the solubility chart.

They both provide the same information; the chart is easier to read for some, the rules are easier to remember for others.

Sample question: Complete the following reactions. Use the solubility table to predict whether precipitates will form in each of the reactions.

(a) $Pb(NO_3)_{2(aq)} + KI_{(aq)} \longrightarrow$

(b) $BaCl_{2(aq)} + Na_2SO_{4(aq)} \longrightarrow$

Solution:

(a) $Pb(NO_3)_{2(aq)} + 2\ KI_{(aq)} \longrightarrow PbI_{2(s)} + 2\ KNO_{3(aq)}$

(b) $BaCl_{2(aq)} + Na_2SO_{4(aq)} \longrightarrow BaSO_{4(s)} + 2\ NaCl_{(aq)}$

Separating Ions in Solution

Figure 1: Separating solid from solution by filtration. (*Source:* CK-12 Foundation, *License:* CC-BY-SA)

When a chemist has a solution that contains two or more ions and he/she wishes to physically separate the ions, the differences in solubilities can be used. Suppose that a chemist has a solution that contains both Pb^{2+} and Zn^{2+} ions. If these two ions were dissolved in the solution as nitrates, then the only anion present is the nitrate ion. If the chemist added some NaCl to the solution, the zinc ions would remain in solution because $ZnCl_2$ is soluble but the lead ions and the chloride ions would form an insoluble compound, $PbCl_2$, and form a precipitate. The chemist could then pour this mixture through a piece of filter paper and the dissolved zinc ions would pass through the filter paper with the solution but the solid $PbCl_2$ would be filtered out. Therefore, the chemist would have separated the zinc ions (now in the solution) and the lead ions (now in the filter paper). The process for separating and identifying ions by selective precipitation and filtration is known as ***gravimetric analysis*** . Analytical chemistry is a sub-discipline of chemistry. The task of analytical chemists is to identify the substances present in materials and to make quantitative measurements on them. In order to identify what substances are present, it is often necessary to isolate (separate) the ions from other ions that might be present. In earlier times, much of this work was done by gravimetric analysis. In modern times, a large amount of the identification of ions in solution is done by instrumentation.

If you are called upon to determine a process for separating ions from each other, you should look in the solubility table to determine a reagent that will form a precipitate with one of the ions but not with the other.

The Reactions Can be Written as Ionic Equations

Remember earlier when we said that we should visualize $NaCl_{(aq)}$ as $Na^{+}{}_{(aq)}$ and $Cl^{-}{}_{(aq)}$ and $AgNO_{3\ (aq)}$ as $Ag^{+}{}_{(aq)}$ and $NO_3{}^{-}{}_{(aq)}$? This is so we could write chemical reactions as **formula equations.** Equation 12 is a formula equation.

$NaCl_{(aq)} + AgNO_{3\ (aq)} \rightarrow NaNO_{3\ (aq)} + AgCl_{(s)}$ (Equation 12)

The ionic solids discussed in the previous section were written together in a formula form. In an ***ionic equation,*** the separated ions are written in the chemical equation. Let's rewrite Equation 12 as a total ionic equation which is a better representation of a double replacement reaction.

$Na^{+}{}_{(aq)} + Cl^{-}{}_{(aq)} + Ag^{+}{}_{(aq)} + NO_3{}^{-}{}_{(aq)} \rightarrow Na^{+}{}_{(aq)} + NO_3{}^{-}{}_{(aq)} + AgCl_{(s)}$ (Equation 13)

Sample question: Write the ionic equation for each of the following.

(a) $BaCl_{2\ (aq)} + Na_2SO_{4\ (aq)} \rightarrow 2\ NaCl_{(aq)} + BaSO_{4\ (s)}$

(b) $2\ K_3PO_{4\ (aq)} + 3\ Ca(NO_3)_{2\ (aq)} \rightarrow 6\ KNO_{3\ (aq)} + Ca_3(PO_4)_{2\ (s)}$

Solution:

(a) $Ba^{2+}{}_{(aq)} + 2\ Cl^{-}{}_{(aq)} + 2\ Na^{+}{}_{(aq)} + SO_4{}^{2-}{}_{(aq)} \rightarrow 2\ Na^{+}{}_{(aq)} + 2Cl^{-}{}_{(aq)} + BaSO_{4\ (s)}$

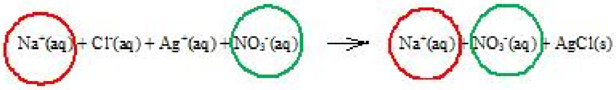
(b) $6\ K^{+}{}_{(aq)} + 2\ PO_4{}^{3-}{}_{(aq)} + 3\ Ca^{2+}{}_{(aq)} + 6\ NO_3{}^{-}{}_{(aq)} \rightarrow 6\ K^{+}{}_{(aq)} + 6\ NO_3{}^{-}{}_{(aq)} + Ca_3(PO_4)_{2\ (s)}$

The Essential Information is Contained in a Net Ionic Equation

If you look at Equation 13, what do you notice is the same on both sides of the equation?

$Na^{+}{}_{(aq)} + Cl^{-}{}_{(aq)} + Ag^{+}{}_{(aq)} + NO_3{}^{-}{}_{(aq)} \rightarrow Na^{+}{}_{(aq)} + NO_3{}^{-}{}_{(aq)} + AgCl_{(s)}$ (Equation 13)

Do you see that $Na^{+}{}_{(aq)}$ and $NO_3{}^{-}{}_{(aq)}$ appear on both sides of this equation in the same form?



$Na^{+}(aq) + Cl^{-}(aq) + Ag^{+}(aq) + NO_3^{-}(aq) \rightarrow Na^{+}(aq) + NO_3^{-}(aq) + AgCl(s)$

(Equation 13)

These ions, because they appear on both sides of the equation and in the same form, are called spectator ions. Think of the phrase "spectator ion". What does it sound like to you? Does it sound like the ion is just in the container watching the reaction? Well, that's kind of what a spectator ion is doing. A ***spectator ion*** is an ion in the ionic equation that appears in the same form on both sides of the equation indicating they do not participate in the overall reaction. Therefore $Na^+(aq)$ and $NO_3^-(aq)$ are spectator ions for this reaction. So what is the overall reaction? Well, let's remove the spectator ions and see.

$Ag^+_{(aq)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)}$ (Equation 14)

Without the spectator ions, we see only the ions that are responsible for forming the solid silver chloride. This equation, represented in Equation 14, is the net ionic equation. The ***net ionic equation*** is the overall reaction that results when spectator ions are removed from the ionic equation. The net ionic equation gives us all of the essential information we need; what ions we need to form our solid. Really, whether we had sodium chloride or potassium chloride is irrelevant, what was important was that the chloride ion and the silver ion were present.

Sample question: Write the net ionic equation for each of the following. Name the spectator ions.

(a) $Ba^{2+}_{(aq)} + 2\ Cl^-_{(aq)} + 2\ Na^+_{(aq)} + SO_4^{2-}{}_{(aq)} \rightarrow 2\ Na^+_{(aq)} + 2\ Cl^-_{(aq)} + BaSO_{4(s)}$

(b) $6\ K^+_{(aq)} + 2\ PO_4^{3-}{}_{(aq)} + 3\ Ca^{2+}_{(aq)} + 6\ NO_3^-{}_{(aq)} \rightarrow 6\ K^+_{(aq)} + 6\ NO_3^-{}_{(aq)} + Ca_3(PO_4)_{2(s)}$

Solution:

(a) $Ba^{2+}_{(aq)} + 2\ Cl^-_{(aq)} + 2\ Na^+_{(aq)} + SO_4^{2-}{}_{(aq)} \rightarrow 2\ Na^+_{(aq)} + 2\ Cl^-_{(aq)} + BaSO_{4(s)}$

$Ba^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)} \rightarrow BaSO_{4(s)}$ net ionic equation

$Cl^-_{(aq)}$ and $Na^+_{(aq)}$ = spectator ions

(b) $6\ K^+_{(aq)} + 2\ PO_4^{3-}{}_{(aq)} + 3\ Ca^{2+}_{(aq)} + 6\ NO_3^-{}_{(aq)} \rightarrow 6\ K^+_{(aq)} + 6\ NO_3^-{}_{(aq)} + Ca_3(PO_4)_{2(s)}$

$3\ Ca^{2+}_{(aq)} + 2\ PO_4^{3-}{}_{(aq)} \rightarrow Ca_3(PO_4)_{2(s)}$ net ionic equation

$K^+_{(aq)}$ and $NO_3^-{}_{(aq)}$ = spectator ions

Lesson Summary

- A solubility chart is a grid showing the possible combinations of cations and anions and their solubilities in water. It is used to determine whether a precipitate is formed in a chemical reaction. The solubility rules are a list of rules dictating which combinations of cations and anions will be soluble or insoluble in water.
- A total ionic equation is one in which all of the ions in a reaction are represented. A net ionic equation is one in which only the ions that produce the precipitate are represented.

Review Questions

1. What is more valuable to use for determining solubility: a solubility chart or a set of solubility rules? **(Intermediate)**

2. If you were told to visualize $Cu(NO_3)_2(aq)$, what might this mean to you? **(Intermediate)**

3. Use the solubility rules to determine the following solubilities in water.

Solubility Rules

1. All group 1 metals and ammonium compounds are soluble.
2. All nitrates, chlorates, and bicarbonates are soluble.
3. Halides are soluble except for Ag^+, $Hg_2{}^{2+}$, and Pb^{2+}
4. Sulfates are soluble except for Ag^+, Ba^{2+}, Ca^{2+}, $Hg_2{}^{2+}$, Sr^{2+}, and Pb^{2+}
5. Carbonates, chromates, phosphates, and sulfides are insoluble except those from rule #1.
6. Hydroxides are insoluble except for those in rule #1, and Ba^{2+}.

Which of the following compounds is soluble in water? **(Intermediate)**

(a) $PbCl_2$

(b) Hg_2Cl_2

(c) $(NH_4)_2SO_4$

(d) $MgCO_3$

(e) $AgNO_3$

(f) $MgCl_2$

(g) KOH

(h) $PbSO_4$

4. When only the ions that produce a precipitate are shown for a chemical equation, what type of reaction exists? **(Intermediate)**

(a) spectator equation

(b) molecular equation

(c) ionic equation

(d) net ionic equation

5. If you wanted to separate a solution of Al^{3+}(aq) from a solution of Fe^{2+}(aq), which of the following would be the best possible reaction? **(Intermediate)**

(a) add HCl

(b) add NaOH

(c) add H_2S

(d) none of the above

6. If you wanted to separate a solution of $Ag^{+}_{(aq)}$ from a solution of $Hg_2{}^{2+}_{(aq)}$, which of the following would be the best possible reaction? **(Intermediate)**

(a) add HBr

(b) add HNO_3

(c) add NaOH

(d) none of the above

7. Complete the following reactions: **(Intermediate)**

(a) $Na_2S(aq) + ZnCl_2(aq) \rightarrow$

(b) $(NH_4)_2CO_3(aq) + CaCl_2(aq) \rightarrow$

8. Write the ionic equations for the balanced molecular equations from question 5. **(Intermediate)**

9. Write the net ionic equations for the ionic equations from question 6. **(Intermediate)**

10. Identify the spectator ions for the ionic equations from question 6. **(Intermediate)**

Vocabulary

solubility chart	A grid showing the possible combinations of cations and anions and their solubilities in water.
solubility rules	A list of rules dictating which combinations of cations and anions will be soluble or insoluble in water.
formula equation	A chemical equation written such that the aqueous solutions are written in formula form.
total ionic equation	A chemical equation written such that the actual free ions are shown for each species in aqueous form.
net ionic equation	The overall reaction that results when spectator ions are removed from the ionic equation.
spectator ions	The ions in the total ionic equation that appear in the same form on both sides of the equation indicating they do not participate in the overall reaction.

Review Answers

1. Answers will vary but basically it does not matter whether you use the set of rules or the solubility chart. They both provide the same information; the chart is easier to read for some, the rules are easier to remember for others.

2. Answers may vary. Students should include in their answer that $Cu(NO_3)_2(aq)$ is the equivalent to $Cu^{2+}(aq)$ and 2 x $NO_3{}^{-}(aq)$ ions. In a container of water, $Cu(NO_3)_2(aq)$ would form ions in solution.

3.

(a) insoluble

(b) insoluble

(c) soluble

(d) insoluble

(e) soluble

(f) soluble

(g) soluble

(h) insoluble

4. (d) net ionic equation

5. (b) add NaOH

6. (a) add HBr

7. (complete equations provided)

8. (write ionic equations)

9. (write net ionic equations)

10. (Identify spectator ions)

23. Chemical Kinetics

Rate of Reactions

Lesson Objectives

- Define chemical kinetics and rates of reactions.
- Write the rate expression and the units for the rate expression.
- Define instantaneous rate.
- Calculate instantaneous rate using a tangent line.

Introduction

In this chapter the study of chemical kinetics will be explored. ***Chemical kinetics*** is the study of rates of chemical reactions and what factors affect the rate of reactions. These factors include concentration, temperature, pressure, surface area, and the effect of a catalyst. Many chemical reactions are required to be sped up or slowed down depending on the nature of the reaction. For example, when food is placed in the refrigerator the temperature is decreased to keep the food from decomposing. The rate of reaction is slowed down by decreasing the temperature. Chemical kinetics plays an important role both in industry and in our daily lives. As we work through this chapter gaining insight into the background of this topic, we will learn more about how the science and the math of this wonderful branch of chemistry work in our world. To begin, we will introduce some of the basic concepts of chemical kinetics.

Change in Concentration Over Time

The term ***rate of reaction*** is used to denote the measure of the rate at which the products are formed in a time interval or the rate at which the reactants are consumed over a time interval. A reaction rate measures how fast or how slow a reaction is. The rusting of a piece of metal, like a car part, has a slow reaction rate because the iron oxidizes in the air in a relatively long time period. A forest fire has a fast reaction rate since it consumes trees in its path in a very short time interval. Reaction rates can be measured in change in mass per unit time (grams/second) or in charge in molarity per unit time (mols/liter/second).

Symbolically, the reaction rate is given the letter r in expressions. Therefore to write the expression for the reaction rate, you can write the following.

$$r = \frac{\Delta concentration}{\Delta time}$$

Remember that the symbol Δ means the *change in*.

Sample question:

For the reaction $H_{2(g)} + I_{2(g)} \rightarrow 2\,HI_{(g)}$, under certain conditions the [HI] = 0.50 mol/L at 25 s and 0.75 mol/L at 40 s. What is the rate of production of HI? Note: Remember that the brackets indicate concentration

Solution:

$$r = \frac{\Delta[HI]}{\Delta t} = \frac{(0.75 - 0.50)\text{ mol/L}}{(40. - 25)\text{ s}} = \frac{0.25\text{ mol/L}}{15\text{ s}} = 1.7 \times 10^{-2}\text{ mol/L}\cdot\text{s}$$

Therefore, the rate of production of HI is 1.7×10^{-2} mol/L·s.

Units for Rate of Reaction

Notice in the sample question in the previous section that the units to measure the reaction rate are in mol/L·s. Therefore, the units are measuring the concentration/time or the M/time. This expression of the units for reaction rate is consistent to allow for comparison of rates. In other words, if all reaction rates were to use the same units, we can compare one rate to the other. For example, with the HI reaction under a different set of conditions, we found that the reaction rate was found to be 2.5 mol/L·s for these conditions. Then, we could predict that the new set of conditions are favorable for this reaction since the reaction rate was faster for the production of HI in the same time interval.

Graphing Instantaneous Rate

Instantaneous rate is defined as the rate of change at a particular moment. For example, a police officer stops a car for speeding. The radar gun on a police cruiser is set to measure the speed of a motorist as the motorist comes close to the cruiser. The driver of the vehicle is stopped doing 65 miles/hour in a 50 mile/hour zone. The cruiser measured the rate of speed at that instant in time when the driver passed the police officer. This is instantaneous rate. If we were to take all of the measures of instantaneous rate and graph them, we would obtain a curve of the overall speed (or the average speed) of the vehicle. The same is true for reactions. For reactions, the instantaneous rate is the rate of the reaction at a specific time in the reaction sequence. If you were to graph the rate of the reactant being consumed versus time, the graph would look like Figure 1. As the reaction proceeds, the concentration of the reactants decreases over time.

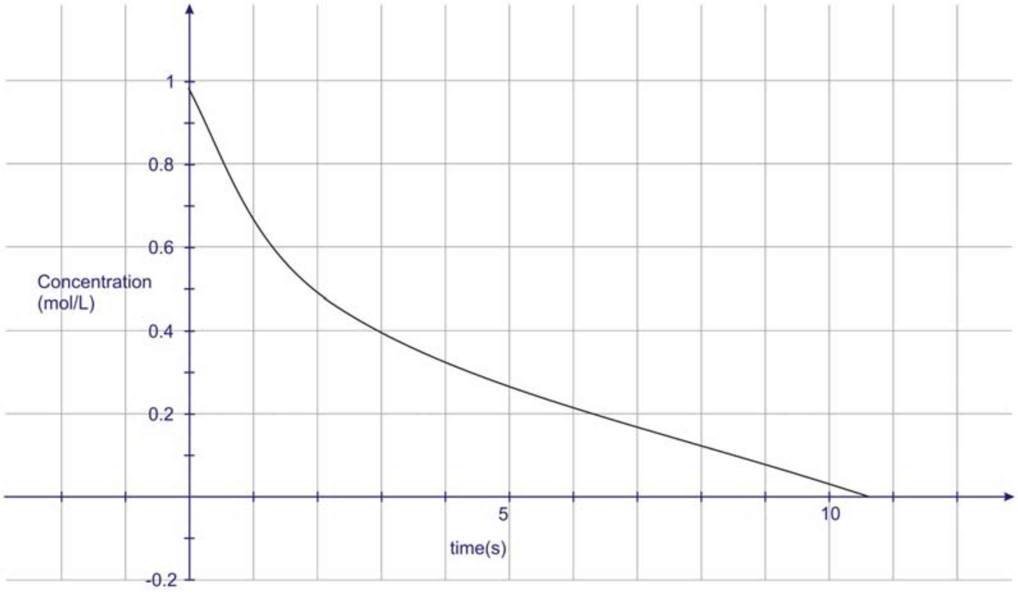


Figure 1: Graph of Concentration vs Time.

The initial rate of the reaction is found when t = 0 s, or when the reaction is just beginning. It is at this point when the maximum amount of the reactant is present. To find the instantaneous rate, or the rate at any given time in the reaction, a tangent line is drawn to this curve. Then the slope of the tangent line is found for a point on the curve. For example, we wanted to know the instantaneous rate at t = 2 s. After drawing the tangent line (see Figure 2), we can calculate the slope of the tangent line to find the instantaneous rate at t = 2 s.

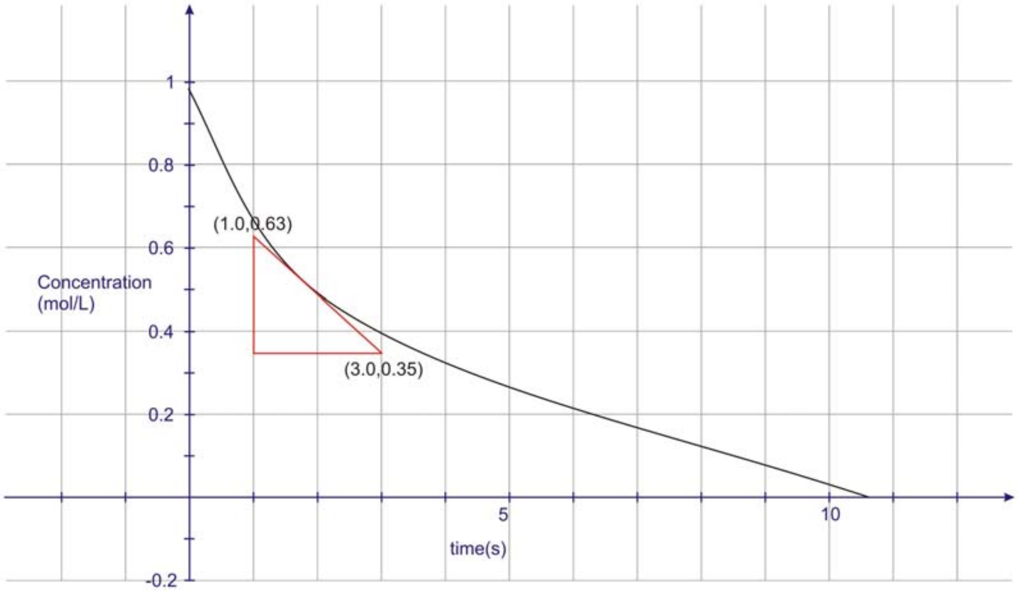


Figure 2: Graph of Concentration vs Time With Tangent Line.

$$\text{rate} = \frac{y_2 - y_1}{x_2 - x_1} = \frac{0.35 - 0.63}{3.0 - 1.0} = \frac{-0.28\ \text{mol/L}}{2.0\ \text{s}} = -0.14\ \text{mol/L·s}$$

or rate = 0.14 mol/L·s since the rate decreases with time for reactants.

Lesson Summary

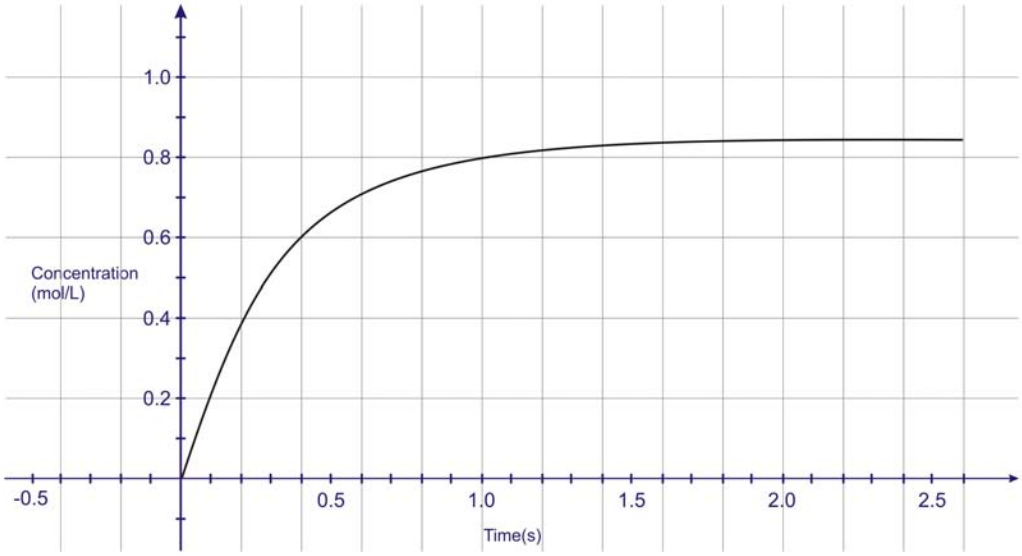
- Chemical kinetics is the study of rates of chemical reactions and how factors affect rates of reactions. The term rate of reaction is used to denote the measure at which the products are formed over a time interval or the rate at which the reactants are consumed over a time interval.
- The units to measure the reaction rate are in mol/L·s. Instantaneous rate is defined as the rate of change at a particular moment.

Review Questions

1. What is the rate of production of $NO_{2(g)}$ in the system below given that the concentration of $NO_{2(g)}$ is 0.40 mol/L at 45 s and 0.85 mol/L at 80 s. **(Intermediate)**

$$NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}$$

2. For the graph below, draw a tangent line at t = 0.40 s, and calculate the instantaneous rate. **(Intermediate)**



3. Which expression represents the rate for the product formation of the following reaction? **(Intermediate)**

$Mg_{(s)} + 2\ HCl_{(aq)} \rightarrow MgCl_{2(aq)} + H_{2(g)}$

(a) rate = $\frac{\Delta[Mg]}{\Delta t}$

(b) rate = $\frac{\Delta[HCl]}{\Delta t}$

(c) rate = $\frac{\Delta[MgCl_2]}{\Delta t}$

(d) All of these are accurate representations of the rate.

4. Which statement represents a rate? **(Beginning)**

(a) The speed of a car is 50 km/h.

(b) Half the product is produced.

(c) A family consumes 5 L of milk.

(d) I ran for 45 minutes.

5. Which statement about the instantaneous rate of a reaction is correct? **(Intermediate)**

(a) The higher the rate, the lesser the slope of a line on a concentration-time graph.

(b) The instantaneous rate is the slope of the tangent to a line on a concentration-time graph.

(c) The instantaneous rate is the slope of the cosine to a line on a concentration-time graph.

(d) All of these statements are correct.

6. In the following reaction, what is the rate of production of NO gas if the concentration decreases from 0.32 mol/L at 56 s and 0.94 mol/L at 78 s? **(Intermediate)**

$4\ NH_{3(g)} + 5\ O_{2(g)} \longrightarrow 4\ NO_{(g)} + 6\ H_2O_{(g)}$

(a) -35 mol/L·s

(b) -2.8×10^{2} mol/L·s

(c) 2.8×10^{-2} mol/L·s

(d) 35 mol/L·s

7. It takes 15 minutes for the concentration of a reactant to decrease from 0.45 mol/L to 0.030 mol/L. What is the rate of reaction in mol/L·s? **(Intermediate)**

Vocabulary

chemical kinetics	The study of rates of chemical reactions and how factors affect rates of reactions.
rate of reaction	The measure at which the products are formed over a time interval or the rate at which the reactants are consumed over a time interval.
instantaneous rate	The rate of change at a particular time interval.

Review Answers

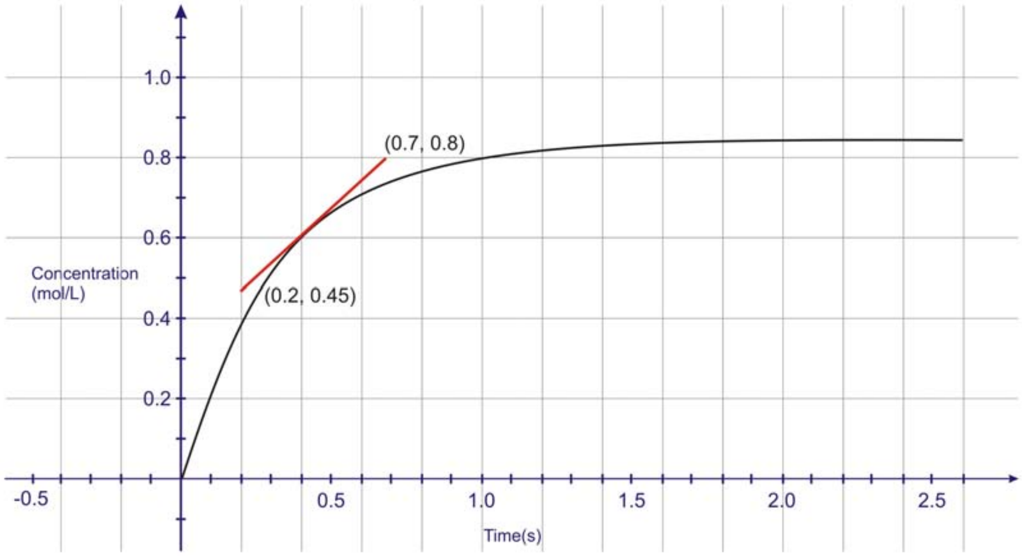
1.

$NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}$

$$r = \frac{\Delta[NO_2]}{\Delta t} = \frac{(0.85 - 0.40)\ \text{mol/L}}{(80. - 45)\ \text{s}} = \frac{0.45\ \text{mol/L}}{35\ \text{s}} = 0.013\ \text{mol/L·s}$$

Therefore the rate of production of NO_2 is 1.3×10^{-2} mol/L·s.

2.



$$\text{rate} = \frac{y_2 - y_1}{x_2 - x_1} = \frac{0.80 - 0.45}{0.7 - 0.2} = \frac{0.35\ \text{mol/L}}{0.5\ \text{s}} = 0.7\ \text{mol/L·s}$$

rate = 0.7 mol/L·s (the rate increases with time for products)

3. c

4. (a) The speed of a car is 50 km/h.

5. (b) The instantaneous rate is the slope of the tangent to a line on a concentration-time graph.

6. (c) 2.8×10^{-2} mol/L·s

7. 15 min = 900 s

rate of disappearance of reactant = $\frac{c_2 - c_1}{t_2 - t_1} = \frac{0.45\text{ mol/L} - 0.030\text{ mol/L}}{900.\text{ s}} = 4.7 \times 10^{-4}$ mol/L·s

Collision Theory

Lesson Objectives

- Define the collision theory.
- Describe the conditions for successful collisions.
- Explain how the kinetic molecular theory applies to the collision theory.
- Describe the rate in terms of the conditions of successful collisions.

Introduction

Consider the chemical reaction $CH_4 + 2\ O_2 \longrightarrow CO_2 + 2\ H_2O$. In the reactants, the carbon atoms are bonded to hydrogen atoms and the oxygen atoms are bonded to oxygen atoms. Each atom in the reactants is bonded to its full capacity and therefore, cannot form any more bonds. In the products, the carbon atoms are bonded to oxygen atoms and the hydrogen atoms are bonded to oxygen atoms. The bonds that are present in the products cannot form unless the bonds in the reactants are first broken. Breaking bonds requires an input of energy. If the atoms in the reactants were in the form of carbon atoms, hydrogen atoms, and oxygen atoms, they would have a much higher potential energy that they have in the form of CH_4 and O_2 molecules. Therefore, in order to get the reactant molecules into a form that will allow them to form new bonds, the old bonds must be broken and this requires that their potential energy be raised considerably.

The energy to break the old bonds comes from the kinetic energy of the reactant particles. The reactant particles are moving around in their random motion and their average kinetic energy is related to their temperature. If a reaction is to occur, the kinetic energy of the reactants must be high enough that when the reactant particles collide, the collision is forceful enough to break the old bonds. Once the old bonds are broken, the atoms in the reactants would be available to form new bonds. At that point, the new bonds of the products could be formed. When the new bonds are formed, potential energy is given off. The potential energy that is given off becomes kinetic energy and is absorbed by the surroundings (primarily the products, the solvent solution if there is one, and the reaction vessel).

Chemists have chosen to give a name to the group of particles that exist for a split second just after the reactant bonds have been broken and before the product bonds form. This group of un-bonded particles is called the **activated complex**. The *activated* part comes from the fact that these atoms are ready to form bonds and the *complex* part comes from the fact that the group of particles is a jumble of particles from all the reactant molecules. A successful collision would proceed as follows:

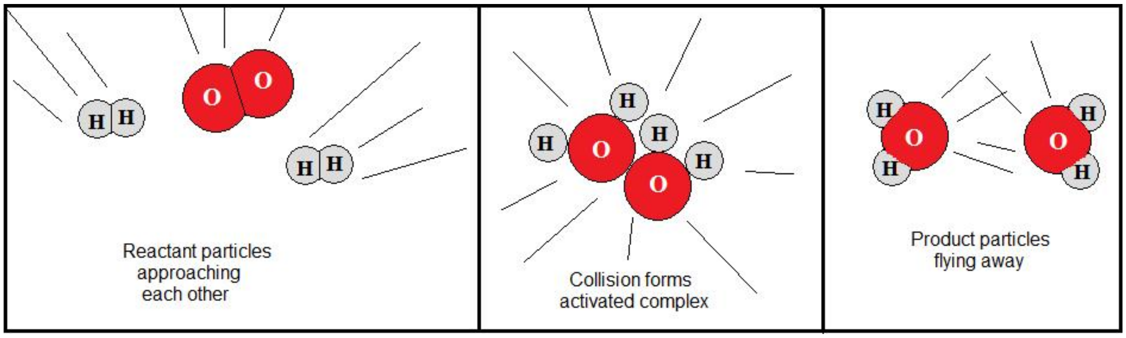


Figure 1: This collision is successful and results in reaction.

(*Created by:* Richard Parsons, *License:* CC-BY-SA)

Reactants → input of energy → activated complex → output of energy → products.

All three groups of particles, the reactants, the activated complex, and the products have a precise amount of potential energy in their bonds. The potential energy of the activated complex is called the **threshold energy**. This threshold energy is the minimum potential energy that must be reached in order for a reaction to occur. The input of energy that is necessary to raise the potential energy of the reactants to this threshold energy is called the ***activation energy***. The activation energy must be provided from the kinetic energy of the reactant particles during the collision. In those cases where the reactants do not collide with enough energy to break the old bonds (inadequate activation energy), the reactant particles will simply bounce off each other and remain reactant particles.

How Reactions Occur

We know that a chemical system can be made up of atoms (H_2, N_2, K), ions (NO_3^-, Cl^-, Na^+), or molecules (H_2O, CH_3CH_3, $C_{12}H_{22}O_{11}$). We also know that in a chemical system, these particles are moving around in a random motion. The ***collision theory*** explains why reactions occur at this particle level between these atoms, ions, and/or molecules. The collision theory provides us with the ability to predict what conditions are necessary for a successful reaction to take place. These conditions include:

(1) The particles must collide with each other.

(2) The particles must have proper orientation.

(3) The particles must collide with sufficient energy to break the old bonds.

A chemical reaction involves breaking bonds in the reactants, re-arranging the atoms into new groupings (the products), and the formation of new bonds in the products. Therefore, not only must a collision occur between reactant particles but the collision has to have sufficient energy to break all the reactant bonds that need to be broken in order to form the products. Some collision geometries need less collision energy than others. The optimal collision geometry requires the smallest amount of particle kinetic energy for the reaction to occur. The amount of kinetic energy the reactant particles must have in order to break the old bonds is called the ***activation energy***. The activation energy is the minimum amount of kinetic energy the reactant particles must have in order for a successful collision to occur, assuming optimal geometry. If the reactant particles collide with less than the activation energy, the particles will rebound (bounce off each other), and no reaction will occur.

The reaction rate, discussed in the previous section is proportional to the number of successful collisions per second.

Collision Theory and the Kinetic Molecular Theory

The ***kinetic molecular theory*** provides the foundation for the collision theory. The kinetic molecular theory tells us about the particles involved in the collisions. Part of the kinetic molecular theory maintains that the collision between particles are "perfectly elastic". The term "perfectly elastic" is a term from physics which means that kinetic energy in conserved in the collision. That is, if no bonds are broken so no KE is converted to PE, the colliding particles simply rebound and total KE after the collision is exactly the same as the total KE before the collision. The kinetic molecular theory states that gas molecules consist of particles that are moving in random motion. This random motion is always in a straight line and the particles deviate only when there is a collision with the walls of a container or with another particle. The only collisions of any consequence are those between other particles. The kinetic energy, defined as the energy of motion, is dependent on the temperature of the system. As the temperature is increased, the kinetic energy of the particles increases and the particles move at a faster pace. With the particles moving faster, they are more likely to collide and will collide with more energy.

In the chapter on kinetic-molecular theory, it was discussed that the particles in a sample of material are not all at exactly the same temperature. The temperature of a substance is the **average kinetic energy** of all the particles. Some of the particles have more than the average kinetic energy and some have less. The particles of the substance actually have a *distribution* of kinetic energies and the temperature of the substance is an expression of the average kinetic energy. Therefore, it is not only possible but likely, that in the mass of reactants for a reaction, some of the reactant particles will have sufficient KE to react and some of the reactant particles will not.

In a slow reaction, the majority of molecules do not have the minimum amount of energy necessary for a reaction to take place. In Diagram 1, the graph illustrates the number of molecules in the system versus the kinetic energy of these molecules. The area under the curve represents the total number of particles. The area shaded in red shows the number of molecules that **DO** have sufficient energy for a successful collision. The minimum amount of energy necessary for a reaction is known as the ***activation energy*** .

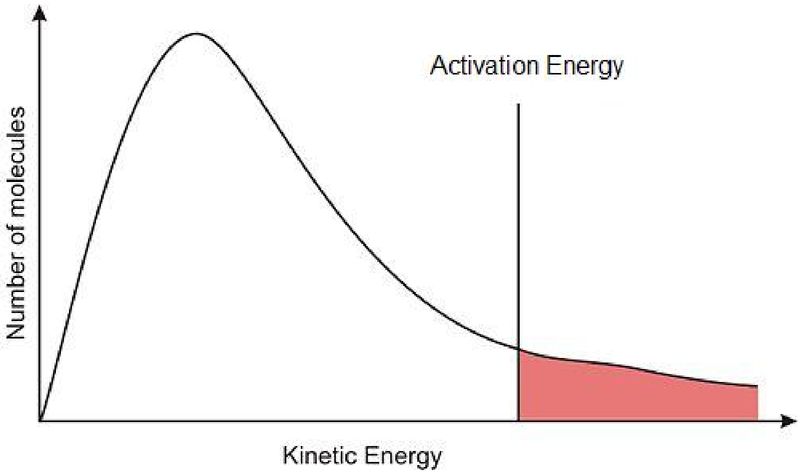


Figure 1: Kinetic Energy vs. Number of Molecules.

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If the temperature is increased, the average kinetic energy of the particles increases and the number of molecules with sufficient kinetic energy for a successful collision would also increase. Figure 2 show changes for the increased temperature.

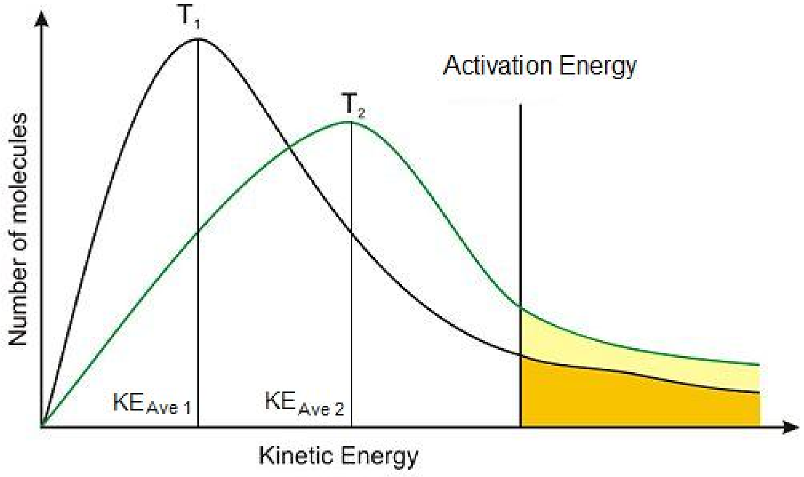

Figure 2: Kinetic Energy vs. Number of Molecules at Two Temperatures.

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At the higher temperature (T_2), the number of molecules with energy greater than the activation energy increases. Therefore the number of molecules with kinetic energy great enough to have successful collisions increases with increasing average kinetic energy.

Reactions May Occur When Particles Collide

Looking back at the three conditions introduced in the first section, consider the following reaction.

$F_2 + NO_2 \longrightarrow FNO_2 + F$

If there is not enough energy, the particles will simply rebound off each other and bonds will not be broken. The original reactants will remain.

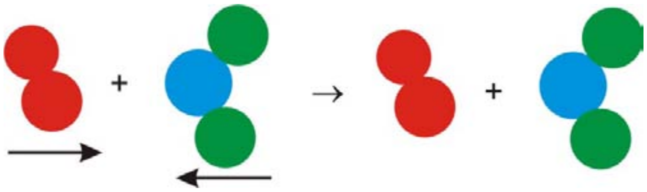

Figure 3: An unsuccessful collision results in rebound.

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In order to have a successful collision, the particles must collide with enough energy and with the correct geometry to break the F_2 and NO_2 bonds and form the FNO_2 and F products. The F would then further react with another element as it is not normally found unreacted (or just as F alone).

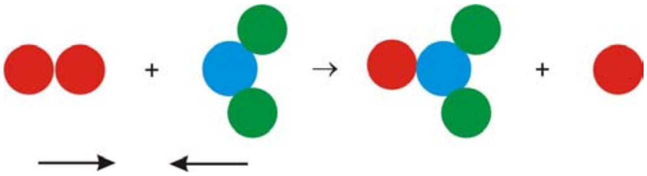

Figure 4: An successful collision results in reaction.

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Rate of Reaction Dependent On Various Factors

As stated at the beginning of the lesson, there are three conditions that must occur in order for a successful collision to occur. First of all, the reactant particles must collide. The total number of collisions per second is known as the ***collision frequency,*** whether these collisions are successful or not. The collision frequency depends on the concentration of the particles in the container, the temperature of the reaction and the size of the particles themselves. Second, the particles must collide with the proper orientation. And third, the particles must collide with sufficient energy. Since then, we have learned that the kinetic energy is related to the force of the particles. Therefore the particles have to achieve an energy greater than the threshold energy to have successful collisions. From this knowledge we can conclude that the rate of the reaction depends on the fraction of molecules that have enough energy and that collide with the proper orientation, and the rate depends on the collision frequency itself.

Putting this all together we get the following:

Rate = collision frequency × collision energy × collision geometric orientation

Where the collision frequency is the first factor of a successful collision, the collision geometric orientation is the second factor of a successful collision, and the collision energy is the third factor of a successful collision.

Lesson Summary

- The collision theory explains why reactions occur between atoms, ions, and/or molecules and allows us to predict what conditions are necessary for a successful reaction to take place.
- The kinetic molecular theory provides the foundation for the collision theory on the molecular level. The minimum amount of energy necessary for a reaction to take place is known as the threshold energy.
- With increasing temperature, the kinetic energy of the particles increase and the number of particles with energy greater than the activation energy increases.
- The total number of collisions per second is known as the ***collision frequency***, whether these collisions are successful or not. Reaction rate = collision frequency × collision energy × collision geometric orientation.

Review Questions

1. According to the collision theory, it is not enough for particles to collide in order to have a successful reaction to produce products. Explain **(Intermediate)**

2. Due to the number of requirements for a successful collision, according to the collision theory, the percentage of successful collisions is extremely small. Yet, chemical reactions are still observed at room temperature and some at very reasonable rates. Explain. **(Intermediate)**

3. What is a basic assumption of the kinetic molecular theory? **(Intermediate)**

(a) all particles will lose energy as the velocity increases

(b) all particles will lose energy as the temperature increases

(c) all particles will increase velocity as the temperature decreases

(d) all particles are in random motion

4. According to the collision theory, what must happen in order for a reaction to be successful? **(Intermediate)**

I. particles must collide

II. particles must have proper geometric orientation

III. particles must have collisions with enough energy

(a) I, II

(b) I, III

(c) II, III

(d) I, II, III

5. What would happen in a collision between two particles if there was insufficient kinetic energy and improper geometric orientation? **(Intermediate)**

(a) the particles would rebound and there would be no reaction

(b) the particles would keep bouncing off each other until they eventually react, therefore the rate would be slow

(c) the particles would still collide but the byproducts would form

(d) the temperature of the reaction vessel would increase

6. Illustrate the successful collision that would occur between the following. **(Intermediate)**

$2\ NO + 2\ H_2 \longrightarrow N_2 + 2\ H_2O$

Further Reading / Supplemental Links

http://en.wikipedia.org/wiki

Vocabulary

collision theory	Explains why reactions occur at this particle level between atoms, ions, and/or molecules; even more important from the collision theory is the ability to predict what conditions are necessary for a successful reaction to take place.
kinetic molecular theory	Provides the foundation for the collision theory on the atomic level; the collisions between particles are considered to elastic in nature.
threshold energy	The minimum amount of energy necessary for a reaction to take place.
collision frequency	The total number of collisions per second.

Review Answers

1. According to the collision theory, particles must collide with enough energy to force the reactant particle bonds to break and the product bonds to form. As well, reactant particles must collide with the correct geometric orientation to form the products.

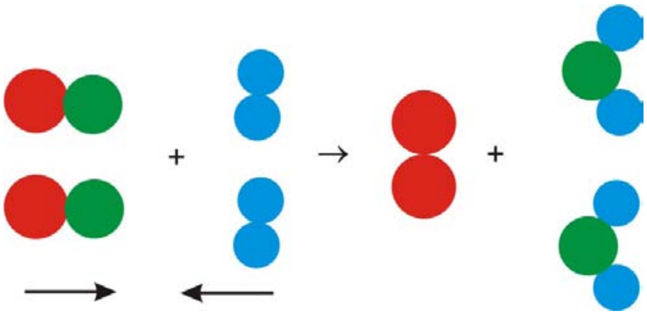
2. For some reactions there is sufficient activation energy present in the environment so that any collisions that occur have the possibility of being a successful collision and produce the products.

3. (d) all particles are in random motion

4. (d) I, II, III

5. (a) the particles would rebound and there would be no reaction

6. (see below)



Potential Energy Diagrams

Lesson Objectives

- Define enthalpy, activation energy, activated complex.
- Describe and draw the difference between endothermic and exothermic potential energy diagrams.
- Draw and label the parts of a potential energy diagram.

Introduction

In the previous lesson the kinetic molecular theory was discussed in relation to the collision theory. The kinetic molecular theory was used to help understand the effect of increasing the temperature on the number of effective collisions in a reaction.

In this lesson, we go beyond the theoretical perspectives of the collision theory to consider how particle collisions can be represented in energy diagrams. Potential energy diagrams in the study of kinetics show how the potential energy changes during collisions from reactants and products. In this first lesson, we will examine the features of such diagrams.

Internal Energy of Reactants and Products, ΔH

As stated in the introduction, potential energy diagrams illustrate the potential energy of the reactants and products for a chemical reaction and how this energy changes during a reaction. Take a look at the potential energy of the reaction drawn in Figure 1.

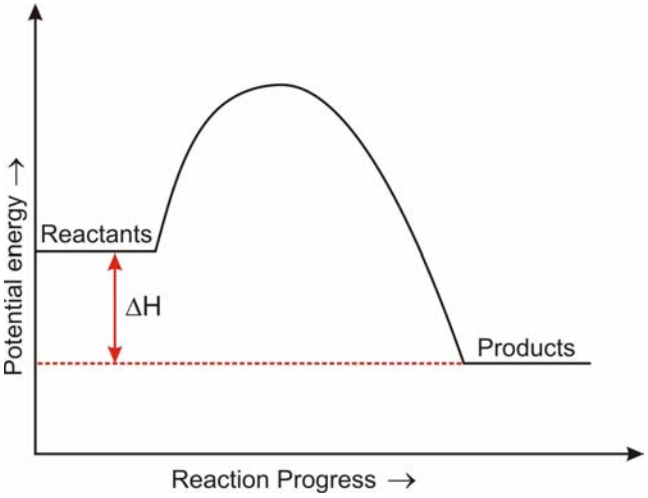


Figure 1: A Potential Energy Diagram.

(*Created by:* Therese Forsythe, *License:* CC-BY-SA)

The y-axis represents the potential energy. The ***potential energy*** measures the energy stored within the bonds and phases of the reactants and products. This potential energy represents the ***internal energy*** of the molecules and, in chemistry, is often called ***enthalpy*** . The x-axis represents the reaction progress. Chemical reactions proceed (or are read) from left to right. Therefore, looking at the potential energy diagram, the reactants are usually found to the left on the diagram and the products on the right.

The enthalpy of a substance is sometimes called **heat content**. The potential energy stored in the bonds of the substance was thought of as heat stored as potential energy. When a reaction occurs, the enthalpy or heat content of the reactants changes into the enthalpy or heat content of the products. The enthalpy of the reactants and products is almost never the same. Therefore, when a reaction occurs, there is a change in the amount of potential energy stored in the bonds between the reactants and the products. If the bonds of the products store more energy than the bonds of the reactants, then energy must be taken in during the reaction. If the bonds of the products store less potential energy than the bonds of the reactants, then excess potential energy will be left over and will come out of the reaction as kinetic energy. The difference in the enthalpy or heat content of the reactants and that of the products is expressed as ΔH, or *the change in enthalpy*. Since this energy is either taken in or given off during the reaction, it is also called *the heat of reaction*. Notice that in Figure 1, the enthalpy change of the reaction is noted by the symbol ΔH. The change in enthalpy, ΔH, is the difference between the potential energy of the reactants and the potential energy of the products.

Exothermic and Endothermic Potential Energy Diagrams

There are two types of potential energy diagrams. These two types center on the difference between the energies of the reactants and products. Consider Figures 2A and 2B below.

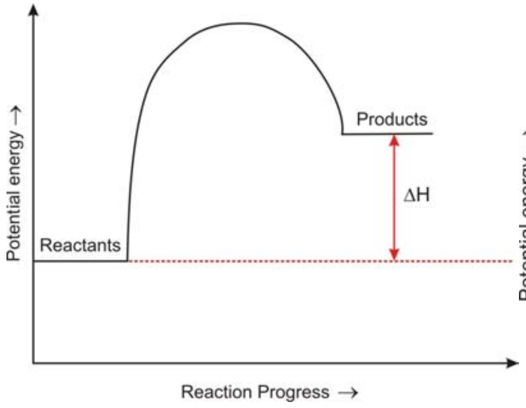


Figure 2A: Endothermic Reaction

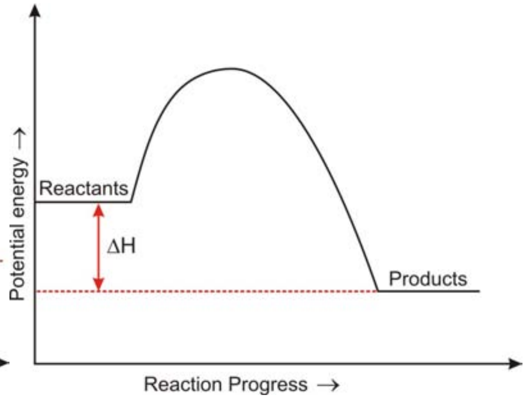


Figure 2B: Exothermic Reaction

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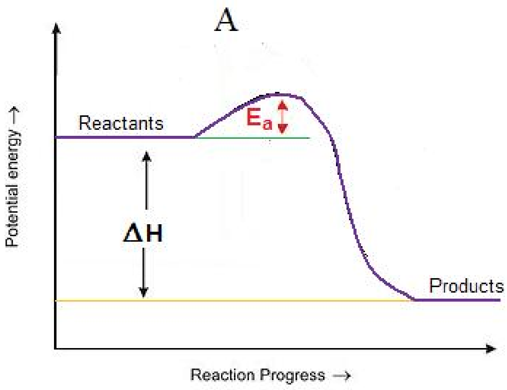
The definition of ΔH is the heat content (enthalpy) of the products minus the heat content (enthalpy) of the reactants, $\Delta H = H_{products} - H_{reactants}$. When the enthalpy of the reactants is greater than the enthalpy of the products, heat will be given off by the reaction and because of the way ΔH is defined, the ΔH will be negative. The opposite is true when the enthalpy of the products is greater than the enthalpy of the reactants.

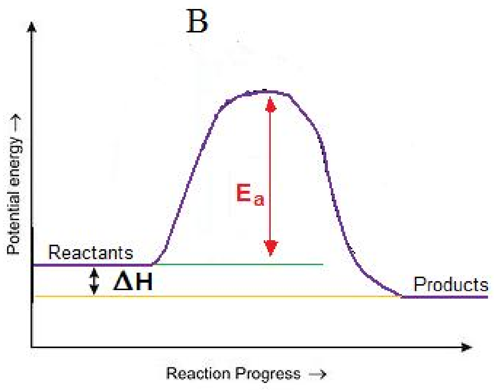
If the difference between the potential energy of the products and the reactants is positive, or $\Delta H > 0$, the reaction is considered to be endothermic (kinetic energy is absorbed and becomes potential energy in the bonds) and is represented by Figure 2A. If the difference between the potential energy of the products and the reactants is negative, or $\Delta H < 0$, the reaction is considered to be exothermic (excess potential energy from the bonds is left over and comes out into the surroundings as kinetic energy) and is represented by Figure 2B.

Activation Energy Barrier

The activation energy in a potential energy diagram represents the minimum amount of energy required to overcome the energy barrier. This energy must be supplied from the collision energy of the reactant molecules. If the molecules do not have sufficient collision energy to provide the activation energy, then the reaction must be heated to increase the kinetic energy of the reactants in order for the reaction to occur. For instance, hydrogen gas and oxygen gas can be kept in the same container at room temperature for long periods of time without reacting. Even though the molecules are colliding, they do not react since there is insufficient activation energy.

In potential energy diagrams, the symbol for activation energy is often designated as E_a. Look at the two exothermic reactions whose PE diagrams are represented in Figures A and B and notice the activation energy marked in each.





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When a reaction has a low activation energy, like A above, most of the reactant molecules have sufficient kinetic energy to react and the reaction will most likely be rapid (a high reaction rate). When a reaction has a high activation energy, like B above, most of the reactant molecules will NOT have enough energy to react and the reaction will most likely be very slow.

Activated Complex

The activated complex is a transitional state between the reactants and products. Consider what is happening in the reaction. The reactant bonds are breaking and the product bonds are forming during successful collisions. In the intermediate stages, a transitional complex is formed that creates a short-lived, very unstable species that is the intermediate between the reactants and products. The activated complex contains the highest amount of energy of all of the species in the reaction. The position therefore is at the top of the activation energy barrier as is shown in Figure 5.

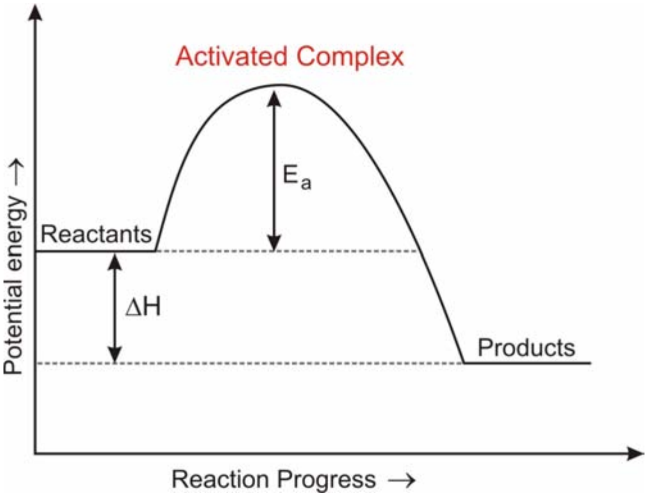

Figure 5: Potential Energy Diagram Showing Activated Complex.

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Sample Question 1: Consider the reaction between H_2 and I_2.

$$H_{2(g)} + I_{2(g)} \rightarrow 2\ HI_{(g)} \qquad \Delta H = 50.\ kJ$$

Under certain circumstances, the enthalpy of the reactants is 20 kJ/mol, the activation energy is 80 kJ, and the enthalpy of reaction is 30 kJ. Draw a potential energy diagram properly labeling the following.

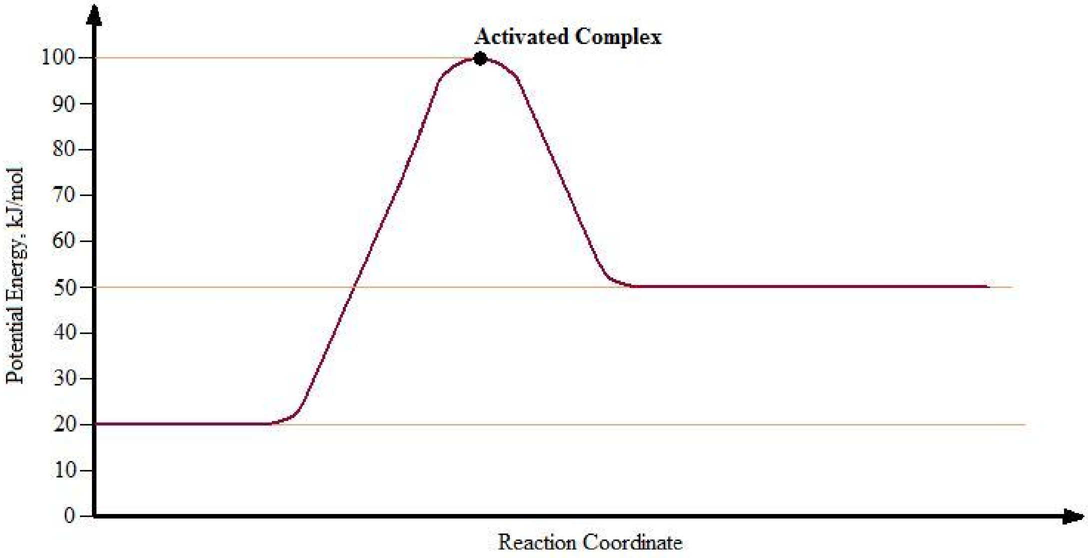
(a) the axes

(b) the activation energy

(c) the change in enthalpy

(d) the activated complex

Solution:



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Sample Question 2:

From the potential energy diagram above, list the values for

(a) the enthalpy of the reactants

(b) the enthalpy of the products

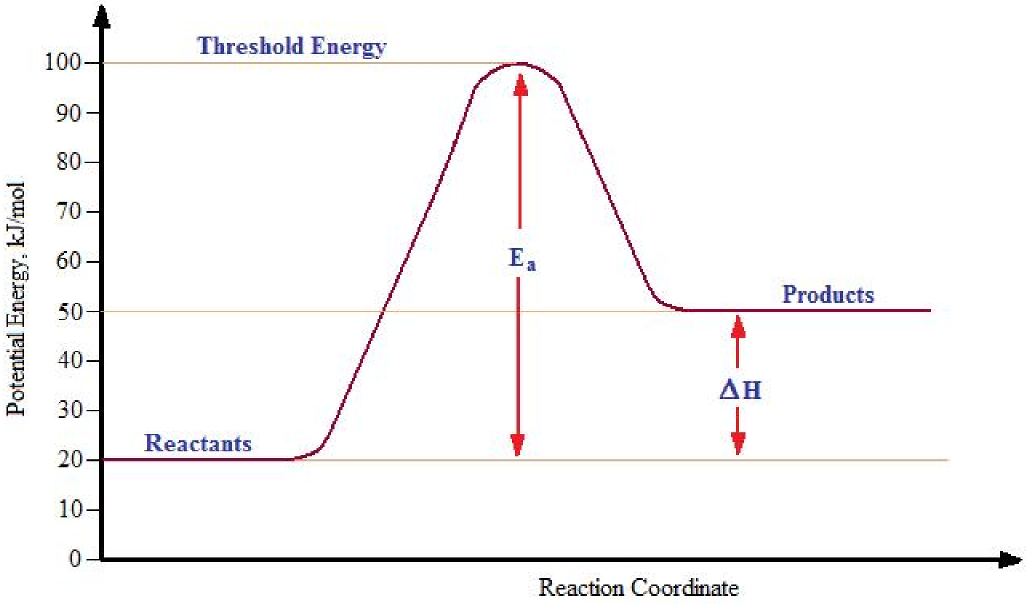
(c) the threshold energy

(d) the activation energy

(e) the change in enthalpy

Solution:

(a) 20 kJ/mol (b) 50 kJ/mol (c) 100 kJ/mol (d) 80 kJ/mol (e) 30 kJ/mol



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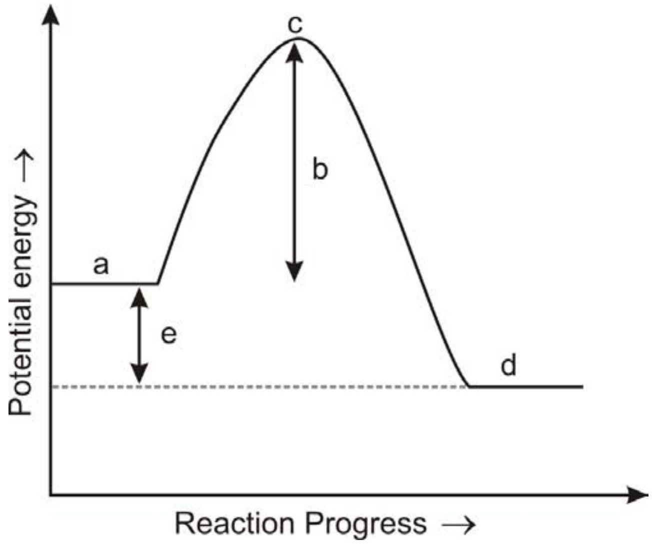
Lesson Summary

- Potential energy diagrams in the study of kinetics show how the potential energy changes during reactions from reactants and products. The ***potential energy*** measures the energy stored within the bonds (both intermolecular and intramolecular) of the reactants and products, therefore is the ***internal energy*** .
- Exothermic reactions have a potential energy difference between the products and reactants that is negative. Endothermic reactions have a potential energy difference between the products and reactants that is positive.
- The threshold energy in a potential energy diagram represents the minimum amount of potential energy necessary for a successful collision to take place. The activation energy is the difference between the energy of the reactants and the threshold energy. The activated complex is a transitional state between the reactants and products.

Review Questions

1. Define and explain the importance of the activation energy. **(Intermediate)**

Use the diagram below to answer questions 2 through 6.



2. Which letter represents the activation energy barrier? **(Beginning)**

(a) a (b) b c) c (d) d

3. Which statement best describes the reaction? **(Intermediate)**

(a) The reaction is exothermic in the forward reaction.

(b) The reaction is endothermic in the forward reaction.

(c) The reaction is exothermic in the reverse reaction.

(d) The reaction is exothermic only at high temperatures.

4. Which letter represents the change in enthalpy for the reaction? **(Beginning)**

(a) b (b) c (c) d (d) e

5. Which letter represents the activated complex for the reaction? **(Beginning)**

(a) a (b) b (c) c (d) d

6. What is an activated complex? **(Intermediate)**

(a) a transitional species that can eventually be isolated

(b) a transitional species of that must be made before the products can be formed

(c) a reactant molecule breaking into a product molecule

(d) part of the activation energy barrier

7. For the following reaction, the activation energy is 60 kJ. **(Intermediate)**

$A_{2(g)} + 2\ B_{(g)} \longrightarrow 2\ AB_{(g)}\ \Delta H = 50\ kJ/mol$

Draw a potential energy diagram properly labeling the following.

(a) The axes

(b) The reactants and products

(c) The activation energy

(d) The enthalpy

Vocabulary

potential energy diagrams	Potential energy diagrams in the study of kinetics show how the potential energy changes during reactions from reactants to products.
potential energy	The potential energy measures the energy stored within the bonds of the reactants and products and therefore is the internal energy.
exothermic reactions	Reactions that have a potential energy difference between the products and reactants that is negative.
endothermic reactions	Reactions that have a potential energy difference between the products and reactants that is positive.
activation energy	The minimum amount of energy that needs to be supplied to the system so that a reaction can occur.
activated complex	A high energy transitional state between the reactants and products.

Review Answers

1. The activation energy is the minimum amount of energy needed to be added to the reactants to produce the activated complex. The products can not be formed without the activated complex being made therefore the activation energy is the key to whether or not the reaction will occur.

2. (b) point b

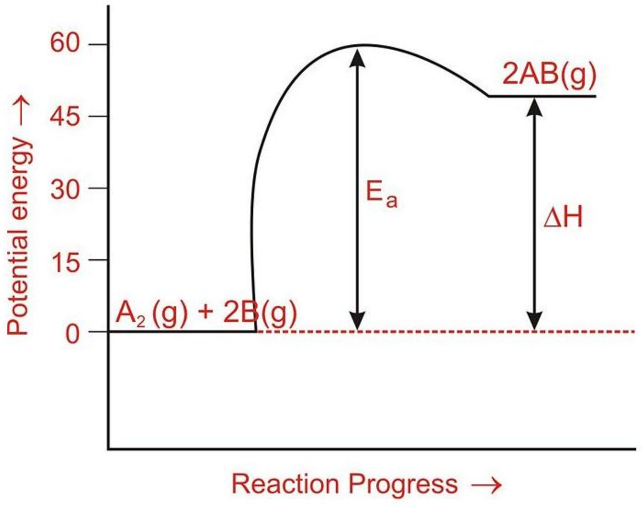
3. (a) the reaction is exothermic in the forward reaction

4. (d) point e

5. (c) point c

6. (b) a transitional species of that must be made before the products can be formed

7. (see below)



Factors That Affect Reaction Rates

Lesson Objectives

- State how the rate of reaction changes as a function of temperature.
- Explain how increased temperature increases the number of particles that can overcome the energy barrier.
- Provide examples of the temperature dependence on the rate in society.
- Describe the effect of increasing the concentration on the rate of a reaction.
- Indicate which reactants in a multi-step process can affect the rate of a reaction.
- Calculate, using experimental data, the relationship between the ratio of the change in concentration of reactants and ratio of the change in rate.
- Describe the surface area to volume ratio.
- Describe the effect of surface area on reaction rate.
- Describe how the change in the surface area affects the collision frequency.
- Describe real world examples of the effect of surface area on reaction rate.
- Define a catalyst.
- Identify a catalyst in a single equation.
- Identify a catalyst in a multi-step process.
- Describe how a catalyst affects the potential energy diagram.
- Explain how a catalyst affects the rate of the reaction.
- Explain how a catalyst affects our everyday lives, particularly with vitamins.

Introduction

Chemists use reactions to generate a product for which they have use. In some cases, the desired product is simply the energy that is released in an exothermic reaction. The energy released is used to heat homes, generate electric power, and so forth. In other reactions, the desired product is some specific compound for which the chemist has some use. For the most part, the reactions that produce some desired compound are only useful if the reaction occurs at a reasonable rate. For example, using a reaction to produce brake fluid would not be useful if the reaction required 8,000 years complete the product. Such a reaction would also not be useful if the reaction was so fast that it was explosive. For these reasons, chemists wish to be able to control reaction rates. In some cases, chemists wish to speed up reactions that are too slow and slow down reactions that are too fast. In order to gain any control over reaction rates, we must know the factors that affect reaction rates.

Chemists have identified many factors that affect the rate of a reaction. Some of these factors can be altered or controlled by chemists and some cannot. The factors that affect reaction rates have been placed in five categories. The first category contains all those factors that **cannot** be altered by chemists. The other four factors will be listed and discussed in detail in this section.

Factors Affecting Reaction Rates

1. The Nature of the Reactants

2. The Temperature of the Reactants
3. The Concentration of the Reactants
4. Surface Area
5. The Presence of a Catalyst

The Nature of the Reactants

There are a number of factors that affect the rate of reaction that cannot be altered. That is, once the reactants are chosen, these factors are permanently determined and cannot be changed. Since chemists can't do anything about these factors, they are lumped together in a single category. We will discuss them here and then not mention them in the remainder of the section. The focus of the remainder of this section will be on those factors affecting reaction rates that chemists can alter and thereby exert some control over reaction rates.

So, what are some of the factors affecting reaction rates that cannot be altered. You may remember from an earlier chapter, the discussion of bond strength. When a bond forms, energy is given off. If a large amount of energy is given off during bond formation, then the same large amount of energy will be required to break the bond. Bonds that give off great amounts of energy when the bond is formed are called strong bonds. Bonds that give off only a small amount of energy when they are formed are called weak bonds and are easily broken - requiring only the same small input of energy to break the bond. If the molecules in the reactants have strong bonds, then a large activation energy will be required under room conditions and the reaction rate will most likely be very slow. Since the bond strengths in the reactants cannot be changed, this factor affecting reaction rates is not alterable and therefore, it is placed in the "Nature of the Reactants" category.

Consider the number of bonds that need to be broken in the reactants. If a reaction involves combining silver ions and chloride ions in solution, you might note that there are **zero** bonds to be broken. In a solution, silver ions and chloride ions have no bonds to break. All that has to occur for these ions to react is that the ions have to come in contact. A reaction between such ions in solution will be almost instantaneous. Compare this to a reaction involving a reactant molecule that has a hundred bonds that have to be broken. Look at all the bonds that have to broken if the reactants for a reaction are $C_{41}H_{84}$ + 83 O_2. These reactants have so many bonds to break that there is no way a single collision could break them all. There are so many bonds to break that this reaction will have to occur with a long series of successive collisions. Such a reaction will always be slow under normal conditions. Once again, the number of bonds to be broken is dependent on the reactants involved in the reaction and cannot be changed. This factor, also, must go into the "Nature of the Reactants" category.

Let's consider one more factor affecting reaction rates that cannot be altered. Suppose you have two reactants that are essentially spheres such as copper atoms and silver ions. These two reactants can collide on any side from any direction and produce a successful collision. Compare that to a reactant whose molecule is shaped like a C and the only successful collision must be inside the opening of the C. For such a reactant, a very special collision geometry is required and very few of the collisions will have this particular geometry. In such cases, again, the reaction will be slow and there is no way to change the shape of the reactant. Reaction rates controlled by special collision geometries also go into the category "The Nature of the Reactants".

Effect of Temperature on Rate of Reaction

Increased Temperature

The rate of reaction was discussed in terms of three factors: collision frequency, the collision energy, and the geometric orientation. Remember that the collision frequency is the number of collisions per second. The collision frequency is dependent, among other factors, on the temperature of the reaction.

Rate = collision frequency × collision energy × collision geometric orientation

When the temperature is increased, the average velocity of the particles is increased. The average kinetic energy of these particles is also increased. The result is that the particles will collide more frequently because the particles move around faster and will encounter more reactant particles but this is only a minor part of the reason why the rate is increased. Just because the particles are colliding more frequently does not mean that the reaction will definitely occur.

The major effect of increasing the temperature is that more of the particles that collide will have the amount of energy needed to have an effective collision. In other words, more particles will have the activation energy needed to overcome the activation energy barrier and form the activated complex. The effect of raising the temperature, therefore, is to produce more activated complexes and, with the greater number of activated complexes that are formed, the faster the rate of reaction.

At room temperature, the hydrogen and oxygen in the atmosphere do not have sufficient energy to attain the activation energy needed to produce water.

$O_{2(g)} + H_{2(g)} \longrightarrow$ no reaction

At any one moment in the atmosphere, there are many collisions occurring between these two reactants. And, when this reaction does occur it is exothermic which tends to mean that the reaction should be happening. But what we find is that water is not formed from the oxygen and hydrogen molecules colliding in the atmosphere because the activation energy barrier is just too high and all the collisions are resulting in rebound. When the necessary energy is supplied to the molecules, the molecules overcome the activation energy barrier, the activated complex is formed, and water is produced:

$O_{2(g)} + 2\ H_{2(g)} \longrightarrow 2\ H_2O_{(L)}$

Decreased Temperature

There are times when the rate of a reaction needs to be slowed down. Using the factors as specified previously, one of ways to accomplish this would be to keep the reactants in separate containers so that there can be no collisions between the particles. At times that might not be practical so lowering the temperature could also be used to decrease the number of collisions that would occur and lowering the temperature would also reduce the kinetic energy available for activation energy. If the particles have insufficient activation energy, the collisions will result in rebound rather than reaction. Using this idea, when the rate of a reaction needs to be lower, keeping the particles from having sufficient activation energy will definitely keep the reaction at a lower rate.

A Generalization for Increased Temperature

The rate of most reactions can be dramatically increased with increased temperature. For reactions that normally occur at room temperature, a general “rule of thumb” is that for every increase of 10°C, the rate will be doubled. And if the temperature for these reactions is increased by 20°C, the rate will be increased by a factor of 4; increasing the temperature by 40°C the rate will be increased by a factor to 16. However, for any specific reaction, the actual rate increase will have to be determined by experimentation.

Examples of Temperature on Reaction Rate

Society uses the effect of temperature on rate every day. Food storage is a prime example of how the temperature effect on reaction rate is utilized by society. Consumers store food in freezers and refrigerators to slow down the processes that cause it to spoil. The decrease in temperature decreases the rate at which the food will break down or be broken down by bacteria.

In the early years of the 20th century, explorers were fascinated with trying to be the first one to reach the South Pole. In order to attempt such a difficult task at a time without most of the technology we take for granted today, they devised a variety of ways of surviving. One method was to store their food in the snow to be used later during their advances to the pole. On some explorations, they buried so much food, that they didn't need to use all of it and it was left. Many years later, when this food was located and thawed, it was found to still be edible.

When milk, for instance, is stored in the refrigerator, the molecules in the milk have less energy. This means that while molecules will still collide with other molecules, few of them will react (which means in this case "spoil") because the molecules do not have sufficient energy to overcome the activation energy barrier. The molecules do have energy and are colliding, however, and so, over time, over time, even in the refrigerator, the milk will spoil. Eventually the higher energy molecules will gain the energy needed to make the activated complex and when enough of these reactions occur, the milk becomes "soured".

However, if that same carton of milk was at room temperature, the milk would react (in other words "spoil') much more quickly. Now most of the molecules will have sufficient energy to overcome the energy barrier and at room temperature many more collisions will be occurring. This allows for the milk to spoil in a fairly short amount of time. This is also the reason why most fruits and vegetables ripen in the summer when the temperature is much warmer. You may have experienced this first hand if you have ever bitten into an unripe banana – it was probably sour tasting and might even have felt like biting into a piece of wood! When a banana ripens, numerous reactions occur that produce all the compounds that we expect to taste in a banana. But this can only happen if the temperature is high enough to allow these reactions to make those products.

Lesson Summary

- With an increase in temperature, there is an increase in the amount of kinetic energy that can be converted into activation energy in a collision and therefore there will be an increase in the reaction rate. A decrease in temperature would have the opposite effect.
- With an increase in temperature there is an increase in the number of collisions which is a minor factor in increasing the rate of reaction. The major reason reaction rate increases with increasing temperature is an increase in temperature increases the number of particles that have sufficient activation energy to overcome the activation barrier and form the activated complex.
- A rule of thumb used for the effect of temperature on the rate is that if the temperature is increased by 10^{o}C, the rate is doubled.

Review Questions

1. Why does an increase in temperature increase the rate of the reaction? **(Intermediate)**

2. Why does higher temperature increase the reaction rate? **(Intermediate)**

(a) more of the reacting molecules will have higher kinetic energy

(b) increasing the temperature causes the reactant molecules to heat up

(c) the activation energy will decrease

(d) increasing the temperature causes the potential energy to decrease

3. When the temperature is increased, what does not change? **(Intermediate)**

(a) number of collisions

(b) activation energy requirement

(c) number of successful collisions

(d) all of the above change

4. What is the “rule of thumb” used for the temperature dependence on the rate? **(Intermediate)**

5. The “rule of thumb” for the temperature effect on reaction rates is that a reaction rate will double for each rise in temperature of 10°C. The rate of reaction for a hypothetical reaction was found to be 0.62 mol/L-s at 6°C. What would be the rate at 46°C?

Vocabulary

effective collision A collision that results in a reaction.

Review Answers

1. Answers will vary but answers should include the fact that the fraction of molecules with energy greater than the threshold energy increases. With an increase in temperature the energy factor increases. An increase in temperature will in fact increase the number of successful collisions meaning that more particles will have sufficient energy to overcome the activation energy barrier and form the activated complex.

2. (a)

3. (b)

4. The “rule of thumb” used for the temperature dependence on the rate is that if the temperature is increased by 10°C, the rate is doubled.

5. The temperature rises 4 x 10°C, therefore the rate doubles four times.

Rate = 0.62 mol/L·s × 2× 2× 2× 2

Or

Rate = 0.62 mol/L·s x 2^4

Rate = 9.92 mol/L·s

Effect of Concentration

Increasing Concentration

If you had an enclosed space, like a classroom, and there was one red ball and one green ball flying around the room with random motion and undergoing perfectly elastic collisions with the walls and with each other, in a given amount of time, the balls would collide with each other a certain number of times determined by probability. If you now put two red balls and one green ball in the room under the same conditions, the probability of a collision between a red ball and the green ball would exactly double. The green ball would have twice the chance of encountering a red ball in the same amount of time. In terms of chemical reactions, a similar situation exists. Particles of two gaseous reactants or two reactants in solution have a certain probability of undergoing collisions with each other in a reaction vessel. If you double the concentration of either reactant, the probability of a collision doubles. The rate of reaction is proportional to the number of collisions per unit time. If one concentration of one of the reactants is doubled, the number of collisions will also double. Assuming that the percent of collision that are successful does not change, then having twice as many collisions will result in twice as many successful collisions. The rate of reaction is proportional to the number of collisions per unit time and increasing the concentration of either reactant increases the number of collisions and therefore, increases the number of successful collisions and the reaction rate.

Some reactions occur by a single collision between two reactant molecules while other reactions occur by a series of collisions between multiple reactant particles. We will consider the case of the single step now and the case of the multiple step reactions later in the unit.

The rate of a single collision chemical reaction at a given temperature can be expressed as a product of the concentrations of the reactants. For the reaction, $A_{(g)} + B_{(g)} \rightarrow AB_{(g)}$, the reaction rate can be expressed as:

Rate = k[A][B], where k is a constant for the reaction called the reaction constant and [A] and [B] are the molarities of the reactants.

If only the concentration of A is doubled, the equation would become,

Rate = k[2A][B] and the rate would obviously be double the previous rate.

If only the concentration of B is doubled, the equation would become,

Rate = k[A][2B] and once again the rate would obviously be double the previous rate.

If the concentrations of both A and B are doubled, the equation becomes

Rate = k[2A][2B] and now the rate would be 4 times the original rate.

Experimental Determination of Reaction Rate

When the reaction involves a series of collisions, the relationship between the reaction rate and the concentration of any single reaction can only be determined by a laboratory procedure. Consider the reaction below between NO_2 and CO. This reaction does not occur by a single collision but rather in a two step process.

$$\begin{array}{ll} NO_2(g) + \cancel{NO_2(g)} \rightarrow \cancel{NO_3(g)} + NO(g) & \text{(step 1)} \\ \cancel{NO_3(g)} + CO(g) \rightarrow \cancel{NO_2(g)} + CO_2(g) & \text{(step 2)} \\ \hline NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g) & \text{(overall reaction)} \end{array}$$

The effect of the concentration of a reactant on the rate of this multiple step reaction can only be known through experimentation. Let's look at one experiment where it can be determined how the concentration of the reactants affects the rate of the reaction.

Sample question: For the hypothetical reaction A + B $\rightarrow$ C + D, the following data was collected in an experiment to attempt to determine the effect of increasing the concentration of the reactants on the rate.

Trial	**[A] (mol/L)**	**[B] (mol/L)**	**Rate (mol/L·s)**
1	1.0	1.0	5.0×10^{-3}
2	2.0	1.0	5.0×10^{-3}
3	1.0	2.0	$10. \times 10^{-3}$

Determine the effect of increasing the [A] and increasing [B] on the rate of the reaction.

Solution:

Step 1: Try to find two trials where the concentration of A is changing while the concentration of B remains the same.

In this case, in trials 1 and 2, [A] changes while [B] remains constant. Since [A] is changing and [B] is staying the same, any change in the reaction rate is due to the change in [A].

Step 2: Determine the effect of changing the concentration of A on the reaction rate.

From trial 1 to trial 2, the concentration of A has doubled. The reaction rate in these two trials, however, did not change.

Therefore, the concentration of A has no effect on the rate for this reaction.

Step 3: Try to find two trials in which [B] changes while [A] stays the same.

In trials 1 and 3, the concentration of B changes while A stays the same. From trial 1 to trial 3, the concentration of B doubles. The reaction rate also doubled between these two trials. When the concentration of B doubled, the reaction rate also doubled. Therefore, we can conclude that the reaction rate is directly proportional to the concentration of B.

Therefore, when the concentration of A is increased, there is no effect on the rate of the reaction.

Therefore, when the concentration of B is doubled, the rate is doubled. In other words, increasing the concentration of B increases the rate.

Example of the Effect of Concentration on Reaction Rate

The chemical test used to identify a gas as oxygen or not relies on the fact that increasing the concentration of a reactant increases reaction rate. The reaction we call combustion refers to a reaction in which a flammable substance reacts with oxygen. If we light a wooden splint (a thin splinter of wood) on fire and then blow the fire out, the splint will continue to glow in air for a period of time. If we insert that glowing splint into any gas that does not contain oxygen, the splint will immediately cease to glow - that is the reaction stops. Oxygen is the only gas that will support combustion. Air is approximately, 20% oxygen gas. If we take that glowing splint and insert it into pure oxygen gas, the reaction will increase its rate by a factor of five - since pure oxygen has 5 times the concentration of oxygen that is in air. When the reaction occurring on the glowing splint increases its rate by a factor of five, the glowing splint will suddenly burst back into full flame. This test, of thrusting a glowing splint into a gas, is used to identify the gas as oxygen. Only a greater concentration of oxygen than that found in air will cause the glowing splint to burst into flame.

Lesson Summary

- Increasing the concentration of a reactant increases the frequency of collisions between reactants and will, therefore, increase the reaction rate.

Review Questions

1. Explain how concentration affects reaction rate using the collision theory. You may want to include a diagram to help illustrate your explanation. **(Intermediate)**

2. Why is the increase in concentration directly proportional to the rate of the reaction? **(Intermediate)**

(a) The kinetic energy increases.

(b) The activation energy increases.

(c) The number of successful collisions increases.

(d) All of the above.

3. For the reaction below, an experiment shows that if the concentration of $H_{2(g)}$ is doubled, the rate of reaction stays the same. If the concentration of $Cl_{2(g)}$ doubles, the rate of the reaction quadruples. **(Intermediate)**

$$H_{2(g)} + Cl_{2(g)} \rightarrow 2\ HCl_{(g)}$$

What is the explanation for this observation?

(a) The reaction is nearing completion and all $H_{2(g)}$is used up.

(b) The reaction occurs in more than one step.

(c) Excess $Cl_{2(g)}$ has been added.

(d) Not enough information is given.

4. The mechanism for a reaction is as follows:

$NO + Br_2 \rightarrow NOBr_2$ (reaction 1) (slow)

$NOBr_2 + NO \rightarrow 2\ NOBr$ (reaction 2) (fast)

Which of the following would have the greatest effect on the rate of reaction? **(Intermediate)**

(a) Increase [NO]

(b) Increase $[Br_2]$

(c) Increase $[NOBr_2]$

(d) Increase [NO] and $[Br_2]$

5. Consider the following reaction mechanism. For which substance would a change in concentration have the greatest effect on the rate of the overall reaction? **(Intermediate)**

$2\ A \rightarrow B + 2\ C$ (slow)

$B + C \rightarrow D + E$ (fast)

(a) A, B, C

(b) A

(c) B

(d) C

6. (3) The following data were obtained for the decomposition of N_2O_5 in $CCl_{4(aq)}$ at 45°C.

Trial	N_2O_5 mol/L	Rate (mol/L·s)
1	0.316	0.39
2	0.274	0.34
3	0.238	0.29
4	0.206	0.25
5	0.179	0.22

Determine the effect of decreasing the $[N_2O_5]$ on the rate of the reaction. **(Challenging)**

$$\frac{[N_2O_5]_{trial2}}{[N_2O_5]_{trial1}} = \frac{0.274}{0.316} = 0.867$$

$$\frac{\text{rate}_{\text{trial2}}}{\text{rate}_{\text{trial1}}} = \frac{0.34}{0.39} = 0.87$$

Further Reading / Supplemental Links

http://en.wikipedia.org/wiki

Vocabulary

multi-step process Reactions that take more than one step in order to make the products.

Review Answers

1. The collision theory states that an increase in concentration increases the probability of a collision. If there is an increase in the number of collisions per unit time, there will be an increase in the rate of the reaction. A diagram should show two containers of the same volume, one with more particles than the other.

2. (c) The number of successful collisions increases.

3. (b) The reaction occurs in more than one step.

4. (d) Increase [NO] and [Br_2]

5. (b) A

6. Decreasing the concentration of N_2O_5 causes the rate to decrease by the same proportion.

Effect of Surface Area

The Relationship Between Surface and Reaction Rate

The very first requirement for a reaction to occur between reactant particles is that the particles must collide with each other. The previous section pointed out how increasing the concentration of the reactants increases reaction rate because it increased the frequency of collisions between reactant particles. It can be shown that the number of collisions that occur between reactant particles is also dependent on the surface area of reactants. Consider a reaction between reactant RED and reactant BLUE in which reactant BLUE is in the form of a single lump. Then compare this to the same reaction where reactant BLUE has been broken up into many smaller pieces.

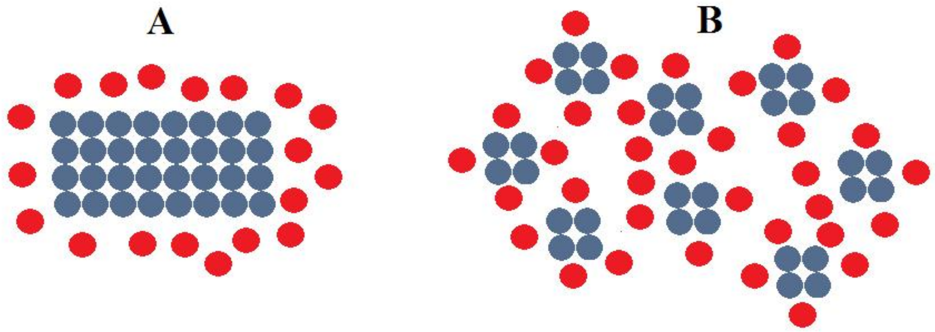


Figure 1: When the large piece of blue molecules is broken into smaller pieces, red molecules can collide with many more blue molecules.

(*Created by:* Richard Parsons, *License:* CC-BY-SA)

In diagram A, only the BLUE particles on the outside surface of the lump are available for collision with reactant RED. The BLUE particles on the interior of the lump are protected by the BLUE particles on the surface. In diagram A, if you count the number of BLUE particles available for collision, you will find that only 20 BLUE particles could be struck by a particle of reactant RED. In diagram A, there are a number of BLUE particles on the interior of the lump that cannot be struck. In diagram B, however, the lump has been broken up into smaller pieces and all the interior BLUE particles are now on a surface and available for collision. In diagram B, more collisions between BLUE and RED will occur, and therefore, the reaction in diagram B will occur at faster rate than the same reaction in diagram A. Increasing the surface area of a reactant increases the frequency of collisions and increases the reaction rate.

The more surface area that is available for particles to react the faster the reaction will occur. You can see an example of this in everyday life if you have ever tried to start a fire in the fireplace. If you hold a match up against a large log in an attempt to start the log burning, you will find it to be an unsuccessful effort. Flammable material like wood requires a significant input of activation energy for the reaction to occur. The reaction between wood and oxygen is an exothermic reaction and once the fire has been started, the heat released by the first reactions to occur will provide the activation energy for the succeeding reactions. However, holding a match against a large log will not cause enough reactions to occur in order to keep the fire going by providing sufficient activation energy for further reactions. In order to start a wood fire, it is common to break a log up into many small, thin sticks called kindling. These thinner sticks of wood provide many times the surface area of a single log. The match will successfully cause enough reactions in the kindling so that sufficient heat is given off to provide activation energy for further reactions.

There have been, unfortunately, cases where serious accidents were caused by the failure to understand the relationship between surface area and reaction rate. One such example occurred in flour mills. A grain of wheat is not very flammable. It takes a significant effort to get a grain of wheat to burn. If the grain of wheat, however, is pulverized and scattered through the air, only a spark is necessary to cause an explosion. When the wheat is ground to make flour, it is pulverized into a fine powder and some of the powder gets scattered around in the air. A small spark then, is sufficient to start a very rapid reaction which can destroy the entire flour mill. In a 10-year period from 1988 to 1998, there were 129 grain dust explosions in mills in the United States. Efforts are now made in flour mills to have huge fans circulate the air in the mill through filters to remove the majority of the flour dust particles. Another example is in the operation of coal mines. Coal, of course, will burn but it takes an effort to get the coal started and once it is burning, it burns slowly because only the surface particles are available to collide with oxygen particles. The interior particles of coal have to wait until the outer surface of the coal lump burns off before they can collide with oxygen. In coal mines, huge blocks of coal must be broken up before the coal can be brought out of the mine. In the process of breaking up the huge blocks of coal, drills are used to drill into the walls of coal. This drilling produces fine coal dust that mixes into the air and then a spark from a tool can cause a massive explosion in the mine. There are explosions in coal mines for other reasons but coal dust explosions contributed to the death of many miners. In modern coal mines, lawn sprinklers are used to spray water through the air in the mine and this reduces the coal dust in the air and eliminates coal dust explosions.

Increasing Surface Area Increases Frequency of Collision

An increase in the surface area allows for an increase in the frequency of collisions between reacting molecules which will increase the rate of reaction. Look at the diagram of a hypothetical tablet below that is going to be used to react with hydrochloric acid (Figure 1A). When the tablet is crushed before the reaction begins, look at the difference in the number of reaction sites at which the hydrochloric acid can react (Figure 1B).

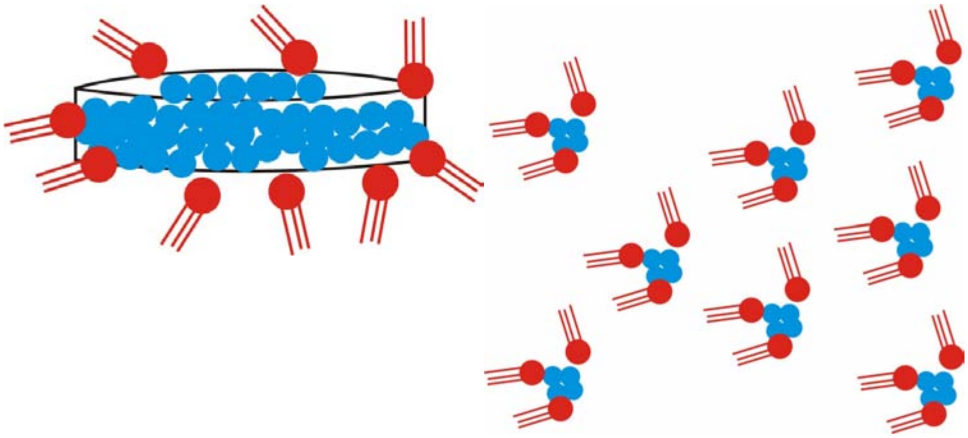


Figure 1A: Low Surface Area. **Figure 1B:** High Surface Area.

(*Created by:* Therese Forsythe, *License:* CC-BY-SA)

An increase in the surface area increases the frequency in collisions and therefore the rate of the reaction is increased.

Examples

A way to study this factor is the following: take two solids, put them together and observe the reaction; then, put one of these solids into solution, add the other solid and observe the reaction. For example: If you were to take a few grams of copper (II) chloride and place them into a beaker along with a piece of aluminum foil, it would take a numbers days if not weeks before you would observe more than just a few changes. However if you were to make a solution of the copper (II) chloride and then add the aluminum foil, you would observe an almost immediate reaction. In this case, the surface area of only one of the reactants was changed, but that change would dramatically affect the rare of reaction because the copper (II) chloride ions would now be totally separated and could individually interact with the atoms present in the aluminum foil.

Lesson Summary

- Increasing the surface area of a reactant increases the number of particles available for collision and will increase the number of collisions between reactants per unit time.
- Increasing the frequency of collisions increases the reaction rate.

Review Questions

1. Why, using the collision theory, do reactions with higher surface are have a faster reaction rates? **(Intermediate)**

2. When does an increase in surface area not increase the rate of reaction? **(Intermediate)**

(a) The rate will not be increased if there is insufficient activation energy present.

(b) The rate will not increase if there is not an increase in collisions.

(c) The rate will not increase if the concentration doesn't change.

(d) The rate will not increase if ΔH does not increase.

3. Choose the substance with the greatest surface in the following groupings: **(Intermediate)**

(a) a block of ice or crushed ice

(b) sugar cubes or sugar crystals

(c) a piece of wood or wood shavings

(d) $O_{2(s)}$ or $O_{2(g)}$

(e) $AgNO_{3(s)}$ or $AgNO_{3(aq)}$

4. Lighter fluid is sometimes used to get a barbeque coals to begin to burn. Give a complete explanation for **(Intermediate)**

(a) the purpose of the lighter fluid; and,

(b) the purpose of the coals.

Vocabulary

surface area to volume ratio	The comparison of the volume inside a solid to the area exposed on the surface.

Review Answers

1. When the area on the surface of a solid is increased, there will be a greater chance for collisions to occur and with sufficient activation energy, the rate of the reaction will increase.

2. (a) The rate will not be increased if there is insufficient activation energy present.

3. (a) crushed ice

(b) sugar crystals

(b) wood shavings

(c) $O_{2(g)}$

(d) $AgNO_{3(aq)}$

4.

(a) The activation energy of the fluid is low so that a match will provide enough energy for it to react. Since the lighter fluid's surface is high and its activation energy is low, it can transfer it can easily transfer the energy needed by the coal to begin to burn.

b) Once the coals have the necessary activation energy, they can begin reacting. And since the coals have low surface area, they will burn slowly and will slowly provide the energy needed to cook the food.

Effect of a Catalyst

Introduction

The final factor that affects the rate of the reaction is the effect of the catalyst. A catalyst is a substance that speeds up the rate of the reaction without itself being consumed by the reaction.

There are a number of catalysts that we recognize. There are surface catalysts which merely provide a surface for intermediate products to adhere to and there are catalysts that are used at the beginning of a reaction but are completely reproduced at the end. The substances called enzymes in biology are catalysts that help carry out numerous chemical reactions in the body. Many commercial preparations of chemicals for industry rely on catalysts to prepare their products more efficiently and cost effectively. For example in the production of sulfuric acid, iron oxide or vanadium oxide is used in combination with platinum as surface catalysts to produce the desired H_2SO_4.

$$2KClO_3(s) \xrightarrow{MnO_2(s)} 2KCl(s) + 3O_2(g) \quad \text{(Equation 1)}$$

In the reaction of potassium chlorate breaking down to potassium chloride and oxygen, a catalyst is available to make this reaction occur much faster than it would occur by itself under room conditions. The catalyst is manganese dioxide and its presence causes the reaction shown above to run many times faster than it occurs without the catalyst. When the reaction has reached completion, the MnO_2 can be removed from the reaction vessel and its condition is exactly the same as it was before the reaction. This is part of the definition of a catalyst . . . that it is not consumed by the reaction.

We already know that we can increase the rate of a reaction by adding one of the reactants to increase the concentration of that reactant and thus increase the reaction rate. But, that added reactant will be consumed by the reaction. A catalyst is a substance that can be added and will increase the reaction rate but will not be consumed by the reaction.

In this lesson, the effect of the catalyst on the reaction rate will be considered as well as its effect on the potential energy diagrams. Let's begin.

A Catalyst is Not a Reactant

As stated in the introduction, a catalyst is defined as a substance that speeds up the rate of the reaction but is itself not consumed by the reaction. In other words, the catalyst is not seen in the reaction as either a reactant or a product. Consider Equation 1 again.

$$2KClO_3(s) \xrightarrow{MnO_2(s)} 2KCl(s) + 3O_2(g) \quad \text{(Equation 1)}$$

Equation 1 is a typical laboratory experiment where potassium chlorate is heated to produce potassium chloride and oxygen gas. The reaction is very slow unless you add manganese dioxide as a catalyst. Manganese dioxide is a black powder; potassium chlorate is a white powder. After heating the potassium chlorate and obtaining the oxygen gas at the end of the reaction, all of the black MnO_2 can be recovered. You should note that the catalyst is not written into the equation as a reactant or product but is noted above the yields arrow. This is standard notation for the use of a catalyst.

Look at the following three-step process below:

$$\begin{array}{l}
ClO^-(aq) + \cancel{H_2O(l)} \rightarrow \cancel{HOCl(aq)} + \cancel{OH^-(aq)} \\
Br^-(aq) + \cancel{HOCl(aq)} \rightarrow \cancel{HOBr(aq)} + Cl^-(aq) \\
\cancel{OH^-(aq)} + \cancel{HOBr(aq)} \rightarrow \cancel{H_2O(l)} + BrO^-(aq) \\
\hline
ClO^-(aq) + Br^-(aq) \rightarrow + Cl^-(aq) + BrO^-(aq)
\end{array}$$

In this three-step process, all of the reactions are added together and all substances that appear on both sides of the equation are eliminated before writing the final overall equation. Notice how $H_2O_{(L)}$ is consumed in the first equation of the sequence and then produced in the final equation of the sequence. Since $H_2O_{(L)}$ is consumed and then produced, it is a catalyst. The presence of the water molecule causes this reaction to occur at a higher rate than it will occur without the presence of water. Therefore, the water is introduced into the reaction and is used in the reaction but it is reproduced at the end of the reaction and so the total amount of it is available at the end. This is the behavior of a catalyst.

Catalysts Provide a Different Path with Lower Activation Energy

Some reactions occur very slowly without the presence of a catalyst. In other words the activation energy for these reactions is very high. When the catalyst is added, the activation energy is lowered because the catalyst provides a new reaction pathway with lower activation energy.

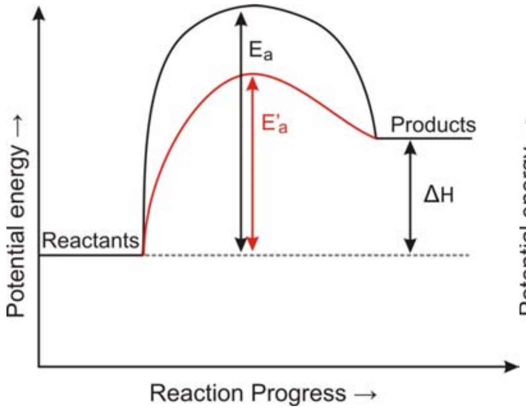


Figure 1

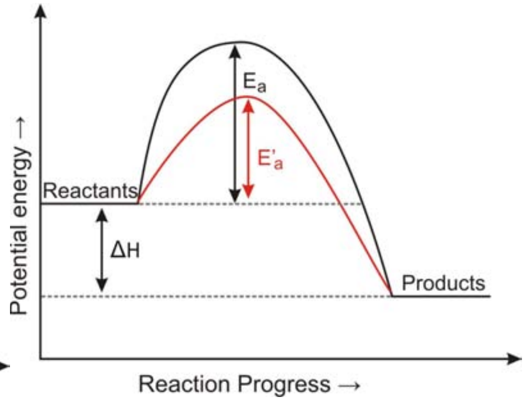


Figure 2

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Remember that the catalyst does not get consumed itself in the reaction so the reactants and product positions are not affected by the addition of the catalyst. In Figure 1, the endothermic reaction shows the catalyst reaction in red with the lower activation energy, designated E'_a . The new reaction pathway has lower activation energy but has no effect on the energy of the reactants, the products, or the value of ΔH.

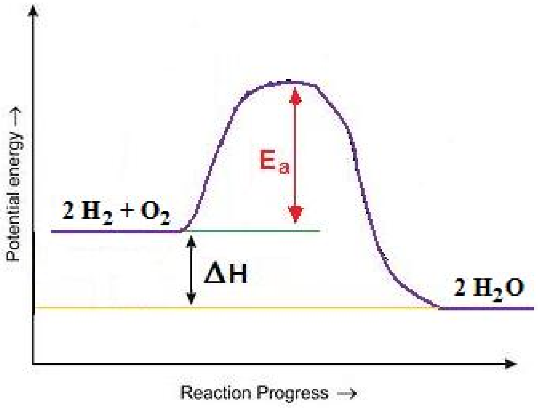
The same is true for the exothermic reaction in Figure 2. The activation energy of the catalyzed reaction (again designated by E'_a) is lower than that of the uncatalyzed reaction. The new reaction pathway provided by the catalyst for the exothermic reaction in diagram 2 affects the energy required for reactant bonds to break and product bonds to form.

Surface Catalysts and Enzymes

An example of a surface catalyst is the behavior of a platinum catalyst in the reaction in which hydrogen and oxygen form water.

$$2\ H_{2(g)} + O_{2(g)} \longrightarrow 2\ H_2O_{(g)}$$

This reaction, as you are probably aware is so slow under room conditions that it essentially doesn't occur. That's why we have hydrogen gas and oxygen gas in our atmosphere without this reaction occurring. Even if hydrogen and oxygen gases are mixed in a reaction vessel, no reaction occurs. This reaction has a very high activation energy requirement and room conditions simply do not provide sufficient energy for the reaction to occur.



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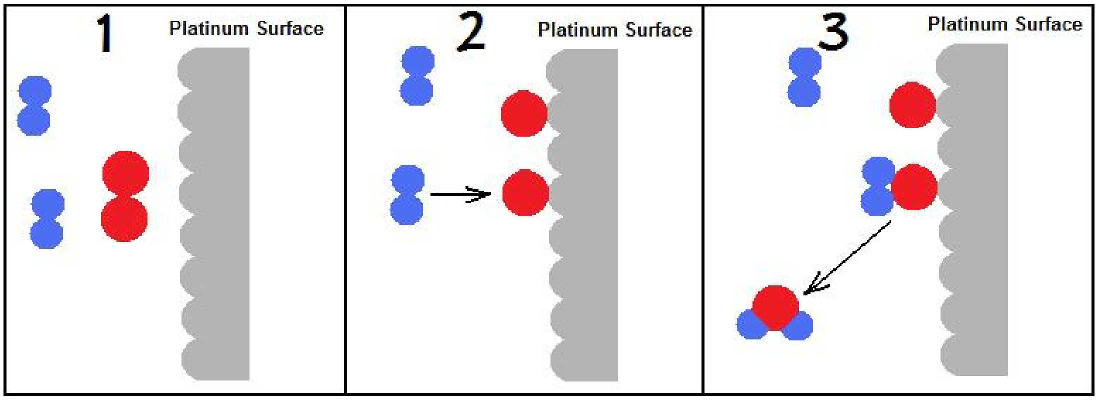
The uncatalyzed reaction between hydrogen gas and oxygen gas requires all the reactant particles to collide in a single collision with enough activation energy to break the bond in both the hydrogen molecules AND break the double bond in the oxygen molecule. Under room conditions, these particles are not nearly energetic enough for a collision to provide that much activation energy and therefore, no reaction occurs.



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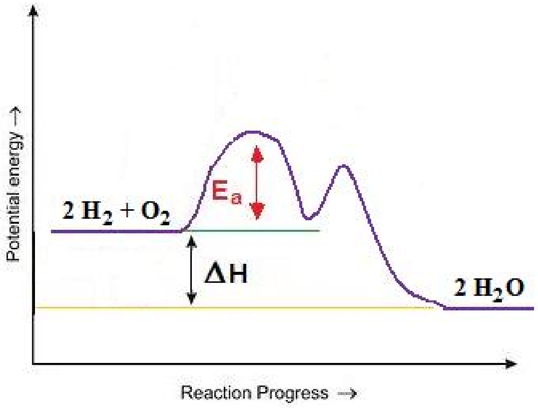
If a platinum surface is available, the oxygen molecules can strike the platinum surface and break the bond holding the oxygen atoms together. The oxygen atoms then adhere to the surface of the platinum. This collision requires less energy than the giant collision necessary when platinum is not present. Later, a hydrogen molecule can collide with one of the oxygen atoms adhered to the platinum surface and this collision breaks the bond in the hydrogen molecule and then the hydrogen and oxygen can combine and leave the surface of the platinum. Eventually, another hydrogen molecule repeats this process with the final oxygen atom. When all the oxygen atoms have left the surface of the platinum, the platinum is exactly the same as it was before the reaction. In this way, the reaction has occurred with several smaller collisions rather than one large one. Room conditions are sufficient to provide the activation energy necessary for the small collisions but not the large one. Therefore, in the presence of a platinum catalyst this reaction will occur at room temperature. The reaction rate has been significantly increased. The fact that the platinum increases the reaction rate but is not permanently consumed, qualifies it as a catalyst in this reaction. As evidence of the success of the platinum as a catalyst for this reaction, if a piece of platinum is dropped into a small container of hydrogen and oxygen gas at room conditions, a small explosion occurs as this reaction goes to completion almost immediately.

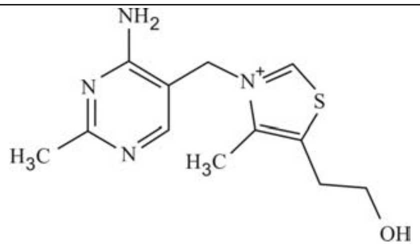


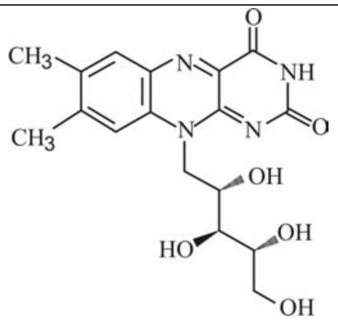
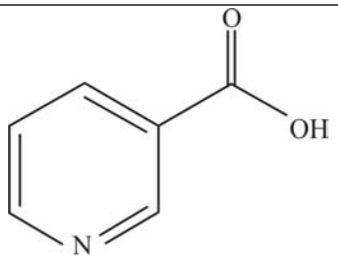
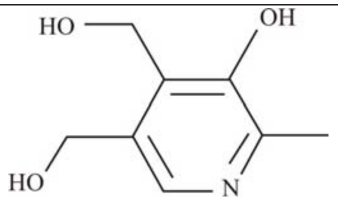
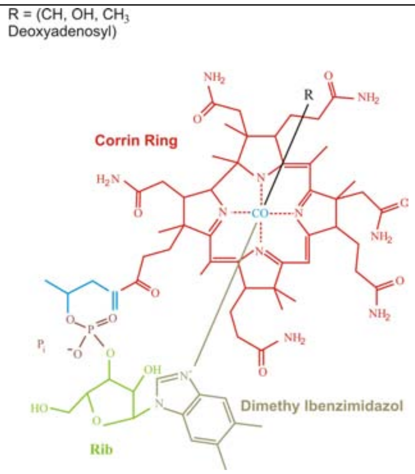
The potential energy diagram for the catalyzed reaction has some parts that have changed and some parts that have not changed. The reactants and products are exactly the same as before because it is the same reaction. Since the products and reactants are the same, they have the same enthalpy stored in their bonds and therefore, the ΔH will be exactly the same for both reactions. The area that has changed is the energy barrier. Each of collisions has a lower activation energy requirement so the energy barrier is lower in the catalyzed reaction than it was in the uncatalyzed reaction. The reaction mechanism for catalyzed reaction is different - the reaction does not occur by the same process. The catalyst provides a different reaction path for the same reaction and the new path has a lower activation energy requirement. The lower activation energy allows for a much faster reaction rate.

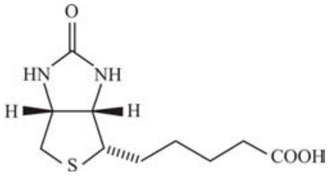
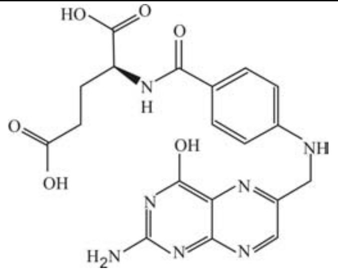
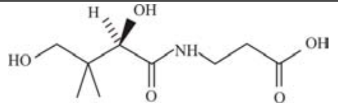
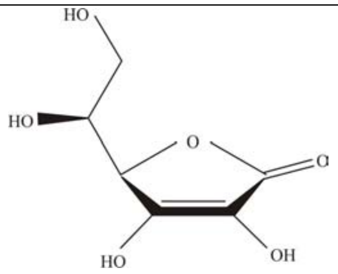
While many reactions in the laboratory can be increased by increasing the temperature, that is not possible for all the reactions that occur in our bodies throughout our entire lives. In fact, the body needs to be maintained at a very specific temperature: 98.6°F or 37°C. Of course there are times, for instance, when the body is fighting an infection, when the body temperature may be increased. But generally, in a healthy person, the temperature is quite consistent. However, many of the reactions that a healthy body depends on could never occur at body temperature. The answer to this dilemma is catalysts or what are also referred to as enzymes. Many of these enzymes are made in your cells since your DNA carries the directions to make them. However, there are a some enzymes that your body must have but are not made in your cells. These catalysts must be supplied to your body in the food you eat and are called vitamins.

One example of these catalysts is the water-soluble vitamins. These vitamins include B_1 (Thiamin), B_2 (Riboflavin), B_3 (Niacin), B_6 (Pyridoxine), B_{12} (Cyanocobalamin), Biotin, Folacin, Pantothenic Acid, and Vitamin C. Table 1 below shows the structure, the use of the different vitamins and where they are found commonly in foods. The role of the vitamin in the body is as a catalyst in metabolism. Remember that catalysts are substances that are not consumed by a reaction. They are used in order to speed up the reaction. The vitamin, itself, does not affect how much of the particular amino acid, protein, or other product that is produced in the reaction to which it is involved. It is important to remember that while these catalysts are not used up in a reaction, a person nonetheless needs to continue to take in vitamins since the body only uses them for a limited amount of time and then they are discarded.

Table 1: Summary Points of Water Soluble Vitamins

Name	Structure	Some important Functions	Commonly Found
B_1 (Thiamin)		• Enhances circulation • aids in digestion • great for the brain	Peanuts, pork, bran, egg yolk, beans are some examples.

	http://en.wikipedia.org/wiki/Thiamin		
B_2 (Riboflavin)	 http://en.wikipedia.org/wiki/Riboflavin	• Required for the body to use O_2, and the metabolism of amino acids and fatty acids. • B_2 helps activate B_6, helps create B_3 • assists in the working of the adrenal gland	Organ meats, nuts, cheese, eggs, milk leafy green vegetables, fish, whole grains, and yogurt are some examples.
B_3 (Niacin)	 http://en.wikipedia.org/wiki/Niacin	• Is necessary for cell respiration, releasing energy in the metabolism of fats, proteins, and carbohydrates • Is required for circulation, the proper working of the nervous system	Liver, poultry, fish, nuts, cereals, asparagus, seeds, milk, and leafy green vegetables, are some examples.
B_6 (Pyridoxine)	 http://en.wikipedia.org/wiki/Pyridoxine	• Assist with the working of the immune system and cell growth • Is necessary for the metabolism of fats, proteins, and carbohydrates	Brewer's yeast, eggs, chicken, carrots, fish, liver, peas, walnuts are some examples.
B 1 2 (Cyanocobalamin)	 http://en.wikipedia.org/wiki/B12	• B12 assists in the production and maintenance of red blood cells as well as the promotion of energy in the body. • B12 also assists with the metabolism of fats, carbohydrates and proteins. • It is thought that B12 helps speed up thought processes (pardon the pun!)	B12 is present in liver, shellfish, eggs, cheese, fish, but also can be manufactured in the body. An interesting point is that B12 is present in milk but the processing of milk may lead to destruction of the vitamin B12.

Biotin – Vitamin H	 http://en.wikipedia.org/wiki/Biotin	• Biotin is used for cell growth, the production of fatty acids • It assists in the metabolism of fats and proteins. • It works to release energy from food and is also necessary for maintaining blood sugar levels. • It is necessary for healthy tissues such as skin, hair, nervous tissue, healthy glands, and bone marrow.	Cheese, beef liver, cauliflower, eggs, mushrooms, chicken breasts, salmon, spinach, brewer's yeast, and nuts are some examples. Vitamin H is able to be made by the body in small supplies if the body senses a need for this vitamin.
Folacin (Folic Acid) – B_9	 http://en.wikipedia.org/wiki/Folacin	• Necessary for DNA synthesis, cell growth, and red cell formation. • Required for the energy production and in the formation of the iron in the hemoglobin. • B9 is a coenzyme for RNA and DNA synthesis. • B9 is also essential for fetal development	Fresh green vegetables (broccoli, spinach), fruit, beans, whole grains and liver are some examples.
Pantothenic Acid – B_5	 http://en.wikipedia.org/wiki/Pantothenic_Acid	• Supports the adrenal gland by helping to secrete hormones (i.e. cortisone). • Assists in metabolism, especially in the metabolism of fat and carbohydrates. • Helps create lipids, hormones, and hemoglobin • Helps fight allergies • Helps maintain healthy skin, muscles and nerves.	Beef, brewer's yeast, eggs, fresh vegetables, kidney, legumes, liver, mushrooms, nuts, pork, saltwater fish, and whole wheat are some examples.
Vitamin C.	 http://en.wikipedia.org/wiki/Vitamin_C	• needed to produce collagen neurotransmitters, steroid hormones, and carnitine • needed in the conversion of cholesterol to bile acids • promotes healthy cell development, calcium absorption, and tissue growth and repair • enhances iron bioavailability	Leafy green vegetables, berries, citrus fruits, tomatoes, melons, papayas are good examples.

		• works as an antioxidant • is thought to help prevent cataracts and other degenerative diseases, fight against infection, and enhance the immune system	

You can see from Table 1, these water-soluble vitamins act on a large number of the systems in our bodies. One example is Vitamin C. It is only needed to be added to the diet of humans and several kinds of animals.

It is interesting how some of the vitamins work in the body. For some vitamins, their role is to carry the chemical groups between enzymes; therefore they are given the term coenzymes and act as the precursor for enzymes. Their function is essential to the development and/or maintenance of systems within our bodies.

If you look at folic acid as an example, it is responsible for assisting in DNA synthesis. Folic acid has a structure shown below.

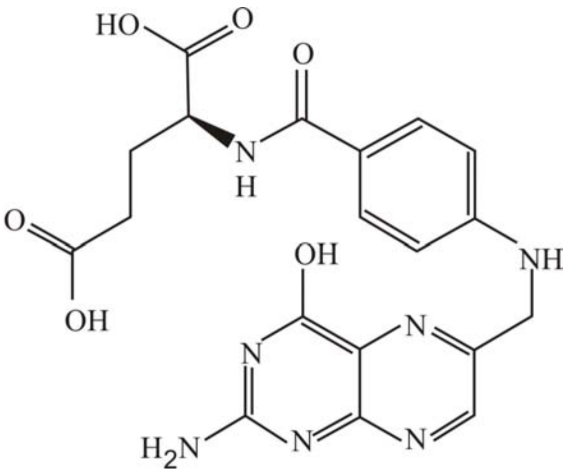


Figure 3A: An example of Folic Acid.

Methyl-tetrahydrofolate is the chemical name for folic acid. Folic acid has the job of supplying thymidine triphosphate (see diagram 4).

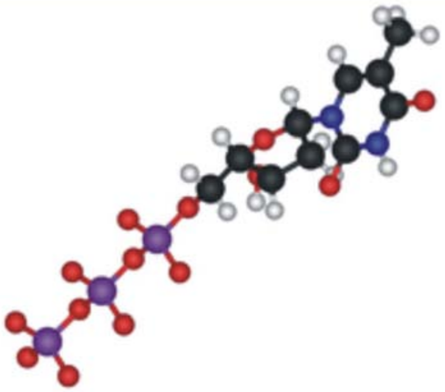


Figure 3B: An example of Thymidine Triphosphate.

In the synthesis of DNA, there are four nucleotide bases required. Thymidine triphosphate is one of these bases and is so important that if it is not present, the DNA synthesis stops. Folic acid (or folacin) supplies this nucleotide base. Neural tube defects such as, spina bifida, are the direct result of a lack of folic acid, specifically thymidine triphosphate. A low amount of this nucleotide base causes the neural tube in the brain to improperly close or not close at all causing serious defects. The lower amount of the base, the more serious the defect.

Lesson Summary

- The catalyst is a substance that speeds up the rate of the reaction without itself being consumed by the reaction. When the catalyst is added, the activation energy is lowered because the catalyst provides a new reaction pathway with lower activation energy.
- The new reaction pathway has lower activation energy but has no effect on the energy of the reactants, the products, or the value of ΔH. Water-soluble vitamins are a common example of a catalyst acting as coenzymes.

Review Questions

1. Draw a potential energy diagram for an exothermic reaction labeling the following. **(Intermediate)**

(a) The activation energy of 125 kJ

(b) The enthalpy of -85 kJ/mol

(c) The reactants and product

(d) The axes

(e) The activation energy for the catalyzed reaction.

2. The main function of a catalyst is to **(Intermediate)**

(a) provide an alternate reaction pathway

(b) change the kinetic energy of the reacting particles

(c) eliminate the slow step

(d) add another reactant

3. What happens when a catalyst is added? **(Intermediate)**

(a) the activation energy of the forward reaction is lowered

(b) the activation energy of the reverse reaction is lowered

(c) the activation energy in general is lowered

(d) the enthalpy of the reaction is lowered

4. Given the reaction mechanism shown below, which species is the catalyst? **(Intermediate)**

$COCl_{2(g)} \rightarrow COCl_{(g)} + Cl_{(g)}$ (fast) (reaction 1)

$Cl_{(g)} + COCl_{2(g)} \rightarrow COCl_{(g)} + Cl_{2(g)}$ (slow) (reaction 2)

$2\ COCl_{(g)} \rightarrow 2\ CO_{(g)} + 2\ Cl_{(g)}$ (fast) (reaction 3)

$2\ Cl_{(g)} \rightarrow Cl_{2(g)}$ (fast) (reaction 4)

(a) $CO_{(g)}$

(b) $COCl_{2(g)}$

(c) $COCl_{(g)}$

(d) $Cl_{(g)}$

5. Catalysts are used in all parts of society from inside our bodies to the largest industries in the world. Give an example of a catalyst and explain its usefulness. **(Intermediate)**

Further Reading / Supplemental Links

http://learner.org/resources/series61.html'''

The ***learner.org*** website allows users to view streaming videos of the Annenberg series of chemistry videos. You are required to register before you can watch the videos but there is no charge. The website has one video that relates to this lesson called ***Molecules in Action*** .

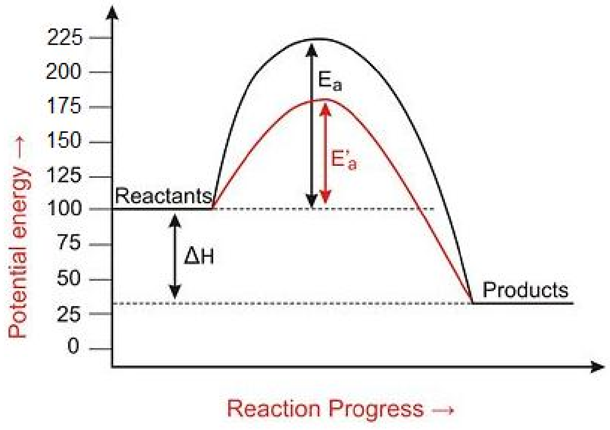
http://www.vitamins-guide.net

http://en.wikipedia.org/wiki

Vocabulary

catalyst A substance that speeds up the rate of the reaction without itself being consumed by the reaction.

Review Answers



1.

2. (a) provide an alternate reaction pathway

3. (c) activation energy in general is lowered

4. (d) Cl(g)

5. In automobiles, the exhaust system takes nitrogen oxides and converts them into $N_{2(g)}$ and $CO_{2(g)}$. In addition, hydrocarbons are converted into $CO_{2(g)}$ and water using a catalyst, usually platinum. The catalytic converted in your car helps to lessen the amount of pollutants released into the environment in your car.

$N_{2(g)}$, $CO_{2(g)}$, and $H_2O_{(g)}$ are less harmful to the environment. Catalysts in industry are used to decrease the amount of money needed to produce the required materials and increase the efficiency to produce these materials.

Reaction Mechanism

Lesson Objectives

- Define reaction mechanisms.
- Identify the rate-determining step.
- Draw a potential energy diagram for a multi-step process.

Introduction

In the last section, the reaction between an uncatalyzed reaction between hydrogen and oxygen was compared to a catalyzed reaction between the same two reactants. It was pointed out that the uncatalyzed reaction required three particles to collide at the same time with sufficient energy to break all the bonds in all the molecules. That uncatalyzed reaction had a very high activation energy and therefore did not occur under room conditions. The catalyzed reaction could occur because it allowed for a series of collisions so the bonds could be broken one at a time, thus requiring less activation energy.

Consider a reaction in which a molecule containing 100 bonds is going to reacted with 50 oxygen molecules. What do you think is the possibility of 51 randomly moving particles to all arrive at exactly the same spot in space so they can have one big collision? You are right, that is not going to happen. And, if it did happen, what are the chances that the collision would be hard enough to break all the bonds in the large reactant and all 50 of the double bonds in the oxygen molecules? Once again, the answer is that the chances are approximately ZERO. Complicated reactions involving many bonds and many molecules do not occur in single collisions. These reactions, instead, occur in a series of collisions. Each collision in the series produces an *intermediate* product that undergoes further collisions until finally, after many collisions, the final products are produced. This long series of collisions producing intermediate products is called a ***reaction mechanism*** .

The reaction below is an example of a multi-step reaction. Nitrogen dioxide and carbon monoxide reactant is a two-step process to form nitrogen monoxide and carbon dioxide. The two steps are shown below.

$$\begin{array}{ll} NO_2(g) + \cancel{NO_2(g)} \rightarrow \cancel{NO_3(g)} + NO(g) & \text{(step 1)} \\ \cancel{NO_3(g)} + CO(g) \rightarrow \cancel{NO_2(g)} + CO_2(g) & \text{(step 2)} \\ \hline NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g) & \text{(overall reaction)} \end{array}$$

In this lesson, we will discuss these multi-step processes, called reaction mechanisms, as well as the individual reactions in the multi-step process.

Most Reactions Have Multi-Steps

As stated in the introduction, when there is a reaction involving more than two reactant particles the likelihood of a successful single collision reaction is small. This is due to the fact that the particles have to have a successful collision with enough energy and the proper orientation. What will happen in these cases is that the overall reaction will take place in a series of single steps, often called elementary steps. An ***elementary step*** is a single, simple step in a multi-step process. An elementary step almost always involves only two particles. The series of elementary steps outline the process of the reaction. Most reactions do not take place in one step but rather occur as a combination of two or more elementary steps. This series of steps is referred to as a ***reaction mechanism.*** Even some two-particle collisions require a reaction mechanism.

In another lesson, it was discussed that the concentration of some reactants can affect the rate of the reaction. The rate of the reaction is dependant on the reactants in the slowest step of the multi-step process. If we look at the reaction below from this same lesson, this is only a two particle collision, $NO_{2(g)}$ and $CO_{(g)}$, and yet it is known that the rate is only affected by the concentration of $NO_{2(g)}$. This indicates that the reaction proceeds by way of a reaction mechanism.

$NO_{2(g)} + CO_{(g)} \longrightarrow NO_{(g)} + CO_{2(g)}$

Sample question: Which of the following reactions would most likely involve a reaction mechanism? Explain.

(a) $2\ I^- + S_2O_8{}^{2-} \longrightarrow I_2 + 2\ SO_4{}^{2-}$

(b) $Cl_{2(g)} \longrightarrow 2\ Cl^-{}_{(g)}$

Solution:

(a) reaction mechanism; three reactant particles are present

(b) elementary step; only one reactant particle is present

Each Step Has Its Own Activated Complex

When there is a single step reaction mechanism, we can draw potential energy diagrams as we have seen earlier in this chapter. However, when there is a multi-step process where two or more elementary steps combine to form one reaction mechanism, the potential energy diagram looks quite different. Look at the reaction mechanism below. This mechanism is involved in the depletion of the ozone layer.

$NO_{(g)} + O_{3(g)} \longrightarrow NO_{2(g)} + O_{2(g)}$ (reaction 1) (slow)

$NO_{2(g)} + O_{(g)} \longrightarrow NO_{(g)} + O_{2(g)}$ (reaction 2) (fast)

The overall reaction is $O_{3(g)} + O_{(g)} \longrightarrow 2\ O_{2(g)}$

If we were to draw the potential energy diagram for this two-step process, it could be represented in Figure 1. Notice that for each reaction in the reaction mechanism, there is an activation energy barrier. Therefore E_{a1} is the activation energy associated with reaction 1 and E_{a2} is the activation energy associated with reaction 2. The slow step has an activation energy barrier that is higher than that of the faster reaction.

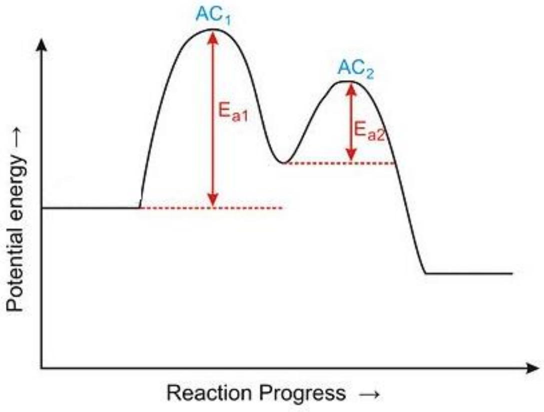


Figure 1: Potential Energy Diagram for a multi-step process

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Each reaction also has its own activated complex. Remember that at the top of the activation energy barrier is the activated complex, the transition state between reactants and products that has the most potential energy. AC_1 is the complex created in the first reaction. AC_2 is the activated complex created in the second reaction. Thus, for this two-step process, there are two activated complexes.

Sample question: Draw the potential energy diagram for the following reaction mechanism ($\Delta H < 0$). Properly label the diagram.

$NO_{2(g)} + F_{2(g)} \rightarrow NO_2F_{(g)} + F_{(g)}$ (reaction 1) (slow)

$NO_{2(g)} + F_{(g)} \rightarrow NO_2F_{(g)}$ (reaction 2) (fast)

Solution:

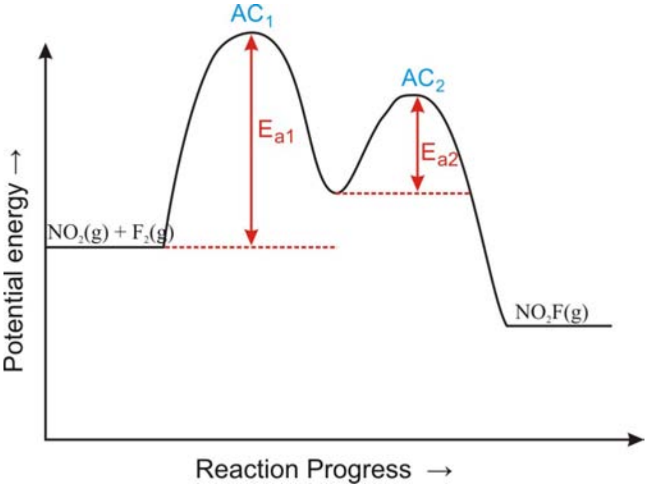

Figure 2: Potential Energy Diagram for a Multi-step Process

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Rate of Reaction is Determined by Slowest Step

In a series of reactions that make up a reaction mechanism, each individual reaction step has its own reaction rate that is determined by the five factors that have been discussed in this chapter. The overall reaction rate for the overall reaction (the sum of all the individual steps) can be determined from the rates of the individual steps. The relationship between the overall rate and the individual rates, however, is not what you might expect. Beginning students often think that to get the overall rate, you would *add up* the individual rates or *average* the individual rates but neither of these is correct. In fact, the overall rate for the reaction is ***exactly the same as the rate of the slowest step*** . Let's look at an example from life to see how this occurs.

Suppose you and two of your friends organize a car wash. You set up an assembly line operation where the cars in position 1 are wetted with a hose, then the cars get in line for position 2 where they are washed with soapy water and rinsed, and then they get in line for position 3 where they are towel dried.

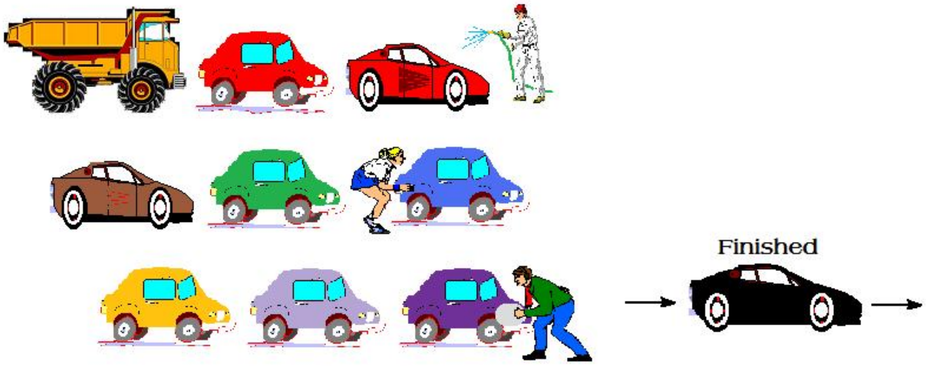

Figure 1: Slowest step in a car wash determines the over all car wash rate.

(*Created by:* Richard Parsons, *License:* CC-BY-SA)

Since you are the leader, you get the job of wetting the cars which takes 3 minutes to accomplish. The job of washing at station 2 takes 18 minutes and the drying job requires 14 minutes. When each job is finished, the car gets in line for the next station. In order to evaluate the efficiency of your assembly line, you count the minutes between the finished cars coming off the end of the line. The time lapse between completed cars is your reaction rate.

Regardless of the picture shown above, you should realize that there will be no cars in the line for station 3. Each car requires 18 minutes in station 2 and when the cars move to station 3, another car immediately goes to station 2. The drying of the first car and the washing of the second car begin at exactly the same time. Since it takes 18 minutes to wash and 14 minutes to dry, the car at station 3 is always finished and gone 4 minutes before the car at station 2. Therefore, the worker at station 3 always stands around and waits for 4 minutes before he gets his next car to dry. The time between cars coming off the line will be the 4 minutes the station 3 worker waits plus the 14 minutes required to dry . . . so the time between cars will be 18 minutes. The reaction rate for this arrangement will be 18 minutes. You should note that this overall reaction rate is exactly the same as the slowest step in the process, namely the wash step at station 2.

Suppose that you now bring in another person to work in your car wash and you assign that person to station 2 so that you have two people washing cars. The time to wash a car now becomes only 9 minutes since you have doubled the work force. Now the wash process will finish before the drying process and cars will back up in line for station 3. Your new arrangement now has a new slowest step - the drying stage is now the slowest step. Therefore, when the worker at station 3 finishes drying a car and the cars leaves the line, another car immediately enters station 3 and the worker immediately begins drying the car. After the worker at station 3 sends a car out, he will take 14 minutes to finish the next car and send it out. With this new organization, the time lapse between cars coming out will now be 14 minutes. The overall reaction rate is faster. The important point is that the slowest step became 14 minutes and the overall rate became 14 minutes.

Suppose once again that you bring another worker and put them at the drying station. The drying process now requires only 7 minutes with two people working. What is the slowest step in the process now? The slowest step is now the washing step again because it takes 9 minutes. Now when the drying station finishes a car, there will be no cars in line because the washing station takes 2 more minutes to wash that it takes to dry. Therefore, once again, the drying station will have to wait for 2 minutes after drying a car before another car comes to station 3. With the 2 minute wait and the 7 minute drying time, the lapse between cars has now become 9 minutes. The overall rate is 9 minutes and the slowest step is 9 minutes. Regardless of how what the process is or how you set up the organization, the overall rate will always be exactly the same as the slowest step.

Let's look at another important point about this concept. We will go back to the original set up with a 3-minute wetting (station 1), an 18-minute washing (station 2), and a 14-minute drying (station 3). Suppose when the first extra worker was brought in, you assigned that person to help with the drying so that the drying time became 7 minutes with the other times remaining the same. What would the overall rate be? The overall rate is exactly the same as the slowest step and the slowest step is the 18-minute washing time. Therefore, you have increased the rate of the drying step but you have NOT affected the overall reaction rate. The only way you can alter the overall reaction rate is to increase the rate of the slowest step. Increasing the rate of steps other than the slowest step does nothing to the overall rate.

In chemical reactions, the speed of the other steps is so much faster than the slow step that the slow step is referred to as the **rate-determining** step. It is the speed of this slowest step that determines the rate of the overall reaction and changing the concentrations of the reactants in this step will change the rate.

Sample question:

In the reaction mechanism below, identify the rate-determining step and write the overall reaction.

$H_2O_{2(aq)} + I^-_{(aq)} \rightarrow IO^-_{(aq)} + H_2O_{(L)}$ (fast)

$H_2O_{2(aq)} + IO^-_{(aq)} \rightarrow I^-_{(aq)} + H_2O_{(L)} + O_{2(g)}$ (slow)

Overall reaction: $2\ H_2O_{2(aq)} \rightarrow 2\ H_2O_{(L)} + O_{2(g)}$

The overall reaction is found by adding the two elementary steps together and cancelling identical species that appear on both sides of the chemical equation, that is, $I^-_{(aq)}$ and $IO^-_{(aq)}$.

Solution:

The slow step (reaction 2) is the rate-determining step. It is the one marked slow. Whatever the reaction rate is for reaction 2, the overall rate will be exactly the same.

Lesson Summary

- A reaction mechanism is a multi-step process that is a combination of two or more elementary steps. An elementary step is a single, simple step in a multi-step process involving one or two particles.
- The rate-determining step is the slowest step in the reaction mechanism and the overall reaction rate will be exactly the same as the rate of the slowest step.

Review Questions

1. Why do most reactions take place in more than one step? **(Intermediate)**

2. The overall rate of a reaction depends on **(Intermediate)**

(a) the temperature

(b) the surface area

(c) the pressure

(d) the slowest step

3. Suppose a reaction takes place according to this reaction mechanism: **(Intermediate)**

$X + Y \rightarrow Z$ (fast)

$X + Z \rightarrow F$ (slow)

Which step in the mechanism is the rate determining step?

4. If you wanted to increase the overall rate of the reaction in Question #2, would increase the concentration of X or Y? Explain **(Intermediate)**

5. The equation for the formation of ammonia is: **(Intermediate)**

$N_{2(g)} + 3\ H_{2(g)} \rightarrow 2\ NH_{3(g)}$

Explain why this equation is not likely to represent the reaction mechanism.

Vocabulary

elementary step	A single, simple step in a multi-step process involving one or two particles.
reaction mechanism	Most reactions do not take place in one step but rather occur as a combination of two or more elementary steps.
rate-determining step	The slowest step in the reaction mechanism.

Review Answers

1. For most reactions, more than one bond between atoms needs to be broken and then bonds between other atoms needs to be formed. This rarely can be done in one step.

2. (d) the slowest step

3. $X + Z \rightarrow F$

4. You would need to increase the concentration of X since it is a reactant in the rate determining step.

5. Since there are three separate hydrogen molecules in which in each one there is one chemical bond that needs to be broken; and, the nitrogen has a chemical bond that has been broken, there must be more than one step to accomplish all of these steps.

24. Chemical Equilibrium

Introduction to Equilibrium

Lesson Objectives

- Describe the three possibilities that exist when reactants come together.
- Identify the three possibilities by looking at a chemical equation.
- Describe what is occurring in a system at equilibrium.

Introduction

Think for a minute about sitting down to a table to eat dinner. There are three possibilities that could happen when you eat dinner. You could (1) finish your entire dinner, (2) you could not want any of it and leave it all on your plate, or (3) you could eat some of it and leave some of it. Reactions have the same possibilities. Reactions also do not always proceed all the way from start to finish. You may have reactions that go to completion so that at the end the reaction vessel contains all products and only products. Some reactions may not start at all so at the end the reaction vessel contains all reactants and only reactants. And some reactions may start but not go to completion, that is, the reaction might start but not go completely to products. In this last case, at the end, the reaction vessel would contain come reactants and some products. In this chapter, we are going to take a closer look at the third type of reaction.

Reaction Possibilities

The Reverse Reaction

Consider the hypothetical reaction $A_{(g)} + B_{(g)} \rightarrow C_{(g)} + D_{(g)}$. Assume this is a single collision reaction so that the formula for reaction rate introduced in the chapter on *Reaction Kinetics* applies. The formula introduced in that chapter applies to reactions where the reaction mechanism is accurately represented by the overall reaction equation. For this reaction, the reaction rate expression would look like this: $R = k[A][B]$.

At this level in chemistry, you won't be working with this rate equation all that much but if you major in science and take a university level chemistry class, you will deal with this equation seriously.

A reaction constant, k, value would look something like this, 0.15 L/mol·s. The units for a reaction rate will be moles per liter per second and the units of the reaction constant must produce the correct units for the reaction rate when multiplied in the equation.

Example:

Calculate the reaction rate for the reaction $A_{(g)} + B_{(g)} \rightarrow C_{(g)} + D_{(g)}$, given the initial concentrations [A] = 0.10 M and [B] = 0.20 M and given the reaction constant, k = 0.015 L/mol·s.

$$R = k[A][B] = \left(0.015\ \frac{\text{L}}{\text{mol}\cdot\text{s}}\right)\left(0.10\ \frac{\text{mol}}{\text{L}}\right)\left(0.20\ \frac{\text{mol}}{\text{L}}\right) = 0.00030\ \text{mol/L}\cdot\text{s}$$

Note: The units for k will be whatever is necessary to make the reaction rate units mol/L·s.

There are some important points to remember about k. The reaction constant, k, is only correct for this reaction at an indicated temperature. If the temperature of a reaction is changed, k will also change. Therefore, the k for a reaction is given at a specified temperature and for every different temperature for this reaction, there would be a different k. It is also important to recognize that for a given k value and given concentrations of A and B, the calculated reaction rate is only true for the very instant the reaction begins. As soon as the reaction begins, A and B will begin to be used to form products and therefore, the concentrations of A and B immediately begin to decrease. As soon as the concentrations of A and B change, the reaction rate will change. Generally, as a reaction runs, the concentrations of the reactants decrease and therefore, the reaction rate would also decrease.

If this reaction between gaseous A and B is carried out in a closed reaction vessel so none of the gaseous products can escape, then as the reaction runs, quantities of C and D are formed and the concentrations of C and D increase. The presence of C and D in the closed vessel provide an opportunity for a ***reverse*** reaction to occur. That is, not only is it possible for particles of A and B to collide and form C and D, but now it is possible for particles of C and D to collide and form A and B.

So, not only is this possible,

$$A_{(g)} + B_{(g)} \rightarrow C_{(g)} + D_{(g)} \qquad \text{(Equation 1)}$$

but this is also possible,

$$A_{(g)} + B_{(g)} \leftarrow C_{(g)} + D_{(g)} \qquad \text{(Equation 2)}$$

Look carefully at equation 2 to make sure you notice that the yields arrow in the equation is pointed backwards. This indicates that for this reaction, the reactants are actually on the product side and the products are on the reactants side, the reaction is running backwards. This is called the *reverse reaction*.

At the very beginning of this reaction, the forward reaction rate is at its highest value because the reactants at are their highest concentration. At the very beginning of this reaction, the reverse reaction will be non-existent because the concentrations of the products are zero. As the reaction runs, the concentrations of the reactants decrease and so the forward reaction rate slows down. As the reaction runs, the concentrations of the products increase and so the reverse reaction rate increases.

Since the forward reaction rate begins with some positive number and decreases and the reverse rate begins at zero and increases, it should be apparent that eventually these two reaction rates must become the same. At that point, when the two reaction rates become equal, the two reactants, A and B, and the two products, C and D, will be used and produced at exactly the same rate. This means that the concentrations of the reactants and products will no longer change. The two reaction rates become equal and constant and the concentrations of all the substances in the reaction become constant. The two equal reaction rates can now continue forever and nothing will change in the reaction vessel. There is no more change in rates or concentrations. This position in a reaction is called ***chemical equilibrium*** .

If the reactants had no color (clear) and one of the products was red, the reaction would begin as a clear container of gases and as the reaction occurred, the color would be become slightly pink as some product appeared and then the pink color would become darker and darker as more and more product was produced. When the reaction reaches equilibrium, the color would no longer change. The properties of the mixture in the reaction vessel that can be observed visually, like color, and those that can measured, like concentrations, are referred to as *macroscopic* properties. When a reaction reaches equilibrium, the macroscopic properties become constant. At the molecular level, however, the process of the two chemical reactions going in opposite directions continues. Chemical equilibrium is often referred to as ***dynamic*** chemical equilibrium to indicate that the molecular processes continue even though we cannot see any change in the contents of the reaction vessel.

When a chemical reaction has reached equilibrium, we represent the reaction with arrows going both directions as shown below.

$$A_{(g)} + B_{(g)} \overset{\leftarrow}{\rightarrow} C_{(g)} + D_{(g)} \qquad \text{(Equation 3)}$$

When the equation uses the double "yields" arrow showing equal reaction rates in both directions, it means that the reaction is AT equilibrium.

You have probably encountered the concept of equilibrium previously in the case of vapor *pressure equilibrium* where the rate of evaporation and the rate of condensation became equal, and in the concept of *solubility equilibrium* where the rates of dissolving and precipitation became equal. Those situations are also a dynamic equilibrium.

Reaction Goes to Completion

When reactants are introduced into a reaction vessel, one possibility is that the reaction will go to completion. For example, if you were to put a piece of magnesium ribbon into a beaker containing 6 M $HCl_{(aq)}$, the magnesium ribbon would react in the solution until all of one of the reactants was used up and no further reaction could occur. The balanced chemical equation could be represented by Equation 1.

$Mg_{(s)} + 2\ HCl_{(aq)} \longrightarrow MgCl_{2(aq)} + H_{2(g)}$ (Equation 1)

This single arrow indicates that the reaction goes to completion meaning that all the reactants undergo a reaction to form products and the reaction stops.

No Reaction Takes Place

Another possibility when reactants are introduced into a reaction vessel is that no reaction occurs. For example, if we were to put a piece of copper in the 6 mol/L $HCl_{(aq)}$ rather than a piece of magnesium, the copper would remain in the $HCl_{(aq)}$ unchanged (see Equation 2).

$Cu_{(s)} + 2\ HCl_{(aq)} \longrightarrow$ no reaction (Equation 2)

Reactions That Appear to Stop Before Reaching Completion

Many chemical reactions fall under a third possibility. These are the reactions where a reaction does occur but it does not proceed all the way so that only products remain at the end. In these reactions, some products and some reactants remains in the flask. When this happens the reaction is said to have reached a state of equilibrium. ***Chemical equilibrium*** occurs when the rate of the forward reaction is equal to the rate of the reverse reaction.

Look at Equation 3.

$2\ N_{2(g)} + 3\ H_{2(g)} \leftrightarrows 2\ NH_{3(g)}$ (Equation 3)

We have seen this type of equation before in earlier chapters. Notice the double arrow. This double arrow indicates the reaction is in equilibrium. This means that the number of $N_{2(g)}$ and $H_{2(g)}$ particles reacting to form $NH_{3(g)}$ is equal to the number of $NH_{3(g)}$ particles reacting to form $N_{2(g)}$ and $H_{2(g)}$.

Sample question: For the reaction $CO_{(g)} + 2H_{2(g)} \leftrightarrows CH_3OH_{(g)}$, describe what is happening to make this an equilibrium reaction.

Solution:

The reaction between carbon monoxide and hydrogen to produce methanol is in equilibrium due to the presence of the double arrows. This means that the number of $CO_{(g)}$ and $H_{2(g)}$ particles reacting to form $CH_3OH_{(g)}$ is equal to the number of $CH_3OH_{(g)}$ particles reacting to form $CO_{(g)}$ and $H_{2(g)}$.

Lesson Summary

- There are three possible ways a reaction can go: It can go to completion (reactants $\longrightarrow$ products); it can just not react at all (reactants $\longrightarrow$ no reaction); it can occur but not go to completion; it would instead, reach chemical equilibrium (reactants ⇔ products).

- Chemical equilibrium occurs when the number of particles becoming products is equal to the number of particles becoming reactants.

Review Questions

1. For the reaction $PCl_{5(g)} \leftrightarrows PCl_{3(g)} + Cl_{2(g)}$, describe what is happening to make this an equilibrium reaction. **(Intermediate)**

Further Reading / Supplemental Links

http://en.wikipedia.org

Vocabulary

chemical equilibrium	A state that occurs when the rate of forward reaction is equal to the rate of the reverse reaction.

Review Answers

1. There is both a forward and reverse reaction that are equal in rate and opposite in direction.

Dynamic Equilibrium

Lesson Objectives

- Define dynamic equilibrium.
- Define the conditions of dynamic equilibrium.

Rate of Forward Reaction is Equal to Rate of Reverse Reaction

We defined chemical equilibrium earlier as a state that occurs when the number of particles becoming the products is equal to the number of particles becoming reactants. Another way to say this is that the forward rate is equal to the reverse rate. Look at Equation 1 below.

$$2\ H_{2(g)} + S_{2(g)} \leftrightarrows 2\ H_2S_{(g)} \quad \text{(Equation 1)}$$

The forward rate is $H_{2(g)}$ and $S_{2(g)}$ reacting to form $H_2S_{(g)}$. The reverse rate is $H_2S_{(g)}$ decomposing to form $H_{2(g)}$ and $S_{2(g)}$. When these two rates are equal, the reaction is in a state of equilibrium. We say the reactions are in a state of dynamic equilibrium. ***Dynamic equilibrium*** is a state where the reaction is reversible and has reached a point such that the rate of the forward reaction is equal to the rate of the reverse reaction. Look at Figure 1 below.

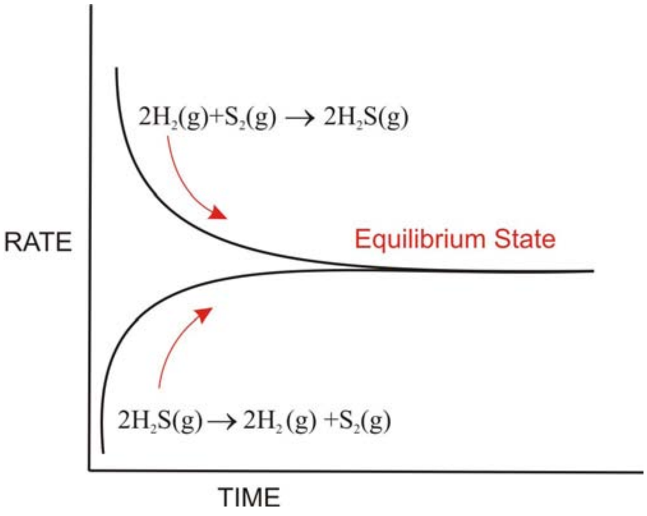

Figure 1: Rate of Forward Reaction = Rate of Reverse reaction.

(*Created by:* Therese Forsythe, *License:* CC-BY-SA)

The figure shows that as the reactants react to form products, the rate of the reaction starts high. This is because there are a lot of reactants particles that are in the reaction vessel at the beginning of the experiment. As the reaction proceeds, the number of reactant particles decrease since the products are being formed from these particles. The result is that, over time, the forward rate is slowing. On the other hand, the opposite is happening for the reverse reaction. Its rate started out low and is building steadily. At the end, you can see that both rates meet at the equilibrium position. In the equilibrium state, the number of particles becoming products equals the number of particles becoming reactants. What is not true, however, is that at equilibrium, the number of reactant particles is equal to the number of product particles. In other words, the concentration of the products does not equal the concentration of the reactants at equilibrium.

For example, look at the reaction represented in Table 1. The data was collected through experimental trials and clearly shows that the [product] does not equal the [reactants] at equilibrium.

Table 1: Data Collected for 2 $NO_{2(g)}$

↔

$N_2O_{4(g)}$ Experiment

Trial	amount of NO_2	amount of N_2O_4 (as reaction proceeds to equilibrium)
1	0.0500 M	0.000
2	0.0320 M	0.0090 M
3	0.0154 M	0.0173 M
4	0.0106 M	0.0197 M
5	0.0100 M	0.0200 M
6	0.0100 M	0.0200 M
7	0.0100 M	0.0200 M
8	0.0100 M	0.0200 M

Equilibrium Will Be Maintained in a Closed System

There are a few more conditions that are necessary for equilibrium to take place. An equilibrium reaction must take place in a closed system in order to actually reach equilibrium. Consider the reaction in which hydrogen peroxide, $H_2O_{2(aq)}$, breaks down to form oxygen gas, $O_{2(g)}$ and liquid water, $H_2O_{(L)}$.

$$H_2O_{2(aq)} \rightarrow O_{2(g)} + H_2O_{(L)}$$

If the oxygen remained in the solution with the water, then it is possible that a reverse reaction could occur where the oxygen gas and water molecules would combine to form hydrogen peroxide.

When this reaction occurs in an open beaker, however, the oxygen bubbles out of the solution and leaves the reaction vessel. Therefore, not all of the products are present in the solution for the reverse reaction to occur. This reaction, in an open beaker, could never come to equilibrium because no reverse reaction is possible. Therefore, in order for a reaction to reach equilibrium, the reaction must occur in a closed system, that is, all the products must remain in the reaction vessel and available for collisions with the other products so that a reverse reaction could occur. Reactions where one of the products escapes from the beaker as a gas will always, eventually, go to completion. Another condition that is required for a reaction to reach equilibrium is that there is no temperature change. Therefore, most reactions at equilibrium are described in this manner, "The reaction between carbon monoxide and oxygen to form carbon dioxide is in equilibrium at constant temperature."

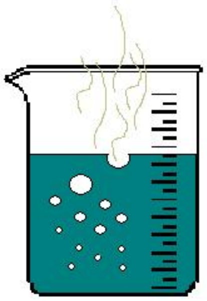

Figure 1: When one product leaves the vessel, no reverse reaction is possible. (*Created by:* Richard Parsons, *License:* CC-BY-SA)

Lesson Summary

- For equilibrium to occur, the rate of the forward reaction must equal the rate of the reverse reaction. A dynamic equilibrium is a state where the rate of the forward reaction is equal to the rate of the reverse reaction.
- For equilibrium to occur, the number of particles becoming products equals the number of particles becoming reactants. For equilibrium to occur, the reaction must take place in a closed system and at constant temperature.

Review Questions

1. What does the term dynamic equilibrium mean? **(Intermediate)**

2. List all of the conditions of a dynamic equilibrium? **(Intermediate)**

3. Of the following conditions, which do you think would not be required for a dynamic equilibrium? **(Intermediate)**

(a) rate of the forward reaction equals the rate of the reverse reaction.

(b) reaction occurs in an open system

(c) reaction occurs at a constant temperature

(d) reaction occurs in a closed system

4. Which of the following systems, at room temperature and pressure, can be described as a dynamic equilibrium? **(Intermediate)**

(a) an open flask containing air, water and water vapor

(b) a glass of water containing ice cube cubes and cold water

(c) a closed bottle of soda pop

(d) an open flask containing solid naphthalene

5. Is each of the following in a state of equilibrium? Explain. **(Intermediate)**

(a) ice cubes are melting in a glass of water with a lid on it

(b) Crystals of potassium dichromate are dissolved in water until the water becomes a uniform orange color and a small amount of crystal remains in the closed container.

(c) An apple that is left on the counter for a few days, it dries out and turns brown.

6. If the following table of concentration vs. time was provided to you for the ionization of acetic acid. How would you know when equilibrium was reached? **(Intermediate)**

Time (min)	$[HC_2H_3O_2]$ mol/L
0	0.100
0.5	0.099
1.0	0.098
1.5	0.097
2.0	0.096
2.5	0.095
3.0	0.095
3.5	0.095
4.0	0.095
4.5	0.095
5.0	0.095

7. Chemical equilibrium is defined as a state where the reversible process shows that the rate of the forward reaction is equal to the rate of the reverse reaction. What does the term equal mean in this definition? **(Intermediate)**

Further Reading / Supplemental Links

http://en.wikipedia.org/wiki/Chemical_equilibrium

Vocabulary

dynamic equilibrium	A state that continues in which the rate of the forward reaction is equal to the rate of the reverse reaction; or, the number of particles/molecules of the reactant becoming the product is equal to the number of particle/molecules of the product becoming the reactant.

Review Answers

1. Equilibrium is considered dynamic when the forward and reverse reactions continue to take place. Therefore for the reaction $N_{2(g)} + O_{2(g)} \leftrightarrows NO_{(g)}$, The forward reaction of $N_{2(g)}$ and $O_{2(g)}$ forming $NO_{(g)}$ is happening in a closed system as well as the reaction of $NO_{(g)}$ decomposing to form $N_{2(g)}$ and $O_{2(g)}$. The term "dynamic" is used because the two reactions continue after equilibrium is reached.

2. The conditions of a dynamic equilibrium include:

a) The reaction must be in a closed system.

b) The reaction must occur at constant temperature

c) The reaction can be reached from either direction (double arrow)

d) The rate of the forward reaction equals the rate of the reverse reaction

There is no change in concentration of the reactants or products once chemical equilibrium is established (inferred by the equilibrium state).

3. (b) reaction occurs in an open system

4. (c) a closed bottle of soda pop

5. (a) Not in equilibrium. The system is closed because it has a lid on the glass but the rate of the forward reaction is not equal to the rate of the reverse reaction. Ice cubes will melt to form water but water will not freeze at room temperature to form ice cubes.

(b) In Equilibrium. When crystals of $K_2Cr_2O_7$ dissolve in water, the reaction is in equilibrium where as some dissolves to produce the orange color and some remains out of solution as crystals on the bottom of the container.

(c) Not in Equilibrium. The apple is on the counter so it is an open system. The moisture in the apple is drawn out and the apple is decomposing.

6. You could tell when equilibrium was reached because there is no net change in the concentration of the acid. Acetic acid is a weak acid and the ionization of acetic acid is an equilibrium reaction.

$$HC_2H_3O_{2(aq)} \leftrightarrows H^+_{(aq)} + C_2H_3O_2{}^-{}_{(aq)}$$

7. Equal here means that the rate at which the reactants are reacting to yield products is the same as the rate at which the products are reacting to yield reactants.

Equilibrium Constant

Lesson Objectives

- Write equilibrium constant expressions.
- Use equilibrium constant expressions to solve for unknown concentrations.
- Use known concentrations to solve for the equilibrium constants.
- Explain what the value of K means in terms of relative concentrations of reactants and products.

Introduction

You were introduced to two types of equations in the chapter on *Reaction Kinetics*. One of these was the reactions where the overall equation and the reaction mechanism were exactly the same. In those reactions, the reaction occurred with a single collision. The other type of reactions were the reactions where the reaction mechanism consisted of two or more steps and the overall equation was the sum of the equations in the reaction mechanism.

For those reactions that consisted of a single collision, the reaction rate could be expressed by inserting the concentrations of the reactants into the expression

Reaction Rate = $k_F[A][B]$, where A and B were the reactants.

For the reactions that had reaction mechanisms of two or more steps, the relationship between the concentration of a particular reactant and the reaction rate had to be determined experimentally. In fact, however, the rate of these reaction mechanism type reactions can also be expressed in the form of this expression, but which reactants go into the expression and how they go into the expression must be determined experimentally.

In the previous section, you were introduced to the possibility of a reverse reaction. For the reaction between A and B yielding C and D, we have not only the forward reaction,

$A_{(g)} + B_{(g)} \longrightarrow C_{(g)} + D_{(g)}$ Equation 1

but we also could have a reverse reaction.

$A_{(g)} + B_{(g)} \longleftarrow C_{(g)} + D_{(g)}$ Equation 2.

If this reverse reaction occurs, it would be the same simple collision that was involved in the forward reaction. Therefore, the reaction rate of the reverse reaction could be expressed as:

Reaction Rate = $k_R[C][D]$, where the products C and D have become the reactants.

When this reaction reaches equilibrium and the two rates become constant and equal,

$\text{Rate}_{\text{forward}} = \text{Rate}_{\text{reverse}}$ and $k_F[A][B] = k_R[C][D]$.

$k_F[A][B] = k_R[C][D]$

Algebraic manipulation of the expression yields

$$\frac{k_F}{k_R} = \frac{[C][D]}{[A][B]}$$

Since both k_F and k_R are constants, then dividing one constant by another yields another constant. The new constant is called the ***equilibrium constant*** and is symbolized by the capital letter ***K***.

$$\mathbf{K} = \frac{[C][D]}{[A][B]}$$

The Equilibrium Constant

Equilibrium reactions are those that do not go to completion but are in a state where the reactants are reacting to yield products and the products are reacting to produce reactants. In a reaction at equilibrium, the equilibrium concentrations of all reactants and products can be measured. The ***equilibrium constant*** (K) is a mathematical relationship that shows how the concentrations of the products vary with the concentration of the reactants. Sometimes, subscripts are added to the equilibrium constant symbol K, such as K_{eq}, K_c, K_p, K_a, K_b, and K_{sp}. These are all equilibrium constants and are subscripted to indicate special types of equilibrium reactions. These are all equilibrium constants and they all follow the rules for K.

There are some rules about writing equilibrium constant expressions that you must learn. The equilibrium constant expressions you have seen in this section so far have been for the simplest possible reactions and reactions with no exceptions in them. In order to really be able to write equilibrium constant expressions correctly, you have to be able to write for complicated reactions and for reactions that have exceptions to the general rules.

Let's begin with, once more, a very simple equation and its equilibrium constant expression.

$A_{(aq)} + B_{(aq)} \leftrightarrows C_{(aq)} + D_{(aq)}$ and $K = \frac{[C][D]}{[A][B]}$

But suppose the reaction was $2\ A_{(aq)} + B_{(aq)} \leftrightarrows C_{(aq)} + D_{(aq)}$. Writing the equation with a coefficient of 2 in front of the A is exactly the same as writing the equation this way:

$A_{(aq)} + A_{(aq)} + B_{(aq)} \leftrightarrows C_{(aq)} + D_{(aq)}$.

In this second form of the equation, we have just written the A twice instead of using a coefficient to show that two molecules are involved in the reaction. If we write the equilibrium constant expression from this last equation, it would look like:

$$K = \frac{[C][D]}{[A][A][B]}$$

With our great knowledge of algebra, we know that writing [A] x [A] is the same as writing $[A]^2$. Therefore, the equilibrium constant would become

$$K = \frac{[C][D]}{[A]^2[B]}.$$

As you can see, the coefficient in the equation has become an exponent in the equilibrium constant. This same process occurs in this same way for all coefficients in the equation. The general rule for writing equilibrium constant expressions for equations is to write the coefficient of each species in the reaction as an exponent in the equilibrium constant expression. So, for the reaction

$a\ A_{(g)} + b\ B_{(g)} \leftrightarrows c\ C_{(g)} + d\ D_{(g)}$, where the lower case a, b, c, and d are coefficients, the equilibrium constant expression would be:

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}.$$

Here is an example equation and its equilibrium constant expression.

$2\ NO_{2(g)} \leftrightarrows 2\ NO_{(g)} + O_{2(g)}$

$$K = \frac{[NO]^2[O_2]}{[NO_2]^2}$$

Of course, this is chemistry, so there will be a couple of exceptions to the general rule for writing equilibrium constant expressions.

The values in the equilibrium constant expression are concentrations (moles per liter) of reactants and products. There are cases where the concentration of particular reactant or product does not change when it is used or produced. Consider a solid as a reactant. The concentration of a substance is the moles of the substance divided by the volume the substance occupies. In the case of a substance dissolved in a beaker of water, its volume is the same as the volume of the solution. If half of the substance is used up in a reaction, the remaining half is still dissolved in the same volume of water and therefore, its concentration will be cut in half. In the case of a solid reactant, however, it is not dissolved in the water and so its volume is the volume of the solid itself. Therefore, if half of the solid is used in a reaction, the moles remaining become half of what it was, but the volume of the solid also becomes half. Therefore, its concentration stays exactly the same. This is also true of a liquid reactant or product that is undissolved. If the state of a reactant or product is indicated by (aq) or (g), its concentration can change but if its state is indicated by (s) or (L), its concentration cannot change. Since the concentrations of these substances cannot change, their numerical value in the equilibrium constant expression will be a constant. Therefore, they do not need to be included in the equilibrium constant expression . . . that is, the equilibrium constant will still be a constant if those substances are omitted from the expression. Since all other chemists omit solids and liquids from equilibrium constant expressions and calculations, you must do this also.

Here are some examples.

$CO_{(g)} + 3\ H_{2(g)} \leftrightarrows CH_{4(g)} + H_2O_{(g)}$

$K = \frac{[CH_4][H_2O]}{[CO][H_2]^3}$ Note the coefficient of 3 becomes an exponent.

$2\ TiCl_{3(s)} + 2\ HCl_{(g)} \leftrightarrows 2\ TiCl_{4(s)} + H_{2(g)}$

$K = \frac{[H_2]}{[HCl]^2}$ Note the two solids are omitted and the coefficients become exponents.

$P_{4(s)} + 6\ Cl_{2(g)} \leftrightarrows 4\ PCl_{3(s)}$

$K = \frac{1}{[Cl_2]^6}$ Note the solids are omitted and the coefficient becomes an exponent.

$H_2O_{(L)} \leftrightarrows H^+_{\ (aq)} + OH^-_{\ (aq)}$

$K = [H^+][OH^-]$ Note the liquid water is omitted and when the denominator is "1", there is no denominator.

Mathematics with Equilibrium Expressions

The mathematics involved with equilibrium expressions can be from the straightforward to the more complex. For example, look at the sample question below.

Sample question 1:

$SO_{2(g)} + NO_{2(g)} \leftrightarrows SO_{3(g)} + NO_{(g)}$

Determine the value of K when the equilibrium concentrations are: $[SO_2] = 1.20$ M; $[NO_2] = 0.60$ M; $[NO] = 1.6$ M; $[SO_3] = 2.2$ M. Are the reactants or products favored? Explain your answer.

Solution:

Step 1: Write the equilibrium constant expression:

$K = \frac{[SO_3][NO]}{[SO_2][NO_2]}$

Step 2: Substitute in given values and solve:

$K = \frac{(2.2)(1.6)}{(1.20)(0.60)} = 4.9$

The equilibrium constant value is the ratio of the concentrations of the products over the reactants. Therefore, a value of 4.9 for the equilibrium constant indicates that there are more products (numerator) than there are reactants (denominator). The reaction is very close to being at equilibrium with the products slightly favored. If the equilibrium constant is "1" or nearly "1", it indicates that the molarities of the reactants and products are about the same. If the equilibrium constant value was a large number, like 100, or a very large number, like 1×10^5, it indicates that the products (numerator) is a great deal larger than the reactants. That means that at equilibrium, the great majority of the material is in the form of products and we say the "products are strongly favored". If the equilibrium constant is small, like 0.10, or very small, like 1×10^{-12}, it indicates that the reactants are much larger than the products and the reactants are strongly favored. With large K values, most of the material at equilibrium is in the form of products and with small K values, most of the material at equilibrium is in the form of the reactants.

Sample question 2:

At a given temperature, the reaction $CO_{(g)} + H_2O_{(g)} \rightleftarrows H_{2(g)} + CO_{2(g)}$ produces the following concentrations at equilibrium: $[CO] = 0.200$ M; $[H_2O] = 0.500$ M; $[H_2] = 0.320$ M; $[CO_2] = 0.420$ M. Find K.

Solution:

Step 1: Write the equilibrium expression:

$$K = \frac{[H_2][CO_2]}{[CO][H_2O]}$$

Step 2: Substitute the given values and solve:

$$K = \frac{(0.320)(0.420)}{(0.200)(0.500)} = 1.34$$

Sample Question 3:

For the same reaction and the same temperature as in Sample Question 2, the concentrations of the substances at equilibrium become: $[CO] = ?$; $[H_2O] = 0.100$ M; $[H_2] = 0.100$ M; $[CO_2] = 0.100$ M. What is the concentration of CO?

Solution:

Since it is the same reaction at the same temperature, the K value will be the same, 1.34 .

Step 1: Rearrange the equilibrium constant expression for the unknown:

$$K = \frac{[H_2][CO_2]}{[CO][H_2O]} \quad \text{so} \quad [CO] = \frac{[H_2][CO_2]}{K\ [H_2O]}$$

Step 2: Substitute and solve:

$$[CO] = \frac{(0.100)(0.100)}{(1.34)(0.100)} = = 0.0746 \text{ M}$$

The Meaning of the Value of K

The equilibrium constant value for a reaction is the ratio of the product of the products over the product of the reactants and it is an accurate ratio for all reactions with those reactants and products and at the specified temperature. That is, the ratio under those conditions do not change. Suppose we are dealing with the reaction $A + B \rightleftarrows C + D$ at 25°C and the $K = 0.050$. If you carry out this reaction by introducing into the reaction vessel, 0.10 M A and 0.20 M B at 25°C and allow the reaction to come to equilibrium, the K will equal 0.050.

If you carry out this reaction by introducing into the reaction vessel, 1.0 M A and 0.010 M B at this same temperature, the K will equal 0.050 . If you were to carry out this reaction by introducing 1.0 M **C** and 1.0 M **D** at this same temperature, and allow the reaction to reach equilibrium, the K will equal 0.050 . Get the picture? It doesn't matter what concentrations of A and B you begin with, as long as it is the same reaction at the same temperature, the K will be the same number. In fact, it doesn't even matter if you begin with the products instead of the reactants, the K value will still be the same number at the same temperature. The K value is a CONSTANT and that's what being a constant means.

Sometimes, it is useful to recognize for a reaction at equilibrium, whether reactants or products will be favored, that is, will most of the material at equilibrium be in the form of reactants or in the form of products? If the K value for the reaction is approximately 1, the quantities of reactants and products will be about the same. If the K value is less than 1, the reactants are favored so most of the material will be in form of reactants, and if K > 1 most of the material will be in the form of the products (products favored).

For example:

(a) For the reaction: $2\ NO_{2(g)} \leftrightarrows N_2O_{4(g)}$, under specific conditions, K = 1.75 at 25°C. This means that at room temperature, the product, $N_2O_{4(g)}$, is very close to having the same concentration as the reactant, $NO_{2(g)}$.

(b) For the reaction: $2\ NOCl_{(g)} \leftrightarrows 2\ NO_{(g)} + Cl_{2(g)}$ at room temperature under certain conditions, the value of K is 0.0741. Under these conditions, the concentration of the reactants (NOCl) exceeds the concentration of the products because the K < 1 and the reactants are said to be favored.

(c) For the reaction: $HCl_{(g)} \leftrightarrows H^+_{\ (aq)} + Cl^-_{\ (aq)}$ at some temperature, the value of K is 5000 which is telling us that the products are strongly favored and this compound readily dissolves in water.

Lesson Summary

- The equilibrium constant, K, is a mathematical relationship that shows how the concentrations of the products vary with the concentration of the reactants.
- If the value of K is greater than 1, the products in the reaction are favored; if the value of K is less than 1, the reactants in the reaction are favored; if K is equal to 1, neither reactants nor products are favored.

Review Questions

1. Why are solids and liquids not included in the equilibrium constant expression? **(Intermediate)**

2. What does the value of K mean in terms of the amount of reactants and products? **(Intermediate)**

3. What is the correct equilibrium constant expression for the following reaction? **(Intermediate)**

$2\ SO_{2(g)} + O_{2(g)} \leftrightarrows 2\ SO_{3(g)}$

(a) $K = \frac{[SO_2]^2[O_2]}{[SO_3]^2}$

(b) $K = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$

(c) $K = \frac{[2\ SO_2][O_2]}{[2\ SO_3]}$

(d) $K = \frac{[2\ SO_3]}{[2\ SO_2][O_2]}$

4. What is the correct equilibrium constant expression for the following reaction? **(Intermediate)**

$Cu(OH)_{2(s)} \leftrightarrows Cu^{2+}{}_{(aq)} + 2\ OH^{-}{}_{(aq)}$

(a) $K = \frac{[Cu^{2+}][OH^{-}]^2}{[Cu(OH)^2]}$ (b) $K = \frac{[Cu(OH)^2]}{[Cu^{2+}][OH^{-}]^2}$

(c) $K = \frac{1}{[Cu^{2+}][OH^{-}]^2}$ (d) $K = [Cu^{2+}][OH^{-}]^2$

5. Consider the following equilibrium system: **(Intermediate)**

$2\ NO_{(g)} + Cl_{2(g)} \leftrightarrows 2\ NOCl_{(g)}$

At a certain temperature, the equilibrium concentrations are as follows: [NO] = 0.184 mol/L, $[Cl_2]$ = 0.165 mol/L, and [NOCl] = 0.060 mol/L. What is the equilibrium constant for this reaction?

(a) 0.506

(b) 0.648

(c) 1.55

(d) 1.97

6. For the reaction:

$MgCl_{2(s)} + \frac{1}{2}\ O_{2(g)} \leftrightarrows MgO_{(s)} + Cl_{2(g)}$

The equilibrium constant was found to be 3.86 at a certain temperature. If 0.560 mol $O_{2(g)}$ is placed in a 1.00 L container, what is the concentration of $Cl_{2(g)}$ at equilibrium? **(Challenging)**

(a) 0.560 mol/L

(b) 2.16 mol/L

(c) 2.88 mol/L

(d) not enough information is available

7. Write the equilibrium constant expressions for each of the following equations: **(Intermediate)**

(a) $CH_3NH_{2(aq)} + H_2O_{(L)} \leftrightarrows CH_3NH_3{}^{+}{}_{(aq)} + OH^{-}{}_{(aq)}$

(b) $2\ CaSO_{4(s)} \leftrightarrows 2\ CaO_{(s)} + 2\ SO_{2(g)} + O_{2(g)}$

(c) $2\ Fe^{3+}{}_{(aq)} + 3\ S^{2-}{}_{(aq)} \leftrightarrows Fe_2S_{3(s)}$

(d) $Hg_{(L)} + H_2S_{(g)} \leftrightarrows HgS_{(s)} + H_{2(g)}$

Further Reading / Supplemental Links

http://en.wikipedia.org/wiki/Chemical_equilibrium

Vocabulary

equilibrium constant (K)	A mathematical ratio that shows the concentrations of the products divided by concentration of the reactants.

Review Answers

1. Solids and liquids are not included in the equilibrium expression because their concentrations can't change to any great degree in an equilibrium situation.

2. If the numerator and the denominator are close to being the same, then K = 1 and the reaction is in equilibrium. If the denominator is greater than the numerator, the reactant concentrations are greater than the product concentrations and therefore the reactants are favored. The reverse is true for K > 1. If the numerator is less than the denominator, most of the reactants have reacted into products and the value of K is large.

3. (b)

4. (d)

5. (b) 0.648

6. (c) 2.88 mol/L

7.

(a) $K = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]}$

(b) $K = [SO_2]^2[O_2]$

(c) $K = \frac{1}{[Fe^{3+}]^2[S^{2-}]^3}$

(d) $K = \frac{[H_2]}{[H_2S]}$

The Effects of Applying Stress to Reactions at Equilibrium

Lesson Objectives

- State Le Châtelier's Principle.
- Demonstrate on specified chemical reactions how Le Châtelier's Principle is applied to equilibrium systems.
- Describe the effect of concentration on an equilibrium system.
- Demonstrate with specific equations how Le Châtelier's Principle explains the effect of concentration.

- Describe the effect of pressure as a stress on the equilibrium position.
- Describe the pressure effect in Le Châtelier’s Principle.
- Describe the effect of temperature as a stress on an equilibrium system.
- Explain how Le Châtelier’s principle explains the effect of temperature.
- Understand how a catalyst works in equilibrium reactions.
- Explain the effect of a catalyst in equilibrium reactions.

Introduction

When a reaction has reached equilibrium with a given set of conditions, if the conditions are not changed, the reaction will remain at equilibrium forever. The forward and reverse reactions continue at the same equal and opposite rates and the macroscopic properties remain constant.

It is possible, however, to reach into the reaction and alter a condition. For example, you could increase the concentration of one of the products, or decrease the concentration of one of the reactants, or change the temperature. When a change of this type is made in a reaction at equilibrium, the reaction is no longer in equilibrium. If you increased the concentration of one of the reactants, then the forward reaction rate would increase and no longer be equal to the reverse rate. The reaction would again move material toward the products. When you alter something in a reaction at equilibrium, chemists say that you put **stress** on the equilibrium. When this occurs, the reaction will no longer be in equilibrium and the reaction itself will begin changing the concentrations of reactants and products ***until the reaction comes to a new position of equilibrium*** . How a reaction will change when a stress is applied can be explained and predicted. That's the topic of this unit.

Le Châtelier’s Principle

In the late 1800s, a chemist by the name of Henry-Louis Le Châtelier was studying stresses that were applied to chemical equilibria. He formulated a principle from this research and, of course, the principle is called **Le Chatelier's Principle**. Le Châtelier’s principle states that when a stress is applied to a system at equilibrium, the equilibrium will shift in a direction to partially counteract the stress and once again reach equilibrium. For instance, if a stress is applied by increasing the concentration of a reactant, the equilibrium position will shift toward the right, producing more products, to remove that stress. The reverse is also true. If a stress is applied by lowering a reactant concentration, the equilibrium position will shift toward the left, this time producing more reactants, and once again partially counteracting that stress. If a stress is applied by increasing the concentration of a product, the equilibrium position will shift toward the left, reducing the concentration of the product. Again the reverse is true in that if a stress is applied by reducing the concentration of a product, the equilibrium position will shift toward the right and producing more reactant to counteract that stress.

Le Chatelier's principle is not an explanation of what happens on the molecular level to cause the equilibrium shift, it is simply a quick way to determine which way the reaction will run in response to a stress applied to the system at equilibrium.

Effect of Concentration Changes on a System at Equilibrium

Raising or Lowering the Concentration of a Reactant or Product

In a system at equilibrium, the forward and reverse reactions are occurring but they are occurring at exactly the same rate and therefore, there is no **NET** movement of material toward the reactants or products. We can use the same theoretical equation to discuss what happens when concentration changes are made in this reaction at equilibrium

$$A_{(aq)} + B_{(aq)} \leftrightarrows C_{(aq)} + D_{(aq)}$$

At equilibrium the forward and reverse rates are equal and the concentrations of all reactants and products remain constant - which keeps the rates constant. Suppose we add some additional A and thus raise the concentration of A without changing anything else in the system. Since the concentration of A is larger than it was before, the forward reaction rate will suddenly be higher. The forward rate will now exceed the reverse rate. Now, there IS a net movement of material from the reactants to the products. As the reaction runs, the concentrations of the reactants decrease and the concentrations of the products increase.

The displacement of the equilibrium was due to a higher forward reaction rate - so that the two rates were no longer equal. As the reaction uses up reactants, the forward rate that was too high slowly decreases and the reverse rate that was too low slowly increases. The two rates are moving toward each other and will eventually become equal again. They do not return to their previous rates but they do become equal at some other size. The system returns to equilibrium.

This explains why Le Chatelier's principle works in this case. Le Chatelier's principle says that when you apply a stress (adding A), the equilibrium system will shift to partially counteract the applied stress. In this case, the reaction shifts toward the products so that A and B are used and C and D are produced. This reduction of the concentration of A is counteracting the stress you applied (adding A).

Suppose the stress you applied to the original reaction was removing some A instead of adding some. In that case, the concentration of A would decrease and the forward rate would slow down. Once again, the two rates are no longer equal. You should note that removing A has no effect on the reverse reaction rate. The reverse rate is dependent on the concentrations of C and D and removing A has no instantaneous effect on the reverse reaction rate. Therefore, at the instant you remove the A, the forward rate decreases but the reverse rate remains exactly what it was. The reverse rate is now greater than the forward rate and the equilibrium will shift toward the reactants. As the reaction runs backward, the concentrations of C and D decrease, slowing the reverse rate (which was the larger one), and the concentrations of A and B increase, raising the forward rate (which was the slower one). The rates are again moving toward each other and the system will again reach equilibrium. The shift of material from products to reactants increases the concentration of A, thus counteracting the stress you applied (removing A). Le Chatelier's principle again correctly predicts the equilibrium shift.

The effect of concentration on the equilibrium system according to Le Châtelier is as follows: Increasing the concentration of a reactant causes the equilibrium to shift to the right using up reactants and producing more products. Increasing the concentration of a product causes the equilibrium to shift to the left using up products and producing more reactants. The exact opposite is true when either a reactant or product is removed.

Sample Questions

Sample question: For the reaction: $SiCl_{4(g)} + O_{2(g)} \rightleftarrows SiO_{2(s)} + 2\ Cl_{2(g)}$, what would be the effect on the equilibrium system if:

(a) $[SiCl_4]$ increases

(b) $[O_2]$ increases

(c) $[Cl_2]$ increases

Solution:

(a) $[SiCl_4]$ increases:

The equilibrium would shift to the right;

$[Cl_2]$ increase;

more SiO_2 would be produced but that does not increase its concentration since its a solid;

[O_2] would decrease.

(b) [O_2] increases:

The equilibrium would shift to the right;

[$SiCl_4$] decrease;

more SiO_2 would be produced but no change in concentration;

[Cl_2] increase.

(c) [Cl_2] increases:

The equilibrium would shift left;

[$SiCl_4$] and [O_2] increase;

SiO_2 would be used up but no change in concentration because it is a solid.

Let's take a moment to consider a detail which sometimes causes confusion with first year students. That detail involves what happens to the concentration of a reactant or product that is changed. In our theoretical reaction, if you add A, the concentration of A will increase. Then the equilibrium shifts toward the products and A is used. Where does the concentration of A end up, higher or lower than the original concentration? The concentration of A is raised when you add it, then it decreases as the equilibrium shifts, but a new equilibrium will be reached before the concentration of A gets back down to its original concentration. That's why Le Chatelier's principle says "equilibrium will shift to **partially** counteract the applied stress". The concentration of A at the new equilibrium will be higher than its original concentration but lower than the level to which you raised it. The same situation occurs in all raising or lowering of reactants and products. The equilibrium shift will move toward returning the concentration to where it was before you applied the stress but it never quite gets back to the original value before a new equilibrium is established.

Decreasing the concentration of a reactant causes equilibrium to shift to the left, which means that less products will be produced. And, if there is a decrease in concentration in a product, the equilibrium will shift so that the reactants will make more products to adjust for this stress.

Sample Question: For the reaction: $PCl_{3(g)} + Cl_{2(g)} \leftrightarrows PCl_{5(g)}$, which way will the equilibrium shift if:

(a) [PCl_3] decreases

(b) [Cl_2] decreases

(c) [PCl_5] decreases

(a) left (b) left (c) right

Sample Question: Here's a reaction at equilibrium. Note the phases of each reactant and product.

$A_{(aq)} + B_{(s)} \leftrightarrows C_{(aq)} + D_{(aq)}$

Think carefully before answering each of the following questions about this system.

(a) Which way will the equilibrium shift if you add some A to the system without changing anything else?

(b) After A has been added and a new equilibrium is reached, how will the new concentration of D compare to the original concentration of D?

(c) After A has been added and a new equilibrium has been established, how will the new concentration of A compare to the original concentration of A?

(d) After A has been added and a new equilibrium has been established, how will the new concentration of B compare to the original concentration of B?

(e) Which way will the equilibrium shift if you add some C to the system without changing anything else?

(f) After C has been added and a new equilibrium has been established, how will the new concentration of D compare its original concentration?

(g) After C has been added and a new equilibrium has been established, how will the new concentration of A compare its original concentration?

(h) Which way will the equilibrium shift if you add some B to the system without changing anything else?

Answers:

(a) The equilibrium will shift toward the products (forward).

(b) The new concentration of D will be higher than the original.

(c) The new concentration of A will be higher than the original. (But lower than the concentration after A was added.)

(d) Since B is a solid, its concentration will be the same as the original. (There will be less of it since some was used in the equilibrium shift, but the concentration will be the same.)

(e) The equilibrium will shift toward the reactants (backward).

(f) The new concentration of D will be lower than the original.

(g) The new concentration of A will be higher than the original.

(h) Since B is a solid, adding B will not change its concentration and therefore has no effect on the equilibrium.

It is possible that adding some B will increase the surface area of B and therefore increase the forward reaction rate but it will also increase the reverse reaction rate the same amount, hence no shift in equilibrium.

The Haber Process and Concentration Change Effects

The reaction between nitrogen gas and hydrogen gas can produce ammonia, NH_3. Under normal conditions, this reaction does not produce very much ammonia. Early in the 20th century, the commercial use of this reaction was too expensive because of the small yield of ammonia.

$$N_{2(g)} + 3\,H_{2(g)} \leftrightarrows 2\,NH_{3(g)} + \text{energy} \quad \text{(Equation 1)}$$

Fritz Haber, a German chemist working in the early years of the 20th century, applied Le Châtelier's principle to help solve this problem. Decreasing the concentration of ammonia, for instance, by immediately removing it from the reaction container will cause the equilibrium to shift to the right and continue to produce more product. There were a number of other ways that Haber used to make as much product as possible. In later sections, we will study all the conditions that are used to force this equilibrium system to produce an even larger actual yield of ammonia.

Lesson Summary

- Increasing the concentration of a reactant causes the equilibrium to shift to the right producing more products.
- Increasing the concentration of a product causes the equilibrium to shift to the left producing more reactants.
- Decreasing the concentration of a reactant causes the equilibrium to shift to the left producing less products.
- Decreasing the concentration of a product causes the equilibrium to shift to the right producing more products.

Review Questions

1. What is the effect on the equilibrium position if the [reactants] is increased? **(Intermediate)**

2. What is the effect on the equilibrium position if the [reactants] is decreased? **(Intermediate)**

3. Which of the following will cause a shift in the equilibrium position of the equation: **(Intermediate)**

$$2\ C_8H_{18(L)} + 25\ O_{2(g)} \leftrightarrows 18\ H_2O_{(L)} + 16\ CO_{2(g)}$$

I. increase [C_8H_{18}]

II. increase [O_2]

III. decrease [CO_2]

IV. decrease [H_2O]

(a) II and I only

(b) II and III only

(c) II and IV only

(d) I, II, III and IV only

4. Which of the following will cause a shift in the equilibrium position of the equation: **(Intermediate)**

$$CaCO_{3(s)} \leftrightarrows CaO_{(s)} + CO_{2(g)}$$

I. increase [$CaCO_3$]

II. increase [CO_2]

III. decrease [CaO]

IV. decrease [CO_2]

(a) II only

(b) I and III only

(c) II and IV only

(d) I, II, III and IV only

5. For the reaction: $N_2O_{5(s)} \leftrightarrows NO_{2(g)} + O_{2(g)}$, what would be the effect on the equilibrium if: **(Intermediate)**

(a) $[N_2O_5]$ increases

(b) $[NO_2]$ decreases

(c) $[NO_2]$ increases

(d) $[O_2]$ increases

6. Answer the following questions when [CO] is increased in the following system at equilibrium. **(Intermediate)**

$Fe_2O_{3(s)} + 3\ CO_{(g)} \leftrightarrows 2\ Fe_{(s)} + 3\ CO_{2(g)}$

a) Write the equilibrium constant expression.

b) Which direction will this equilibrium shift?

c) What effect will this stress have on $[CO_2]$?

7.. For the reaction: $C_{(s)} + H_2O_{(g)} \leftrightarrows CO_{(g)} + H_{2(g)}$, what would be the effect on the equilibrium system if: **(Intermediate)**

(a) $[H_2O]$ increases

(b) mass of C decreases

(c) [CO] increases

(d) $[H_2]$ decreases

Review Answers

1. Increasing the concentration of the reactant causes the equilibrium to shift right producing more products.

2. Decreasing the concentration of the reactant causes the equilibrium therefore shifts to the left producing more reactants.

3. (b) II and III only

4. (c) II and IV only

5. (a) $[N_2O_5]$ increases will have no effect because $[N_2O_5]$ is a solid.

(b) $[NO_2]$ decreases, the reaction shifts right because NO_2 is a product. The equilibrium position must shift right to remove the stress. The result is that more NO_2 and O_2 being produced.

(c) [NO_2] increases, the reaction shifts left because NO_2 is a product. The equilibrium position must shift left to remove the stress.

(d) [O_2] increases, the reaction shifts left because O_2 is a product. The equilibrium position must shift left to remove the stress.

6.

(a) $K_e = \frac{[CO^2]^3}{[CO]^3}$

(b) forward

(c) increase

7.

(a) Equilibrium will shift in the forward direction

(b) No effect on equilibrium

(c) Equilibrium will shift in the reverse direction

(d) Equilibrium will shift in the reverse direction

The Effect of Effect Changes of Pressure on a System at Equilibrium

The General Effect of Increasing Partial Pressures

A second type of stress studied in Le Châtelier's principle is the effect of changing the pressure of a system at equilibrium. It should be noted that reactants and products that are in solid, liquid, or aqueous state are NOT compressible. Therefore, raising or lowering the pressure on a system that contains only solids, liquids, and/or aqueous solutions will have no effect on the equilibrium. If, however, the reaction at equilibrium contains at least one gas in either the reactants or products, altering the pressure will alter the equilibrium. You should remember from the study of the Kinetic-Molecular Theory that the pressure and volume of a gas are intricately related. Boyle's gas law reminds us that pressure and volume are inversely related. Keep this in mind as you learn the effect of pressure stresses on the equilibrium position.

Suppose we have the following reaction at equilibrium.

$$A_{(aq)} + B_{(aq)} \leftrightarrows C_{(aq)} + D_{(g)}$$

Since the reaction has at least one gaseous substance involved in the reaction, it's equilibrium will be affected by a change in the partial pressure of that gas.

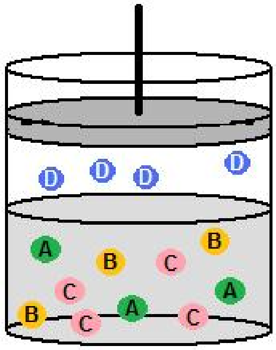

Figure 1: . (*Created by:* Richard Parsons, *License:* CC-BY-SA)

In order for this reaction to reach equilibrium, it would have to be in a closed reaction vessel so the gaseous product could not escape and would stay in contact with the solution so the reverse reaction could occur. There are three ways to increase the pressure in the area above the liquid in the cylinder; 1) add some other gas not involved in the reaction, 2) add some gaseous D into the space above the liquid, and 3) push the piston down so the space above the liquid in the cylinder is decreased. Increasing the pressure in the cylinder by adding a gas not involved in the reaction will increase the total gas pressure in the cylinder but it will not affect the partial pressure of D and therefore, that will not have any effect on the equilibrium of this reaction. Adding some gaseous D to the cylinder is the same thing as adding a reactant or product and has already been discussed in the section on the effect of changing the concentration of a reactant or product. Lowering the piston in the cylinder pushes the D molecules into a smaller space and therefore increases the partial pressure of gaseous D and this increases the concentration of gaseous D in the space above the liquid. Since the concentration of D is increased, the reverse reaction rate will increase and the equilibrium will shift toward the reactants. It is very important to note that **as the equilibrium shifts toward the reactants, the amount of D will decrease as it is used in the shift, and the pressure in the volume above the liquid DECREASES**. Therefore, Le Chatelier's principle also correctly predicts this result. The stress you applied by increasing the pressure above the liquid causes a shift in equilibrium which **tends to counteract the stress you applied**. You raised the pressure, the equilibrium shift tends to lower pressure.

Of course, the reverse of this is also true. If you expand the volume of the cylinder by raising the piston, the partial pressure of D and the concentration of D will decrease. When the concentration of D decreases, the reverse rate slows and the forward reaction rate will drive the equilibrium toward the products. Therefore, the equilibrium shift will increase the concentration and partial pressure of D, thus tending to counteract the stress you applied.

Increasing Pressure Shifts Equilibrium Toward Fewer Moles of Gas

When you have a reaction at equilibrium with gaseous substances on both sides of the equation, the explanation for what happens is more complicated but still understandable with a little thought. Consider equation 1. below.

$$A_{(aq)} + B_{(g)} \leftrightarrows C_{(aq)} + D_{(g)} \qquad \text{(Equation 1)}$$

In this case, there are gaseous substances in both reactants and products. It should be easy to see that if we reduce the volume above this reaction to half of its previous volume, the partial pressures and the concentrations of these two gases will be doubled. Therefore, both reaction rates will increase because concentrations on each side have been increased. If we assume, we are still dealing with single collision reactions so that the forward and reverse rates can be expressed as $R_F = [A][B]$ and $R_R = [C][D]$, then we can see that doubling the concentration of B doubles the forward rate and doubling the concentration of D doubles the reverse rate. Both rates will increase but they increase by the same factor and therefore, the equilibrium will NOT shift.

Suppose, now, that we are dealing with the reaction in Equation 2.

$$A_{(aq)} + B_{(g)} \leftrightarrows C_{(g)} + D_{(g)} \qquad \text{(Equation 2)}$$

This time, we see that there is one gas in the reactants and two gases in the products. If we once again reduce the volume of the gases to half, the partial pressures and the concentrations of the gases will double. Therefore, we double the forward reaction rate because we doubled the concentration of B. In terms of the products, we double the reverse reaction rate once by doubling the concentration of C and then we double the rate again by doubling the concentration of D.

Reverse $\text{Rate}_{\text{OLD}} = k[C][D]$, then by doubling the concentrations of C and D, Reverse $\text{Rate}_{\text{NEW}} = k[2C][2D]$ $4 \times k[C][D]$.

Therefore, the new reverse rate will be four times the original reverse rate. If we double the forward reaction rate and quadruple the reverse rate, the equilibrium shift will be toward the reactants.

When you increase the pressure (by reducing volume) on a reaction at equilibrium, the equilibrium shift will be toward the side that has the fewer moles of gas.

Once again, you should note that Le Chatelier's principle predicts this result. If the equilibrium shift is converting 4 moles of gas to 2 moles of gas, as a backward shift would do, then the shift is reducing the number of moles of gas and the pressure will decrease. You applied a stress by increasing the pressure and the equilibrium shift tends to counteract that stress by reducing pressure.

For a gaseous system at equilibrium, an increase in pressure will cause the equilibrium to shift to the side with the least number of moles (molecules/particles) of gas. This is occurs because the lesser number of moles of gas produces less pressure. Diagram 1 illustrates the decrease in volume/increase in pressure effect on the equilibrium position.

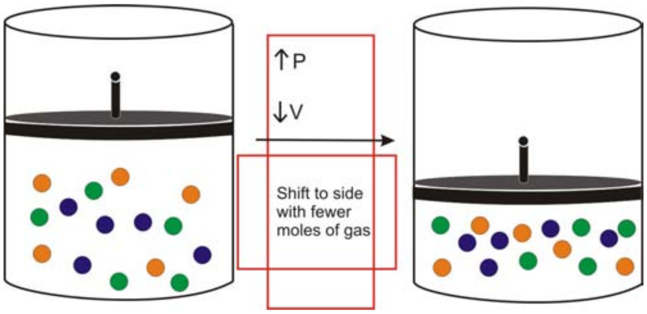

Figure 1: Increase in Pressure Illustration.

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Sample question: For the reaction: $2\ SO_{2(g)} + O_{2(g)} \leftrightarrow 2\ SO_{3(g)}$ what would be the effect on the equilibrium system when the pressure increases.

Solution:

$2\ SO_{2(g)} + O_{2(g)} \leftrightarrows 2\ SO_{3(g)}$

3 moles gas $\leftrightarrows$ 2 moles gas

If the pressure increases, the reaction would shift to the side with the least number of moles of gas. Since there are 3 moles of gaseous reactants and 2 moles of gaseous products, the equilibrium would shift right producing more products, SO_3.

For a gaseous system at equilibrium, a decrease in pressure will cause the equilibrium to shift to the side with the greatest number of moles (molecules/particles) of gas. Once again, this is true because the greater number of moles of gas will produce more pressure. Diagram 2 illustrates a decrease in pressure as it affects the equilibrium position.

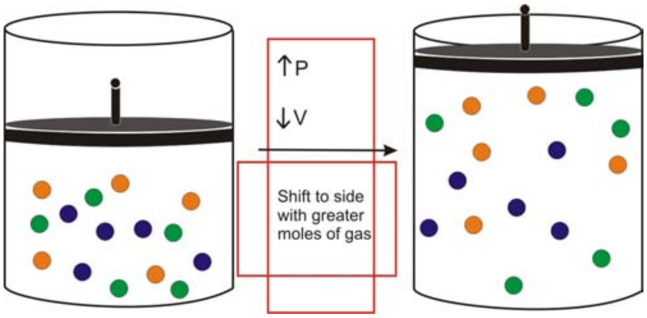

Figure 2: Decrease in Pressure Illustration.

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Sample question: For the reaction: $4\ NH_{3(g)} + 5\ O_{2(g)} \leftrightarrows 4\ NO_{(g)} + 6\ H_2O_{(g)}$, what would be the effect on the equilibrium system if the pressure decreases:

Solution:

$4\ NH_{3(g)} + 5\ O_{2(g)} \leftrightarrows 4\ NO_{(g)} + 6\ H_2O_{(g)}$,

9 moles gas ⟶ 10 moles gas

If the pressure decreases, the reaction would shift to the side with the greater number of moles of gas. Since there are nine moles of gaseous reactants and ten moles of gaseous products, the equilibrium would shift right producing more products.

Increased or Decreased Volume

As is shown in both diagrams 1 and 2, changing the pressure of a gaseous system is often accomplished by changing the volume. The effect of increasing the volume has the same effect as decreasing the pressure. Therefore, increasing the volume of a system will shift the equilibrium to the side with the larger number of moles of molecules/particles. Or, if an equilibrium system has its volume decreased, the side with the lesser number of moles of molecules/particles will be favored.

Sample question: For the reaction: $PCl_{5(g)} \leftrightarrows Cl_{2(g)} + PCl_{3(g)}$ what would be the effect on the equilibrium system when (a) the volume increases; (b) the volume decreases

Solution:

(a) When the volume is increased, pressure decreases and the equilibrium will shift toward the side will more moles of gas. Therefore, $[PCl_5]$ will decrease and $[Cl_2]$ and $[PCl_3]$ will increase.

(b) When the volume is decreased, pressure increases and the equilibrium will shift toward the side will fewer moles of gas. Therefore, $[PCl_5]$ will increase and $[Cl_2]$ and $[PCl_3]$ will decrease.

The Haber Process and the Effect of Pressure Change

Earlier we discussed the reaction that produces ammonia, NH_3:

$N_{2(g)} + 3\ H_{2(g)} \leftrightarrows 2\ NH_{3(g)}$

We also stated that the German chemist Fritz Haber working with Le Châtelier's principle developed a method that produces a maximum amount of the product. Previously we saw that when ammonia is immediately removed from the reaction container, in other words, decreasing the concentration, the equilibrium shifts to make up for the stress and will continue to make more ammonia.

Now we can add one more condition: Since there are 4 moles of gas molecules in the reactants and 2 moles of gas molecules in the product, increasing the pressure (or decreasing the volume) will shift the equilibrium to the right and produce more ammonia. Later, we will discuss one more factor to complete our discussion of the making of ammonia.

Lesson Summary

- An increase in pressure will cause the equilibrium to shift to the side with the lesser number of moles of molecules/particles of gas.
- A decrease in pressure will cause the equilibrium to shift to the side with the greater number of moles of molecules/particles of gas.
- A decrease in volume will also cause the equilibrium to shift to the side with the lesser number of moles of gas.
- An increase in volume will also cause the equilibrium to shift to the side with the greater number of moles of gas.

Review Questions

1. What is the effect on the equilibrium position if the pressure is increased? **(Intermediate)**

2. What is the effect on the equilibrium position if the pressure is decreased? **(Intermediate)**

3. Use Le Châtelier's Principle to predict what will happen to the following equilibrium if the pressure is increased. **(Intermediate)**

$$2\ NH_{3(g)} \leftrightarrows N_{2(g)} + 3\ H_{2(g)}$$

(a) equilibrium position shifts right

(b) equilibrium position shifts left

(c) $[N_2]$ will decrease

(d) $[NH_3]$ will increase

4. Use Le Châtelier's principle to predict what will happen to the following equilibrium if the pressure is decreased. **(Intermediate)**

$$2\ NO_{(g)} + 2\ H_{2(g)} \leftrightarrows N_{2(g)} + 2\ H_2O_{(g)}$$

(a) equilibrium position will not shift

(b) equilibrium position shifts left

(c) $[N_2]$ will increase

(d) [NO] will increase

5. Use Le Châtelier's principle to predict what will happen to the following equilibrium if the volume is decreased. **(Intermediate)**

$2\ NCl_{3(g)} \leftrightarrows N_{2(g)} + 3\ Cl_{2(g)}$

(a) equilibrium position shifts right

(b) equilibrium position shifts left

(c) $[N_2]$ will increase

(d) $[NCl_3]$ will decrease

6. For the reaction: $2\ N_2O_{(g)} + O_{2(g)} \leftrightarrows 4\ NO_{(g)}$, what would be the effect on the equilibrium system if the pressure increases (or the volume decreases)? **(Intermediate)**

7. For the reaction: $2\ IBr_{(g)} \leftrightarrows I_{2(g)} + Br_{2(g)}$, what would be the effect on the equilibrium system if the pressure decreases (or the volume increases)? **(Intermediate)**

8. For the reaction: $H_{2(g)} + CO_{2(g)} \leftrightarrows H_2O_{(g)} + CO_{(g)}$, what would be the effect on the equilibrium system if (a) the pressure increases; and (b) the volume decreases? **(Intermediate)**

9. For the reaction: $3\ NO_{(g)} \leftrightarrows N_2O_{(g)} + NO_{2(g)}$, what would be the effect on the equilibrium system if (a) the pressure increases; and (b) the volume decreases? **(Intermediate)**

Review Answers

1. An increase in pressure (decrease in volume) will cause the equilibrium to shift to the side with the least number of moles (molecules/particles) of gas.

2. An decrease in pressure (increase in volume) will cause the equilibrium to shift to the side with the greatest number of moles (molecules/particles) of gas.

3. b and d

4. d

5. b

6. $2\ N_2O_{(g)} + O_{2(g)} \leftrightarrows 4\ NO_{(g)}$

3 moles gas $\leftrightarrows$ 4 moles gas

If the pressure increases (volume decreasing), the reaction would shift to the side with the least number of moles of gas. Since there are 3 moles of gaseous reactants and 4 moles of gaseous products, the equilibrium would shift left producing more reactants, $N_2O_{(g)}$ and $O_{2(g)}$.

7. 2 moles gas $\leftrightarrows$ 2 moles gas

If the pressure decreases (volume increasing), the reaction would have no shift in the equilibrium system because there are the same number of moles of gas on either side of the equation. Since there are two moles of gaseous reactants and two moles of gaseous products, the equilibrium would not shift right or left.

8. (a) No effect (b) No effect

9. (a) Equilibrium will shift forward (b) Equilibrium will shift forward

The Effect of Changing Temperature on a System at Equilibrium

Increase in Temperature

When the factors that affect reaction rate were discussed, one of the major factors was temperature. Increasing the temperature of any reaction increases the reaction rate. Almost all reactions require activation energy and the higher the temperature of the reactants, the larger the number of particles that have the activation energy. Increasing the temperature of reactants increases their rate of motion which increases the number of collisions and also increasing temperature increases the percentage of successful collisions.

How then, will increasing the temperature of a reaction at equilibrium alter the equilibrium? Equilibrium is the result of the forward and reverse reaction rates becoming equal. It should be clear that increasing the temperature of the reaction vessel will increase both the forward and reverse reaction rates. Will increasing the temperature increase both rates equally? Let's examine the potential energy diagram of a reaction and see if we can gain any insight there. Here is the potential energy diagram for our usual theoretical reaction.

$$A_{(g)} + B_{(g)} \rightarrow C_{(g)} + D_{(g)}$$

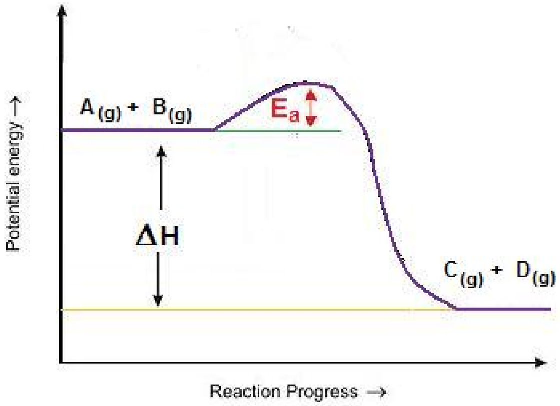

Figure 1: Potential energy diagram with small activation energy.

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As you can see, the forward reaction has a small energy barrier while the reverse reaction has a very large energy barrier. With the reactants and products at the same temperature (as they must be if they are in the same container), it should be apparent that more of the reactant particles will have sufficient activation energy and fewer of the product particles will have sufficient activation energy. Therefore, in this case, the forward reaction will be much faster that the reverse reaction if their concentration of reactants were the same. In the chapter on Reaction Kinetics, we used an energy distribution curve to show the percentage of reactant particles that had sufficient activation energy to react. Here are the energy distribution curves for A and B in the forward reaction and for C and D in the reverse reaction.

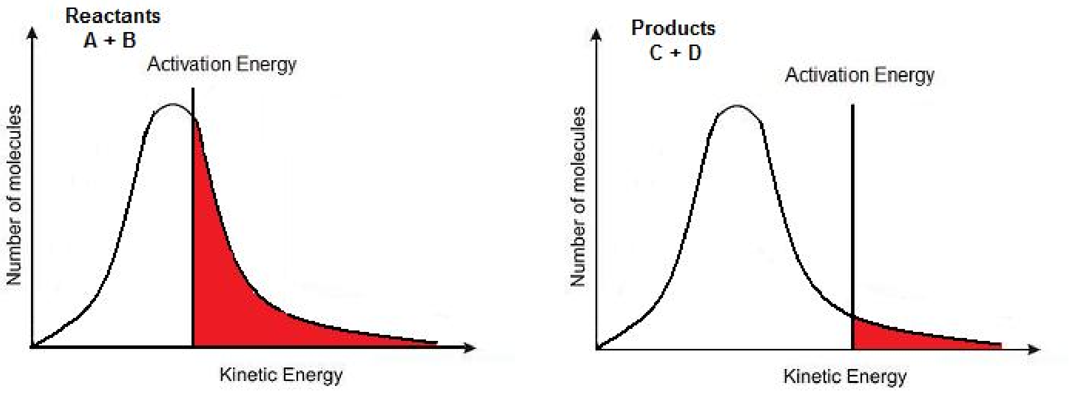

Figure 2: Distribution Curves at Original Temperature.

(*Created by:* Richard Parsons, *License:* CC-BY-SA)

As you can see in the drawing, a much larger percentage of reactant particles have the activation energy required for a successful collision than product particles. Suppose we were to increase the average temperature of these groups of particles by 10°C. The activation energy requirements remain the same for both groups of particles but the average temperature of the entire mass of both groups of particles will increase. On the energy distribution curves, the groups of particles will move up by 10°C but the activation energy remains in place.

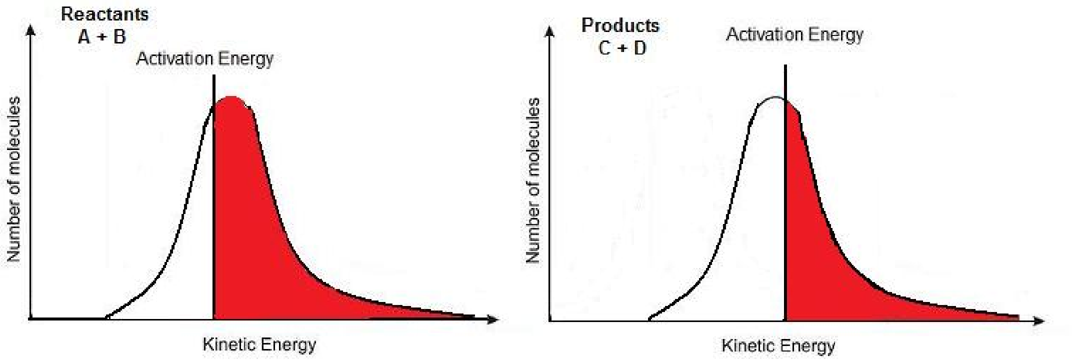

Figure 3: Distribution Curves with 10°C Increase.

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Both reaction rates will increase because both groups of particles have increased the number of particles with sufficient activation energy. The point is to try to determine the factor by which the number of reactions will increase for each side. Looking at the red area for the two reactant distribution curves, we could estimate that the red area has doubled between Figure 1 and Figure 2. The red area for the products, however, has increase by a factor of 5 or 6 times. From this estimate, we could say that the increase in temperature increased the forward reaction rate by a factor of 2 but it increased the reverse rate by a factor of 5. Therefore, with a temperature increase, this equilibrium will shift toward the reactants (backward).

For every reaction, either the forward or reverse reaction will require more activation energy and be slower than the other reaction. The addition of energy to a reaction (heating) increases both reaction rates but it always increases the slower reaction rate more than the faster one. Therefore, heating an exothermic reaction will shift the equilibrium backward and heating an endothermic reaction will shift the equilibrium forward.

You should look at potential energy diagram for exothermic and endothermic reactions and make sure you can always tell whether the forward or reverse reaction is slower and then decide which way an increase in temperature will shift the equilibrium.

The logic for what happens when you lower the temperature of a reaction at equilibrium is just the opposite as that given above for heating a reaction. Cooling a reaction at equilibrium slows both reaction rates but it slows the slower reaction more. Therefore, cooling an exothermic reaction will shift it toward the products and cooling an endothermic reaction will shift the equilibrium toward the reactants.

Le Chatelier's principle also correctly predicts the equilibrium shift when systems at equilibrium are heated and cooled. An increase in temperature is the same as adding heat to the system. Look at the equation 1.

$$2\ SO_{2(g)} + O_{2(g)} \leftrightarrows 2\ SO_{3(g)} \quad \Delta H = -191\ \text{kJ} \quad \text{(Equation 1)}$$

Equation 1 can also be written as:

$$2\ SO_{2(g)} + O_{2(g)} \leftrightarrows 2\ SO_{3(g)} + 191\ \text{kJ} \quad \text{(Equation 2)}$$

What's important to remember about increasing the temperature of an equilibrium system, is the energy can be thought as just another product or reactant. In Equation 2, you can clearly see that the 191 kJ are a product. Therefore when the temperature of this system is raised, the effect will be the same as increasing any other product. For instance, as the temperature is increased, the equilibrium will shift away from the stress and result in increased concentration of each of the reactants and a decrease in concentration of the other product.

$$2\ SO_{2(g)} + O_{2(g)} \leftrightarrows 2\ SO_{3(g)} + 191\ \text{kJ}$$

When the temperature is increased for this reaction, the reaction will shift toward the reactants in an attempt to counteract the increased temperature. Therefore, the $[SO_3]$ will decrease and the $[SO_2]$ and $[O_2]$ will increase.

And, if the temperature for this equilibrium system is lowered, the equilibrium will shift to make up for this stress.

$$2\ SO_{2(g)} + O_{2(g)} \leftrightarrows 2\ SO_{3(g)} + 191\ \text{kJ}$$

When the temperature is decreased for this reaction, the reaction will shift toward the products in an attempt to counteract the decreased temperature. Therefore, the $[SO_3]$ will increase and the $[SO_2]$ and $[O_2]$ will decrease.

Table 1 summarizes the effect temperature has on equilibrium reactions, both endothermic and exothermic.

Table 1: The Effect of Temperature on an Endothermic and an Exothermic Equilibrium System

	Exothermic (- ΔH)	Endothermic (+ ΔH)
Increase Temperature	Shifts left, favors reactants	Shifts right, favors products
Decrease Temperature	Shifts right, favors products	Shifts left, favors reactants

Sample question: Predict the effect on the equilibrium position if the temperature is increased in each of the following.

(a) $H_{2(g)} + CO_{2(g)} \leftrightarrows CO_{(g)} + H_2O_{(g)}\ \Delta H = +\ 40\ \text{kJ/mol}$

(b) $2\ SO_{2(g)} + O_{2(g)} \leftrightarrows 2\ SO_{3(g)} + \text{energy}$

Solution:

(a) $H_{2(g)} + CO_{2(g)} \leftrightarrows CO_{(g)} + H_2O_{(g)}$ $\Delta H = +40$ kJ/mol

The reaction is endothermic. With an increase in temperature for an endothermic reaction, the reactions will shift right producing more products.

(b) $2\ SO_{2(g)} + O_{2(g)} \leftrightarrows 2\ SO_{3(g)}$ + energy

The reaction is exothermic. With an increase in temperature for an exothermic reaction, the reactions will shift left producing more reactants.

Value of K Changes When Temperature Changes

The reaction constant, k, for a reaction is determined for a particular temperature and is correct only at that temperature. The k value is unaffected by changes in concentration, volume, or pressure. The equilibrium constant, K, is the ratio of k_F to k_R, so if the k's don't change, neither will K. Therefore, K is a constant through all changes in concentration, volume, or pressure. When you change the temperature, however, the k values do change and therefore, the K value will also change.

Temperature is the only stress, of all those studied by Le Châtelier (and others) that has the effect of increasing or decreasing the value of the equilibrium constant. It was actually a Dutch chemist, Jacobus Henricus van 't Hoff, who shortly after Le Châtelier's work was known, derived the relationship for how the equilibrium constants change with temperature. He showed that the value of the equilibrium constant is indeed affected by the increase and decrease in temperature. In fact, with an increasing temperature, the value of the equilibrium constant, K, increases if the forward reaction is endothermic and decreases if it is exothermic. The opposite, of course, would be true for a decrease in temperature.

Table 2 extends Table 1 showing how the value of K changes for the endothermic and exothermic reactions.

Table 2: The Effect of Temperature on an Endothermic and an Exothermic Equilibrium System

	Exothermic (- ΔH)	Endothermic (+ ΔH)
Increase Temperature	Shifts left, favors reactants, K ↓	Shifts right, favors products, K ↑
Decrease Temperature	Shifts right, favors products, K ↑	Shifts left, favors reactants, K ↓

Sample question: How does an increase in the temperature affect the concentration of the substance boldfaced in each of the following as well as the value of K?

(a) $\mathbf{SO_{2(g)}}$ + energy $\leftrightarrows S_{(s)} + O_{2(g)}$

(b) $P_{4(s)} + 10\ Cl_{2(g)} \leftrightarrows 4\ \mathbf{PCl_{5(g)}}$ + energy

Solution:

(a) $SO_{2(g)}$ + energy $\leftrightarrows S_{(s)} + O_{2(g)}$; An increase in temperature for an endothermic reaction shifts right, therefore the equilibrium constant (K) increases and the products are favored. This means that the concentration of SO_2 will decrease.

(b) $P_{4(s)} + 10\ Cl_{2(g)} \leftrightarrows 4\ PCl_{5(g)}$ + energy; An increase in temperature for an exothermic reaction shifts left, therefore the equilibrium constant (K) decreases and the reactants are favored. This means that the concentration of PCl_5 will decrease.

The Haber Process and the Effect of Temperature Change

The conditions for making the maximum amount of ammonia in the Haber process include decreasing the concentration of the ammonia (by removing it from the reaction container) and increasing the pressure.

$$N_{2(g)} + 3\ H_{2(g)} \leftrightarrows 2\ NH_{3(g)} + \text{energy}$$

One more factor that will affect this equilibrium system is the temperature. Since the forward reaction is exothermic, lowering the temperature will once again shift the equilibrium system to the right and increase the ammonia that is produced. Specifically the conditions that were found to produce the greatest yield of ammonia are 550°C (in commercial situations this is a "low" temperature) and 250 atms of pressure. Once the equilibrium system is producing the ammonia, the product is removed, cooled and dissolved in water.

Lesson Summary

- For a forward endothermic reaction, an increase in temperature shifts the equilibrium toward the products whereas a decrease in temperature shifts the equilibrium toward the reactant side.
- For a forward exothermic reaction, an increase in temperature shifts the equilibrium toward the reactant side whereas a decrease in temperature shifts the equilibrium toward the product side.
- Increasing or decreasing the temperature causes the K value to change.

Review Questions

1. Why does temperature affect the value of the equilibrium constant? **(Intermediate)**

2. Which direction will an equilibrium system shift for each of the following: **(Intermediate)**

(a) adding energy to a forward exothermic equilibrium system

(b) adding energy to a reverse exothermic equilibrium system

(c) adding energy to a forward endothermic equilibrium system

(d) adding energy to a reverse endothermic equilibrium system

3. At a certain temperature the equilibrium constant for the reaction given below is 7.43.

$$Ag^{+}_{(aq)} + Cl^{-}_{(aq)} \leftrightarrows AgCl_{(s)} \quad \Delta H = -112\ \text{kJ/mol}$$

What would the value of the equilibrium constant be if the reaction were allowed to come to equilibrium at a higher temperature? **(Intermediate)**

(a) less than 7.43

(b) greater than 7.43

(c) the same, 7.43

(d) not enough information is available

4. With an increase in temperature, the equilibrium constant for a certain reaction was found to increase. Consequently what can be said about the concentrations of the reactants and products? **(Intermediate)**

(a) They both increase.

(b) They both decrease.

(c) The (reactants) increase and the (products) decrease.

(d) The (products) increase and the (reactants) decrease.

5. Predict the effect on the equilibrium position if the temperature is increased in each of the following. **(Intermediate)**

(a) $H_{2(g)} + I_{2(g)} \leftrightarrows 2\ HI_{(g)}$ $\Delta H = +51.8$ kJ

(b) $P_4O_{10(s)} + H_2O_{(L)} \leftrightarrows H_3PO_{4(aq)}$ + heat

6. How does an increase in the temperature affect the concentration of the products in each of the following as well as the value of K? **(Intermediate)**

(a) $NO_{2(g)} + NO_{(g)} \leftrightarrows N_2O_{(g)} + O_{2(g)}$ $\Delta H = -43$ kJ

(b) $4\ NH_{3(g)} + 5\ O_{2(g)} \leftrightarrows 4\ NO_{(g)} + 6\ H_2O_{(g)}$ + heat

7. Predict the effect on the equilibrium position if the temperature is increased in each of the following. **(Intermediate)**

(a) $C_2H_{2(g)} + H_2O_{(g)} \leftrightarrows CH_3CHO_{(g)}$ $\Delta H = -151$ kJ/mol

(b) $HC_2H_3O_{2(g)} + H_2O_{(g)}$ + energy $\leftrightarrows CH_3CH_2OH_{(g)} + O_{2(g)}$

8. How does an increase in the temperature affect the concentration of the substance boldfaced in each of the following as well as the value of K? **(Intermediate)**

(a) $N_2O_{2(g)}$ + energy $\leftrightarrows 2\ \mathbf{NO_{2(g)}}$

(b) $2\ C_{(s)} + \mathbf{O_{2(g)}} \leftrightarrows 2\ CO_{2(g)}$ + energy

Use this information to answer questions 9 - 12.

$2\ NOBr_{(g)} \leftrightarrows 2\ NO_{(g)} + Br_{2(g)}$ $\Delta H^{o} = +16.1$ kJ/mol Br_2

The reaction above is at equilibrium in a closed container at 25°.

9. What will happen to the concentration of NO if the temperature is increased? **(Intermediate)**

A. increase B. decrease C. remain unchanged

10. What will happen to the concentration of NOBr if the temperature is increased? **(Intermediate)**

A. increase B. decrease C. remain unchanged

11. What will happen to the concentration of Br_2 if the temperature is increased? **(Intermediate)**

A. increase B. decrease C. remain unchanged

12. What will happen to the value of K_e if the temperature is increased> **(Intermediate)**

A. increase B. decrease C. remain unchanged

Review Answers

1. Since changing the temperature affects the equilibrium by shifting to get rid of the stress. Therefore the concentration of each of the reactants and products will change which then changes the mathematics of determining the K.

2. (a) shifts left

(b) shifts right

(c) shifts right

(d) shifts left

3. less than 7.43

4. d

5. Solution:

(a) $H_{2(g)} + I_{2(g)} \leftrightarrows 2\ HI_{(g)}$ $\Delta H = +51.8$ kJ

The reaction is endothermic. With an increase in temperature for an endothermic reaction, the reactions will shift right producing more products.

(b)$P_4O_{10(s)} + H_2O_{(L)} \leftrightarrows H_3PO_{4(aq)}$ + heat

The reaction is exothermic. With an increase in temperature for an exothermic reaction, the reactions will shift left producing more reactants.

6. **Solution:**

(a) $NO_{2(g)} + NO_{(g)} \leftrightarrows N_2O_{(g)} + O_{2(g)}$ $\Delta H = -43$ kJ

An increase in temperature for an exothermic reaction shifts left, therefore the equilibrium constant, K, decreases and the reactants are favored. This means the concentration of the products will go down.

(b) $4\ NH_{3(g)} + 5\ O_{2(g)} \leftrightarrows 4\ NO_{(g)} + 6\ H_2O_{(g)}$ + heat

An increase in temperature for an exothermic reaction shifts left, therefore the equilibrium constant, K, decreases and the reactants are favored. This means that the concentration of the products will decrease.

7. (a) Equilibrium shift backward (b) Equilibrium shift forward

8. (a) Increase (b) Increase

9. A

10. B

11. A

12. A

The Effect of a Catalyst on a System at Equilibrium

A Catalyst has No Effect on an Equilibrium Position

We have studied the effect of temperature, pressure, and concentration stresses on the equilibrium system from the work of Le Châtelier. A summary of how these stresses affect the equilibrium position are found in Table 1 below.

Table 1: Summary of Le Châtelier Stresses and the Effect on Equilibrium

Stress	**Increase**	**Decrease**
Temperature	Endothermic, forward , shift right Exothermic, reverse, shift left	Endothermic, forward, shifts left Exothermic reverse, shift right
Pressure	Shift to side with least number of moles of gas	Shift to side with greatest number of moles of gas
Concentration	Increase [reactants], shift right Increase [products], shift left	Decrease [reactants], shift left Decrease [products], shift right

Lastly, the effect of a catalyst on the equilibrium position was studied by Le Châtelier to see if the catalyst acting as a stress, would shift the equilibrium position and, if so, how? In this final section of the factors that affect equilibrium as studied by Le Châtelier and others, we will answer this question.

A ***catalyst*** is a substance that increases the rate of a chemical reaction but is, itself, left unchanged, at the end of the reaction. A catalyst provides an alternate pathway that requires less activation energy to form an activated complex so that the products are more easily produced.

There are many catalysts that are used in the laboratory and in our everyday life to affect the rates of reactions. Metals such as platinum are common catalysts. Enzymes in the body are biological catalysts. The biological enzyme used in Equation 1 is a complex protein enzyme that contains a zinc ion. In this reaction to form CO_2 in the body, the enzyme acts as a catalyst to increase the rate of the reaction to obtain equilibrium. Thus for Equation 1, the enzyme will help achieve equilibrium faster, but has **no** effect on the equilibrium position.

$$H_2CO_{3(aq)} \leftrightarrows HCO_3{}^{1-}{}_{(aq)} + H^+{}_{(aq)} \leftrightarrows H_2O_{(L)} + CO_{2(g)}$$ Equation 1

A Catalyst Increases Both Reaction Rates Equally

A catalyst affects the rate of reaction so both the forward and reverse reactions would be changed equally. Equilibrium is a state that the reaction has when the rate of the forward reaction equals the rate of the reverse reaction. This means that there is no effect on a system at equilibrium. The catalyst will increase the rate at which the equilibrium is achieved but once the system is at equilibrium, the catalyst will have no other effect on the equilibrium.

Sample question: Predict the effect on the chemical equilibrium

$4\ NH_{3(g)} + 5\ O_{2(g)} \leftrightarrows 4\ NO_{(g)} + 6\ H_2O_{(g)}$

when each of the following changes are made to the equilibrium system.

(a) $[H_2O]$ is increased

(b) Pressure is decreased

(c) $[NH_3]$ is decreased

(d) Catalyst is added

(e) Volume is decreased

Solution in chart format:

	$4\ NH_{3(g)}$ +	$5O_{2(g)}$	$\leftrightarrows$	$4\ NO_{(g)}$ +	$6\ H_2O_{(g)}$
(a)	↑	↑	←	↓	↑
(b)	↓	↓	→	↑	↑
(c)	↓	↑	←	↓	↓
(d)	no effect				
(e)	↑	↑	←	↓	↓

Lesson Summary

- A catalyst is a substance that increases the rate of a chemical reaction but is, itself, left unchanged, at the end of the reaction.
- A catalyst affects the rate of reaction so both the forward and reverse reactions would be changed equally.
- A catalyst has no effect on the equilibrium position.

Review Questions

1. What is a catalyst? Give an example of a catalyst. **(Intermediate)**

2. How does a catalyst work in an equilibrium reaction? **(Intermediate)**

3. What will the effect of adding a catalyst for the following reaction. **(Intermediate)**

$4\ NH_{3(g)} + 5\ O_{2(g)} \leftrightarrows 4\ NO_{(g)} + 6\ H_2O_{(g)}$ $\Delta H = -905$ kJ

(a) the (products) will increase at equilibrium

(b) the (reactants) will increase at equilibrium

(c) the equilibrium constant will increase for the forward reaction

(d) there will be no effect on the equilibrium concentrations

4. The reaction between nitrogen monoxide and carbon monoxide is represented as follows: **(Intermediate)**

$NO_{(g)} + CO_{(g)} \leftrightarrows \frac{1}{2} N_{2(g)} + CO_{2(g)}$ $\Delta H = -374$ kJ

If a catalyst was added to the system, all of the following would be affected in the system except: **(Intermediate)**

(a) an increase in ΔH

(b) an increase the rate of the reverse reaction.

(c) an increase the rate of the forward reaction.

(d) a change in the reaction path

5. Of the four factors listed below, which factors would not be dependent on the value of the equilibrium constant for the following equation? **(Intermediate)**

$2\ NaNO_{3(s)} \leftrightarrows 2\ NaNO_{2(s)} + O_{2(g)}$

I. concentration of $NaNO_{3(s)}$

II. concentration of $NaNO_{2(s)}$

III. concentration of $O_{2(g)}$

IV. addition of a catalyst

(a) I and II only

(b) III and IV only

(c) I and III only

(d) I, II and IV only

6. In the following reaction, what would Le Châtelier's principle predict to increase the concentration of CO_2? **(Intermediate)**

$C_{(s)} + O_{2(g)} \leftrightarrows CO_{2(g)}$ $\Delta H = -393.5$ kJ/mol

(a) add a catalyst

(b) increase O_2

(c) increase the pressure

(d) increase the temperature

7. Predict the effect on the chemical equilibrium $H_2O_{(g)} + CO_{(g)} \leftrightarrows H_{2(g)} + CO_{2(g)}$, $\Delta H = -42$ kJ when each of the following changes are made to the equilibrium system. What will the effect be on the amount of product produced? **(Intermediate)**

(a) Temperature is increased

(b) Pressure is increased

(c) CO_2 decreases

(d) Catalyst is added

8. Predict the effect on the chemical equilibrium $2\ NaHCO_{3(s)} \leftrightarrows Na_2CO_{3(s)} + CO_{2(g)} + H_2O(g)$, $\Delta H = -635.33$ kJ when each of the following changes are made to the equilibrium system. What will be the effect on the amount of product produced? **(Intermediate)**

(a) Temperature is decreased

(b) Pressure is decreased

(c) $[Na_2CO_3]$ decreases

(d) Catalyst is added

9. Define Le Châtelier's principle. **(Beginning)**

10. What is the main condition for Le Châtelier's principle to be applied? **(Beginning)**

11. Give an example to show how Le Châtelier's principle can be used to allow for more products to be produced where a chemical equilibrium is shifting in response to an applied stress. **(Intermediate)**

12. Answer the following questions if a stress is applied to the product side of the following equilibrium system: **(Intermediate)**

$$4\ NH_{3(g)} + 5O_{2(g)} \leftrightarrows 4\ NO_{(g)} + 6\ H_2O_{(g)}$$

a) What stress is being placed on the equilibrium system?

b) What will the system do to respond to the stress?

c) How will the system try to respond to the stress?

13. Answer the following questions if a stress is applied to the reactant side of the following equilibrium system: **(Intermediate)**

$$2\ NaHCO_{3(s)} \leftrightarrows Na_2CO_{3(s)} + CO_{2(g)} + H_2O_{(g)}$$

a) What stress is being placed on the equilibrium system?

b) What will the system do to respond to the stress?

c) How will the system try to respond to the stress?

14. Answer the following questions if a stress is applied to the reactant side of the following equilibrium system: **(Intermediate)**

$$C_{(s)} + \frac{1}{2} O_{2(g)} \leftrightarrows CO_{(g)}$$

a) What stress is being placed on the equilibrium system?

b) What will the system do to respond to the stress?

c) How will the system try to respond to the stress?

15. Answer the following questions if a stress is applied to the reactant side of the following equilibrium system: **(Intermediate)**

$C_6H_{12(L)} + HBr_{(aq)} \leftrightarrows C_6H_{13}Br_{(aq)}$

a) What stress is being placed on the equilibrium system?

b) What will the system do to respond to the stress?

c) How will the system try to respond to the stress?

16. Predict the effect on the chemical equilibrium $2\ SO_{3(g)} + \text{heat} \leftrightarrows 2\ SO_{2(g)} + O_{2(g)}$, when each of the following changes are made to the equilibrium system. What will the effect be on the amount of product produced? **(Intermediate)**

(a) Temperature is increased

(b) Pressure is increased

(c) $[O_2]$ decreases

(d) Catalyst is added

17. Predict the effect on the chemical equilibrium $2\ N_2O_{4(g)} + \text{heat} \leftrightarrows 2\ NO_{2(g)}$, when each of the following changes are made to the equilibrium system. What will the effect be on the amount of product produced? **(Intermediate)**

(a) Temperature is decreased

(b) Pressure is decreased

(c) $[N_2O_4]$ decreases

(d) Catalyst is added

Review Answers

1. A catalyst is a substance that increases the rate of a chemical reaction but is, itself, left unchanged, at the end of the reaction. Enzymes are examples of biological catalysts.

2. A catalyst affects the rate of reaction so both the forward and reverse reactions would be changed equally. These substances speed up both the forward and reverse rates to get to the equilibrium state faster. Therefore there is no effect on the equilibrium position.

3. (d) there will be no effect on the equilibrium concentrations

4. (a) an increase in ΔH

5. (d) I, II and IV only

6. (b) increase O_2

7. (a) $H_2O_{(g)} + CO_{(g)} \leftrightarrows H_{2(g)} + CO_{2(g)}$, $\Delta H = -42$ kJ/mol

(b) Temperature is increased: reaction is exothermic, therefore when the temperature is increased the reaction shifts left and the amount of product decreases.

(c) Pressure is increased; there are 2 moles of gaseous products and 2 moles of gaseous reactants therefore there is no effect on the reaction when the pressure increases.

(d) $[CO_2]$ decreases; CO_2 is a product, therefore when there is an decrease in the product concentration the reaction equilibrium shifts right and the amount of product increases.

Catalyst is added; a catalyst does not affect the equilibrium position so there is no effect on amount of product formed.

8. (a) $2\ NaHCO_{3(s)} \leftrightarrows Na_2CO_{3(s)} + CO_{2(g)} + H_2O_{(g)}$, $\Delta H = -\ 635.33$ kJ

(b) Temperature is decreased: reaction is exothermic, therefore when the temperature is decreased the reaction shifts right and the amount of product increases.

(c) Pressure is decreased; there are 2 moles of gaseous products and 0 moles of gaseous reactants therefore the reaction shifts to the product side or the side with the greatest number of moles of gas.

(d) $[Na_2CO_3]$ decreases; Na_2CO_3 is a product, but it is a solid so since solids do not affect the equilibrium constant, it will have no effect on the equilibrium position or the amount of products.

Catalyst is added; a catalyst does not affect the equilibrium position so there is no effect on amount of product formed.

9. Le Châtelier's principle states that if you apply a stress to an equilibrium system, the equilibrium position will shift to offset that stress and regain equilibrium.

10. The reaction must be in equilibrium in order to apply Le Châtelier's principle to it. Otherwise you cannot apply this principle.

11. Answers will vary but students could use any equilibrium reaction like the one shown below and then state something similar.

$N_{2(g)} + 2\ O_{2(g)} \leftrightarrows 2\ NO_{2(g)}$; by adding a stress(like increased pressure or decreased volume) to the reactant side (left side), the equilibrium position is shifted toward the right and thus causing the production of more products.

12. (a) A stress is being applied to the right hand side (product side) of the equilibrium system.

(b) The system will respond by shifting the equilibrium position to the left.

(c) The system will respond by producing more reactants, in this case NH_3 and O_2.

13. (a) A stress is being applied to the left hand side (reactant side) of the equilibrium system.

(b) The system will respond by shifting the equilibrium position to the right.

(c) The system will respond by producing more reactants, in this case CO_2 and H_2O.

14. (a) A stress is being applied to the left hand side (reactant side) of the equilibrium system.

(b) The system will respond by shifting the equilibrium position to the right.

(c) The system will respond by producing more reactants, in this case, CO.

15. (a) A stress is being applied to the right hand side (product side) of the equilibrium system.

(b) The system will respond by shifting the equilibrium position to the left.

(c) The system will respond by producing more reactants, in this case HBr.

16. (a) Equilibrium will shift forward.

(b) Equilibrium will shift in the reverse direction.

(c) Equilibrium will shift forward.

(d) No shift in equilibrium.

17. (a) Equilibrium will shift forward.

(b) No shift in equilibrium.

(c) Equilibrium will shift in the reverse direction.

(d) No shift in equilibrium.

Further Reading / Supplemental Links

http://en.wikipedia.org/wiki

Vocabulary

Le Châtelier's Principle	Applying a stress to an equilibrium system causes the equilibrium position to shift to offset that stress and regain equilibrium.
The Haber Process	A commercial method that makes the maximum amount of ammonia using the Le Châtelier's Principle.
exothermic reaction	A reaction in which the heat content of the reactants is greater than the heat content of the products; the excess energy is given off as a product.
endothermic reaction	A reaction in which the heat content of the reactants is less than the heat content of the products; energy is needed to be added to the reactants in order to form the products.
catalyst	A substance that increases the rate of a chemical reaction but is, itself, left unchanged, at the end of the reaction.

Slightly Soluble Salts

Lesson Objectives

- Define solubility product constants.
- Write solubility product constant expressions.

- Calculate solubility product constants.

Introduction

The dissolving equations for solid salts provide an interesting set of equilibrium constant expressions. These dissolving equations will always have a solid as the only reactant and the resulting aqueous ions as the products. Here are some dissolving equations for salts to remind you how they appear.

$NaCl_{(s)} \longrightarrow Na^+_{(aq)} + Cl^-_{(aq)}$

$Zn(IO_3)_{2(s)} \leftrightarrows Zn^{2+}_{(aq)} + 2\ IO_3^-{}_{(aq)}$

$PbCl_{2(s)} \leftrightarrows Pb^{2+}_{(aq)} + 2\ Cl^-_{(aq)}$

Since equilibrium constant expressions for equations always omit solids, the equilibrium constant expressions for these equations will have a denominator of "1", so no denominator will be shown. Here are the equations with their equilibrium constant expressions.

$NaCl_{(s)} \longrightarrow Na^+_{(aq)} + Cl^-_{(aq)}$ $K = [Na^+][Cl^-]$

$Zn(IO_3)_{2(s)} \leftrightarrows Zn^{2+}_{(aq)} + 2\ IO_3^-{}_{(aq)}$ $K = [Zn^{2+}][IO_3^-]^2$

$PbCl_{2(s)} \leftrightarrows Pb^{2+}_{(aq)} + 2\ Cl^-_{(aq)}$ $K = [Pb^{2+}][Cl^-]^2$

In this final section of the chapter we will look at solubility equilibria.

Salts in an Equilibrium System

The equilibrium constants for slightly soluble salts are especially useful because of the large amount of information that can be acquired from mathematical calculations available with these equations. Consider the dissociation of copper(II) hydroxide (Equation 4)

$Cu(OH)_{2(s)} \leftrightarrows Cu^{2+}_{(aq)} + 2\ OH^-_{(aq)}$ (Equation 1)

Copper (II) hydroxide dissolves in solution only slightly. The resulting solution is saturated; and in order for an equilibrium system to be established, excess solid must also be in the container. In fact, the equilibrium constant for the reaction shown in Equation 1 is 2.2×10^{-20}. This very small value for K means that the salt dissolves very little in solution and very few $Cu^{2+}_{(aq)}$ or $OH^-_{(aq)}$ ions are actually formed in the solution process. However it is still an equilibrium system if there is excess salt in the container.

Sample question: Tooth enamel consists of the compound hydroxyapatite. It has a formula $Ca_5(PO_4)_3OH$ and has an equilibrium constant of 6.8×10^{-37}. Write the dissociation equation and comment on the value of the equilibrium constant.

Solution:

$Ca_5(PO_4)_3OH_{(aq)} \leftrightarrows Ca_5(PO_4)_3^+{}_{(aq)} + OH^-_{(aq)}$

$K = 6.8 \times 10^{-37}$. This value is very small indicating that there is not much dissociation occurring which is a good thing. This means that tooth enamel will not readily dissociated into the ions and stay as enamel on your teeth (something you want to happen!)

Solubility Product Constant

Equation 5 represents the dissociation of iron (II) hydroxide.

$Fe(OH)_{2(s)} \leftrightarrows Fe^{2+}{}_{(aq)} + 2\ OH^{-}{}_{(aq)}$ (Equation 5)

The equilibrium expression would be:

$K = [Fe^{2+}][OH^{-}]^{2}$

Since the reactants are solids (as they would always be for the dissolving of a solid in solution), the equilibrium constant expression has the concentration of the reactants multiplied together raised to the power of their coefficients and no denominator shown. Since these reactions are so specialized, their equilibrium constants are given their own name, ***solubility product constants*** and have the subscripted symbol K_{sp}.

Sample question: Write the dissociation reaction and the solubility product constant expression for each of the following solids.

(a) $PbSO_{4(s)}$

(b) $Al(OH)_{3(s)}$

Solution:

(a) $PbSO_{4(s)} \leftrightarrows Pb^{2+}{}_{(aq)} + SO_4{}^{2-}{}_{(aq)}$ $Ksp = [Pb^{2+}][SO_4{}^{2-}]$

(b) $Al(OH)_{3(s)} \leftrightarrows Al^{3+}{}_{(aq)} + 3\ OH^{-}{}_{(aq)}$ $Ksp = [Al^{3+}][OH^{-}]^{3}$

Mathematics for K_{sp}

Conclusions from K_{sp} Size

When looking at the solubility product constant, we can see qualitatively how the ion concentrations affect the value of the constant. Take, for example, the dissociation of lead iodide.

$PbI_{2(s)} \leftrightarrows Pb^{2+}{}_{(aq)} + 2\ I^{-}{}_{(aq)}$ $K_{sp} = [Pb^{2+}][I^{-}]^{2} = 7.90 \times 10^{-9}$

We can see that there are twice as many iodide ions as there are lead ions in the equilibrium system. Notice, too, that this number is very low indicating that little dissociation is occurring.

For the dissociation of silver chromate, there are twice as many silver ions as there are chromate ions. The value of K_{sp} is even lower meaning the amount of dissociation for silver chromate is even smaller.

$Ag_2CrO_{4(s)} \leftrightarrows 2\ Ag^{+}{}_{(aq)} + CrO_4{}^{-}{}_{(aq)}$ $K_{sp} = [Ag^{+}]^{2}[CrO_4{}^{-}] = 1.10 \times 10^{-12}$

Sample problem: Compare the amount of dissociation of the two sulfates listed below.

(a) Barium sulfate: $BaSO_{4(s)} \leftrightarrows Ba^{2+}{}_{(aq)} + SO_4{}^{2-}{}_{(aq)}$ $K_{sp} = 1.10 \times 10^{-10}$

(b) Silver sulfate:: $Ag_2SO_{4(s)} \leftrightarrows 2\ Ag^+_{(aq)} + SO_4^{2-}{}_{(aq)}$ $K_{sp} = 1.20 \times 10^{-5}$

Solution:

For barium sulfate, there are equal amounts of the sulfate and barium ions formed when barium sulfate dissolves. The K_{sp} is low meaning that the amount of barium sulfate that does dissolve is low.

For silver sulfate in (b), there are twice as many silver ions as sulfate ions and the K_{sp} is much higher meaning that more of the silver sulfate will dissolve in solution forming ions.

Calculating K_{sp} From Solubility

The K_{sp} of a slightly soluble salt can be calculated from its solubility. Solubilities are usually given in grams/liter but occasionally are given in moles/liter. If the solubility is given in moles/liter, you can follow the same process as demonstrated below except you skip the first step.

Given the solubility of copper (I) bromide to be 0.0287 grams/liter, the molarity of the dissolved CuBr can be determined, and from the molarity of the dissolved CuBr, the molarity of the individual ions in solution can be calculated.

$$\text{mols CuBr dissolved} = \frac{0.0287\ \text{g/L}}{143.5\ \text{g/mol}} = 0.000200\ \text{M} = 2.00 \times 10^{-4}\ \text{M}$$

$$CuBr_{(s)} \leftrightarrows Cu^+_{(aq)} + Br^-_{(aq)}$$

In this case, the reacting ratio between the moles of solid dissolved and the moles of ions in solution is 1:1, so when 2.00×10^{-4} mol/L of CuBr dissolve, the concentration of the ions in solution will be $[Cu^+] = 2.00 \times 10^{-4}$ mol/L and $[Br^-] = 2.00 \times 10^{-4}$ mol/L.

The K_{sp} expression for the dissolving of CuBr is $K_{sp} = [Cu^+][Br^-]$. Substituting the now known values for the concentrations of the ions into the K_{sp} expression will

yield the K_{sp} value after calculation.

$K_{sp} = [Cu^+][Br^-] = (2.00 \times 10^{-4})(2.00 \times 10^{-4}) = 4.00 \times 10^{-8}$. Units for K_{sp} values are usually not expressed.

The process is only slightly more complicated for salts with more complicated formulas. Consider the salt calcium phosphate. The solubility of calcium phosphate is 5.10×10^{-5} g/L. First, we convert the solubility in grams/liter to moles/liter.

$$\text{molarity } Ca_3(PO_4)_2 \text{ dissolved} = \frac{5.10 \times 10^{-5}\ \text{g/L}}{310.\ \text{g/mol}} = 1.67 \times 10^{-7}\ \text{M}$$

Then, using the dissolving equation, we determine the molarity of the ions in solution.

$$Ca_3(PO_4)_{2(s)} \leftrightarrows 3\ Ca^{2+} + 2\ PO_4^{3-}$$

For every mol/L of calcium phosphate that dissolves, there will be 3 times as much calcium ion and 2 times as much phosphate ion in solution. Therefore,

$[Ca^{2+}] = (3)(1.67 \times 10^{-7}\ \text{M}) = 5.01 \times 10^{-7}$ M and

$[PO_4{}^{3-}] = (2)(1.67 \times 10^{-7}\ M) = 3.34 \times 10^{-7}\ M.$

We finish the calculation by writing the K_{sp} expression and substituting the molarities of the ions into the expression and calculate.

$K_{sp} = [Ca^{2+}]^3[PO_4{}^{3-}]^2 = (5.01 \times 10^{-7})^3(3.34 \times 10^{-7})^2 = 1.4 \times 10^{-32}$

Calculating Solubility From K_{sp}

Not only can the K_{sp} be calculated from the solubility but the solubility can be calculated from the K_{sp}. The logic is similar and just as easy but the arithmetic is somewhat more difficult.

Given the K_{sp} for AgBr as $K_{sp} = 1.60 \times 10^{-10}$, we can use the dissolving equation and some algebra to calculate the concentrations in mols/L of each ion in solution.

$AgBr_{(s)} \leftrightarrows Ag^+ + Br^-$

If we allow x to represent the mols/L of AgBr that dissolves, then, since the reacting ratios in the equation are all ones, x will represent both $[Ag^+]$ and $[Br^-]$. We can then write the K_{sp} expression for AgBr, set it equal to the given K_{sp} value, substitute the assigned variables into the equation and solve.

$K_{sp} = [Ag^+][Br^-] = 1.60 \times 10^{-10}$

$(x)(x) = 1.60 \times 10^{-10}$

$x = 1.26 \times 10^{-5}\ M$ (Not so tough, today's calculators will find square roots for you.)

The molar concentrations of the ions in solution are both 1.26×10^{-5} M and according to the dissolving equation, the molarity of AgBr will be the same so the solubility of AgBr is 1.26×10^{-5} M. To find the solubility of AgBr in grams/liter, we simply need to multiply the moles/liter by the molar mass and we will get the solubility in grams/liter.

Solubility of AgBr in g/L = $(1.26 \times 10^{-5}$ mols/L)(188 g/mol) = 2.4×10^{-3} g/L

This problem becomes more difficult mathematically when the formula of the salt is more complicated. Let's try lead (II) fluoride. Here is the dissolving equation, the K_{sp} expression, and the given K_{sp} value for PbF_2.

$PbF_{2(s)} \Leftrightarrow Pb^{2+} + 2\ F^-$

$K_{sp} = [Pb^{2+}][F^-]^2 = 4.0 \times 10^{-8}$

Once again, we let x represent the solubility of PbF_2 in moles/liter and therefore, the concentration of lead ions in solution will be x and the concentration of fluoride ions in solution will be 2x. Substitute these variables into the K_{sp} expression and solve for x.

$[Pb^{2+}][F^-]^2 = 4.0 \times 10^{-8}$

$(x)(2x)^2 = 4.0 \times 10^{-8}$

$4x^3 = 4.0 \times 10^{-8}$

$x^3 = 1.0 \times 10^{-8}$

Now, the question is, do you know how to take a cube root? Some of you may have a calculator with a cube root button and some may not. Another way to take the cube root of a number with your calculator is to 1) take the log of the number, 2) divide the log by 3, and then 3) take the inverse log of the result. The answer to this step will be the cube root of the original number.

$x = 2.2 \times 10^{-3}$ mol/L

When we assigned the variables, x represented the molarity of the lead ions in solution but x also represented the molarity of lead (II) fluoride that had dissolved, so this is the solubility in moles/liter and to get grams/liter, we multiply by the molar mass.

Solubility of $PbF_2 = (2.2 \times 10^{-3}$ mol/L)(245 g/mol) = 0.53 g/L

You should look back at the assignment of variables and determine the molarity of fluoride ions in solution. There will be questions where you are asked to find the concentrations of the ions in solution from K_{sp}. You would use this same process but the answers would come from the solution for x.

Lesson Summary

- Equilibrium constants for slightly soluble salts are called solubility product constants.

Review Questions

1. What is the solubility product constant? Give an example. **(Intermediate)**

2. Why is solubility considered a special case for chemical equilibria? **(Intermediate)**

3. Nickel hydroxide is a slightly soluble salt. Its dissociation reaction is represented below. **(Intermediate)**

$Ni(OH)_{2(s)} \rightleftarrows Ni^{2+}{}_{(aq)} + 2OH^-{}_{(aq)}$

Which of the following best represents the solubility product constant expression, K_{sp}?

(a) $K_{sp} = \frac{[Ni^{2+}][OH^-]}{[Ni(OH)_2]}$ (b) $K_{sp} = \frac{[Ni^{2+}][OH^-]^2}{[Ni(OH)_2]}$

(c) $K_{sp} = [Ni^{2+}][OH^-]$ (d) $K_{sp} = [Ni^{2+}][OH^-]^2$

4. The K_{sp} for AgBr is 5.0×10^{-13}. What is $[Ag^+]$ at equilibrium? **(Intermediate)**

(a) 5.0×10^{-13} mol/L

(b) 7.1×10^{-7} mol/L

(c) 2.5×10^{-13} mol/L

(d) not enough information is given

5. The K_{sp} for PbF_2 is 3.60×10^{-8}. What is $[F^-]$ at equilibrium? **(Intermediate)**

(a) 3.60×10^{-8} mol/L

(b) 3.33×10^{-3} mol/L

(c) 4.16×10^{-3} mol/L

(d) 2.08×10^{-3} mol/L

6. Magnesium hydroxide is the key component in milk of magnesia, the suspension used to cure indigestion. It has an equilibrium constant of 6.3×10^{-10}. Write the dissociation equation and comment on the value of the equilibrium constant. **(Intermediate)**

7. Write the dissociation reactions for the following salts as well as the K_{sp} expressions. **(Intermediate)**

(a) Calcium fluoride

(b) chromium(II) carbonate

(c) Arsenic(III) sulfide

Further Reading / Supplemental Links

http://en.wikipedia.org/wiki

Vocabulary

solubility product constant, K_{sp} Equilibrium constant for a slightly soluble salt.

Review Answers

1.Equilibrium constants for slightly soluble salts are called solubility product constants. Examples will vary.

$Ag_2S_{(s)} \rightleftharpoons 2\ Ag^+_{(aq)} + S^{2-}_{(aq)}$ $K_{sp} = [Ag^+]^2[S^{2-}]$

2.Solubility is considered a special case for chemical equilibria because for slightly soluble salts the reactions of the salts dissolving in solution are actually an equilibrium reaction. In these reactions, as more of the solid dissolves, more of the ions in solution combine to form solids.

3. (d)

4. (b)

5. (d)

6. $Mg(OH)_{2(s)} \rightleftharpoons Mg^{2+}_{(aq)} + 2\ OH^-_{(aq)}$

$K_{sp} = 6.3\ 10^{-10}$ which is very small. This means that there are very few ions in solution and mostly $Mg(OH)_2$ particles in the suspension.

7. (a) Calcium fluoride: $CaF_{2(s)} \rightleftharpoons Ca^{2+}_{(aq)} + 2\ F^-_{(aq)}$; $K_{sp} = [Ca^{2+}][F^-]^2$

(b) chromium(II) carbonate: $CrCO_{3(s)} \rightleftharpoons Cr^{2+}_{(aq)} + CO_3{}^{2-}_{(aq)}$; $K_{sp} = [Cr^{2+}][CO_3{}^{2-}]$

(c) Arsenic(III) sulfide: $As_2S_{3(s)} \leftrightarrows 2\ As^{3+}{}_{(aq)} + 3\ S^{2-}{}_{(aq)}$; $K_{sp} = [As^{3+}]^2[S^{2-}]^3$

25. Acids

Arrhenius Acids

Lesson Objectives

- Define an Arrhenius acid and know some examples of acids.
- Define operational and conceptual definition.
- Explain the difference between operational and conceptual definitions.
- Describe the properties of acids.
- Describe some of the reactions that acids undergo.

Introduction

In previous chapters you may remember learning about electrolytes and you may even remember reading about Svante Arrhenius. Arrhenius worked a great deal with specific types of electrolyte solutions known as acids and bases. He set the groundwork for our current understanding on acid-base theory. We will begin our study of acids and bases with Arrhenius's theories starting with his famous definitions. This was quite an accomplishment for a scientist in the late 19th century with very little technology but with the combination of knowledge and intellect available at the time. Arrhenius led the way to our understanding of how acids and bases differed, their properties, and their reactions.

We may not realize how much acids and bases affect our lives. Have you ever thought of drinking a can of soda pop and actually drinking acid? Have you looked at bottles of household cleaners and noticed what the main ingredients were? Have you ever heard a shampoo commercial and heard them say that the shampoo was "pH balanced" and wondered what this meant and why it is so important for hair? Thanks to the beginning work of Arrhenius in the latter part of the 19th century, we started to learn about acids and bases; our study continued and is constantly growing. Let's begin our study of this wonderful branch of chemistry.

Definition of Arrhenius Acid

Take a look at all of the following chemical equations. What do you notice about them? What is common for each of the equations below?

$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$ (Equation 1)

Hydrochloric acid

$HNO_{3(aq)} \rightarrow H^+_{(aq)} + NO_3^-{}_{(aq)}$ (Equation 2)

Nitric acid

$HClO_{4\,(aq)} \rightarrow H^+_{(aq)} + ClO_4^-{}_{(aq)}$ (Equation 3)

Perchloric acid

One of the distinguishable features about acids is the fact that acids donate H^+ ions in solution. If you notice in all of the above chemical equations, all of the compounds ionized to produce H^+ ions. This is the one main, distinguishable characteristic of acids and the basis for the Arrhenius definition of acids. Arrhenius defined an ***acid*** as a substance that produces H^+ ions in solution.

Most acids can be easily identified because their formula begins with H. Notice this is the case with the three acids in the equations above. This, of course, is not always the case. Sometimes acids are written a little differently so that the H is not written first. Let's look at the chemical equation for acetic acid (Equation 4). It can sometimes be written in a different manner (Equation 5), which is typical for weak acids.

$HC_2H_3O_{2\ (aq)} \rightarrow H^+_{(aq)} + C_2H_3O_2{}^-_{(aq)}$ (Equation 4)

$CH_3COOH_{(aq)} \rightarrow H^+_{(aq)} + CH_3COO^-_{(aq)}$ (Equation 5)

Thus, there are two ways you could identify an acid. You could check to see if the compound formula begins with an H, this would be a primary indicator. Then write the ionization equation, if the ionization equation reveals that the H^+ ion is released, the compound is definitely an acid.

Sample question 1: Which of the following compounds are acids? For those that are acids, write the ionization reaction.

(a) H_2SO_4

(b) NaOH

(c) C_6H_5COOH

Solution:

(a) H_2SO_4 looks like it is an acid because the formula begins with an H. We check by writing the ionization equation and see that the compound dissociates to give H^+ ions and therefore is definitely an acid.

$H_2SO_{4\ (aq)} \rightarrow 2\ H^+_{(aq)} + SO_4{}^{2-}_{(aq)}$

(b) NaOH has Na^+ as a cation, not H^+ (or starts with a cation other than H^+) and is therefore not an acid. By writing the dissociation equation we see that NaOH is definitely not an acid.

$NaOH_{(s)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$

(c) C_6H_5COOH does not start with hydrogen but when we write the ionization equation, we reveal that the compound ionizes to give H^+ ions in solution and is therefore an acid.

$C_6H_5COOH_{(aq)} \leftrightarrows H^+_{(aq)} + C_6H_5COO^-_{(aq)}$

Properties of Acids

Acids are a special group of compounds because it has been found that they have their own set of properties. This helps to identify them from other compounds. Thus, if you had a number of compounds that you were wondering whether these were acids or otherwise, you could identify them by their properties. But what exactly are the properties? Think about the last time you tasted lemons. Did they taste sour, sweet, or bitter? Lemons taste sour. This is another property of acids. Another property of acids is that they turn blue litmus paper red. Litmus paper is an indicator paper that is used to identify whether a substance is an acid or a base. If blue litmus paper turns red when it is dipped into a solution, then the solution is an acid. Figure 1 shows litmus paper and its reaction with an acid solution.

Figure 1: Blue Litmus Paper and Its Reaction With Acids.

(*Created by*: Therese Forsythe, *License:* CC-BY-SA)

The properties of acids such as sour taste and turning blue litmus red are parts of the operational definition of acids. ***Operational definitions*** describe how the acids behave. Operational definitions differ from conceptual definitions because with ***conceptual definitions*** , there is an attempt to explain why the acid is behaving the way it is. Let's look at the reaction between hydrochloric acid and sodium hydroxide. Hydrochloric acid ionizes and produces an H^+ ion.

$HCl_{(aq)} \rightarrow H^+{}_{(aq)} + Cl^-{}_{(aq)}$ (Equation 1)

Hydrochloric acid

Sodium hydroxide, on the other hand, dissociates to produce the sodium ion and the hydroxide ion. Look at Equation 6.

$NaOH_{(s)} \rightarrow Na^+{}_{(aq)} + OH^-{}_{(aq)}$ (Equation 6)

When hydrochloric acid and sodium hydroxide react, we get the following chemical equation (Equation 7).

$HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(L)}$ (Equation 7)

Notice how the products of Equation 7 are table salt and water. When an acid (HCl) reacts with a base (NaOH), a salt and water are produced. Therefore the acid has neutralized the base. The conceptual definition for the neutralization would state that the H^+ ions and the OH^- ions react to form neutral water molecules. This is true for all reactions between acids and bases.

Sample question: Write the reaction between HNO_3 and KOH. Explain how the acid is neutralizing the base.

Solution:

$HNO_{3\ (aq)} + KOH_{(aq)} \rightarrow KNO_{3\ (aq)} + HOH_{(L)}$

As with the case with HCl and NaOH, the H^+ ions from $HNO_{3\ (aq)}$ and the $OH^-{}_{(aq)}$ ions from the $KOH_{(aq)}$ combine to form neutral water. This means that the acid has neutralized the base. If we were to write the total ionic equation for this reaction, we would see:

Total Ionic: $H^+{}_{(aq)} + NO_3{}^-{}_{(aq)} + K^+{}_{(aq)} + OH^-{}_{(aq)} \rightarrow K^+{}_{(aq)} + NO_3{}^-{}_{(aq)} + H_2O_{(L)}$

The net ionic equation then reveals that the acid neutralizes the base. Net ionic: $H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(L)}$

Acids React with Metals

We have learned that part of the conceptual definition of acids is that they neutralize bases. Another part of this definition is that they react with metals to produce hydrogen gas. Look at the chemical reactions below. What type of reactions are these?

$Zn_{(s)} + 2\ HCl_{(aq)} \rightarrow ZnCl_{2\ (aq)} + H_{2\ (g)}$ (Equation 8)

$Mg_{(s)} + 2\ HCl_{(aq)} \rightarrow MgCl_{2\ (aq)} + H_{2\ (g)}$ (Equation 9)

$Ba_{(s)} + 2\ HCl_{(aq)} \rightarrow BaCl_{2\ (aq)} + H_{2\ (g)}$ (Equation 10)

Notice that each of these reactions is a single replacement reaction. Single replacement reactions involve the reaction between a single element and a compound. In the cases shown above, the single displacement reactions all involve a metal reacting with an acid. What do you notice that is the same in the product side of the equation for all three equations? They all produce hydrogen gas (H_2). This is another part of the conceptual definition of acids. Acids react with most metals to produce hydrogen gas.

Sample question: Write the reaction between:

(a) magnesium and sulfuric acid.

(b) calcium and acetic acid

Solution:

(a) $Mg_{(s)} + H_2SO_{4(aq)} \rightarrow MgSO_{4(aq)} + H_{2(g)}$

(b) $2\ CH_3COOH_{(aq)} + Ca_{(s)} \rightarrow Ca(OOCCH_3)_{2(aq)} + H_{2(g)}$

Acids in Our Environment

Acids are present in our everyday lives. Think about the last time you took an aspirin or a vitamin C tablet. Aspirin is acetylsalicylic acid while vitamin C is ascorbic acid; both are acids that can produce H^+ ions when ionizing in water. Acetic acid ($HC_2H_3O_2$) is a component of vinegar, hydrochloric acid (HCl) is stomach acid, phosphoric acid (H_3PO_4) is commonly found in dark soda pop, sulfuric acid (H_2SO_4) is used in car batteries and formic acid (HCO_2H) is what causes the sting in ant bites. The list goes on and on. We interact with acids on a daily basis so some knowledge of their properties and interactions is essential.

Sample question: Write the names of three common acids other than the ones listed here.

Solution:

Hydrofluoric acid, HF – used to etch glass

Nitric acid, HNO_3, – used to etch metals

Citric acid, $C_3H_5(COOH)_3$ – sour taste in citrus fruits

Lesson Summary

- Arrhenius defined an acid as a substance that donates H^+ ions when dissociating in solution. Operational definitions describe observed properties of how acids behave.
- Conceptual definitions describe why acids behave the way they do.
- Properties of acids include: affect indicators (turn blue litmus paper red), taste sour, neutralize bases, react with metals to produce hydrogen gases.

Review Questions

1. Explain the difference between a conceptual definition and an operational definition. **(Beginning)**

2. What are the properties of acids? Give a common example. **(Beginning)**

3. Which statement best describes a characteristic of acid solutions? **(Beginning)**

(a) They react with some metals to form hydrogen gas.

(b) They turn red litmus paper blue.

(c) They taste bitter.

(d) They are made from non-metal oxides.

4. Which of the following is the Arrhenius definition of an acid? **(Beginning)**

(a) An acid is a substance that donates protons.

(b) An acid is a substance that accepts protons.

(c) An acid is a substance that dissolves in water to form OH^- ions.

(d) An acid is a substance that reacts with water to form H^+ ions.

5. Which of the following will react with acids and produce hydrogen gas? **(Intermediate)**

(a) chlorine

(b) ammonia

(c) carbon

(d) magnesium

6. Write the reaction for each of the following: **(Intermediate)**

(a) hydrofluoric acid + sodium hydroxide

(b) potassium hydroxide + hydrogen sulfide

(c) dissociation of iodic acid

(d) zinc + hydrochloric acid

Further Reading / Supplemental Links

http://en.wikipedia.org/wiki

Vocabulary

Arrhenius acid	A substance that produces H^+ ions in solution.
operational definitions	Definitions that describe how something behaves. (i.e. the operational definition of acids includes tastes sour and turns blue litmus red).
conceptual definitions	Definitions that describe why something behaves the way it does. (i.e. the conceptual definition of acids includes reacting with bases to neutralize them).

Review Answers

1. A conceptual definition describes why a substance behaves the way it does whereas an operational definition describes how it behaves.

2. Acids taste sour, turn blue litmus paper red, neutralize bases, and react with acids to produce $H_2(g)$. A common example is a lemon (although answers will vary).

3. (a) They react with some metals to form hydrogen gas.

4. (d) An acid is a substance that reacts with water to form H^+ ions.

5. (d) magnesium

6.

(a) $HF_{(aq)} + NaOH_{(aq)} \longrightarrow NaF_{(aq)} + H_2O_{(L)}$

(b) $2\ KOH_{(aq)} + H_2S_{(aq)} \longrightarrow K_2S_{(aq)} + 2H_2O_{(L)}$

(c) $HI_{(aq)} \longrightarrow H^+{}_{(aq)} + I^-{}_{(aq)}$

(d) $Zn_{(s)} + 2HCl_{(aq)} \longrightarrow ZnCl_{2\ (aq)} + H_{2\ (g)}$

Strong and Weak Acids

Lesson Objectives

- Distinguish between strong and weak acids.
- Identify strong and weak acids from given choices.
- Describe how strong and weak acids differ in terms of concentrations of electrolytes.

Introduction

A great number of people associate a strong acid with its ability to react with skin, essentially “melting´ it away from bone. It was only recently on a popular crime show that this very acid chemistry know-how was used as a method for a crime. This crime show used sulfuric acid. Why sulfuric acid and not acetic acid? What makes the difference? How can we tell if an acid is strong or weak? How does this relates to the electrolyte lesson we have learned previously, considering that the acids are a combination of the H^+ cation and the anion? The answers to these questions and more will be found in the lesson that follows.

The Hydronium Ion

As has been discussed in an earlier chapter, ions in solution are hydrated. That is, water molecules are attached to the ions by the attraction between the charge on the ion and oppositely charged end of the polar water molecules. A positive ion in solution will be surrounded by water molecules with the negative ends of the polar water molecule oriented toward the positive ion. A negative ion in solution will be surrounded by water molecules with the positive ends of the water molecules oriented toward the negative ion. When we write the formula for these ions in solution, we do not show the attached water molecules. It is simply recognized by chemists that ions in solution are always hydrated.

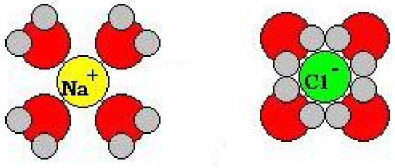


Figure 1: Hydrated ions in solution. (*Created by:* Richard Parsons, *License:* CC-BY-SA)

The hydrogen ion in solution is also hydrated in the same as all other ions. Many chemists feel that it is important in the case of hydrogen ion to show that it is attached to water. They choose not to show that the hydrogen ion is surrounded by four water molecules, but show only that it has one water molecule attached. When you add a hydrogen ion, H^+ to one water molecule, H_2O, the result is a positively charged ion consisting of three hydrogens and one oxygen, H_3O^+. This ion has been given the name ***hydronium ion***. Many authors show this hydronium ion in every case where a hydrogen ion is represented in an equation, but other authors show it only sometimes. Expressing the hydrogen ion as a hydronium ion complicates equations somewhat because if the hydrogen ion is shown as a hydronium ion, then the other side of the equation must contain a water molecule to balance the equation.

$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$ (not showing hydronium)

$HCl_{(aq)} + H_2O_{(L)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$ (showing hydronium)

You will need to recognize that sometimes the hydrogen ion is shown simply as a hydrogen ion and sometimes, it is shown as a hydronium ion and you will need to be able to deal with it in either form.

Strong Acids

In an earlier chapter, ionization was defined as certain covalently bonded molecules reacting with water and producing ions in solution. Ionization reactions involve chemical changes. It is the amount of ionization that is essential in determining if an acid is strong or weak. ***Strong acids*** are defined are ones that completely ionize or undergo 100% ionization (See Equation 1).

$HCl_{(g)} + H_2O_{(L)} \longrightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$ (Equation 1)

Notice in equation 1 that there is a single arrow separating the products from reactants. This single arrow indicates that when the reaction has stopped, there are no $HCl_{(g)}$ molecules remaining in the solution, only $H^+_{(aq)}$ ions and $Cl^-_{(aq)}$ ions. This is characteristic of a strong acid.

There are only six common strong acids. These acids are shown in Table 1. Each of the acids found in this table, like HCl, completely ionize in water.

Table 1: Strong Acids

Name	Symbol
Hydrochloric Acid	HCl
Hydrobromic Acid	HBr
Hydroiodic Acid	HI
Nitric Acid	HNO_3
Perchloric Acid	$HClO_4$
Sulfuric Acid	H_2SO_4

Weak Acids

Unlike their strong acid counterparts, ***weak acids*** do not ionize 100%. The less ionization that takes place, the weaker the acid since there will be fewer H^+ ions in solution. For example, acetic acid ionizes only about 5% meaning that when acetic acid is placed in water, only about 5% of the acetic acid molecules separate into H^+ ions and $C_2H_3O_2^-$ ions (See Equation 2).

$$HC_2H_3O_{2(aq)} \leftrightarrows H^+_{(aq)} + C_2H_3O_2^-{}_{(aq)} \qquad \text{(Equation 2)}$$

Notice, as well, that in the above equation our arrow has been replaced with a double arrow indicating that the reaction reaches equilibrium. When this reaction reaches equilibrium, the container holds mostly acetic acid molecules and a little bit of hydronium (or H^+) ions and a little bit of acetate ions.

Let's look at citric acid. Citric acid, $C_6H_8O_7$, is commonly found in everyday products like lemons and limes, and even soft drinks. It is the substance responsible for making the sour taste of these foods and drinks. Citric acid only ionizes a little more than 3% and is therefore classified as a weak acid. If we were to write an ionization reaction for citric acid, it would appear as written in Equation 3.

$$C_6H_8O_{7(aq)} + H_2O_{(L)} \leftrightarrows H_3O^+_{(aq)} + C_6H_7O_7^-{}_{(aq)} \qquad \text{(Equation 3)}$$

Notice how, as with Equation 2, the double arrow indicates the reaction has reaches equilibrium. As with all weak acids, when this reaction reaches equilibrium, there is mostly $C_6H_8O_{7(aq)}$ and some hydronium ion and some citrate ion, $C_6H_7O_7^-{}_{(aq)}$ in the solution.

Remember that all acids that are not one of the six listed in Table 1 are weak. These weak acids do not completely ionize in water. Even though these weak acids are very soluble, they dissolve as molecules and only a few of the molecules break into ions in the solution.

Sample question: Write ionization equations for only those acids that are weak.

(a) Sulfuric acid (H_2SO_4)

(b) Hydrofluoric acid (HF)

(c) Trichloroacetic acid (CCl_3COOH)

Solution:

(a) H_2SO_4 is a strong acid (one of the six).

(b) HF is a weak acid (not one of the six): $HF(aq) \leftrightarrows H^+(aq) + F^-(aq)$

(c) CCl_3COOH is a weak acid (not one of the six): $CCl_3COOH_{(aq)} \leftrightarrows H^+{}_{(aq)} + CCl_3COO^-{}_{(aq)}$

Strong and Weak Electrolytes

Non-electrolytes have been described as solutions that do not conduct electricity and electrolytes are those that do conduct electricity. However, electrolytes do have varying degrees of strength. If a solution has a large number of ions present in it, it is called a ***strong electrolyte*** whereas an electrolyte solution that has only a few ions present is called a ***weak electrolyte*** . A strong acid completely ionizes in water solution, there are lots of ions in solution and the ions make the solution a strong electrolyte. A weak acid produces only a few ions in solution and therefore is classified as a weak electrolyte. Such a solution will only conduct a small electric current.

Lesson Summary

- Strong acids undergo 100% ionization in water (i.e. hydrochloric acid, HCl). Weak acids undergo less than 100% ionization (i.e. acetic acid, $HC_2H_3O_2$).
- All acids that are not one of the six are weak and also if they are not one of the six, do not completely ionize in water. *Weak electrolytes are solutions that conduct electricity to a lesser extent than strong electrolyte solutions.

Review Questions

1. What is the difference between a strong and weak acid? Show an example of each. **(Intermediate)**

2. In terms of electrolyte solutions, how would you distinguish between a strong acid and a weak acid? **(Intermediate)**

3. All of the following are weak acids except? **(Beginning)**

(a) $HClO_3$

(b) $HC_2H_3O_2$

(c) HF

(d) HCl

4. Which compound is a strong acid? **(Beginning)**

(a) $HClO_2(aq)$

(b) $H_2CO_3(aq)$

(c) formic acid

(d) perchloric acid

5. Which one of the following compounds is not a strong electrolyte? **(Beginning)**

(a) $CH_3COOH(aq)$

(b) $HClO_4(aq)$

(c) HI(aq)

(d) NaOH(aq)

6. Which of the following is usually referred to as strong acid in water solution? Write the ionization reactions. **(Intermediate)**

(a) HF

(b) HNO_2

(c) H_2CO_3

(d) HSO_4^-

(e) HNO_3

(f) $HClO_4$

Further Reading / Supplemental Links

http://en.wikipedia.org/wiki

Vocabulary

strong acids	Acids that completely ionize or undergo 100% ionization in solution (i.e. HCl).
weak acids	Acids that do not completely ionize or undergo 100% ionization in solution (i.e. $HC_2H_3O_2$).

Review Answers

1. A strong acid completely ionizes in solution. An example is hydrochloric acid.

$$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$$

A weak acid only partially ionizes in solution. An example is acetic acid.

$$HC_2H_3O_2(aq) \leftrightarrows H^+(aq) + C_2H_3O_2^-(aq)$$

3. Electrolyte solutions will conduct electricity and when connected to an LED light will cause the LED light to glow. If the acid solution is a strong acid, the LED light will glow brightly. If the acid solution is a weak acid, the LED light will not glow brightly. The weaker the acid is, the more dim the light.

4. (d) HCl

5. (d) perchloric acid

6. (a) $CH_3COOH(aq)$

7.

(a) HF = weak; $HF(aq) \leftrightarrows H^+(aq) + F^-(aq)$

(b) HNO_2 = weak; $HNO_2(aq) \leftrightarrows H^+(aq) + NO_2^-(aq)$

(c) H_2CO_3 = weak; $H_2CO_2(aq) \leftrightarrows H^+(aq) + HCO_3^-(aq)$

(d) HSO_4^- = weak; $HSO_4^-(aq) \leftrightarrows H^+(aq) + SO_4^{2-}(aq)$

(e) HNO_3 = strong; $HNO_3(aq) \rightarrow H^+(aq) + NO_3^-(aq)$

(f) $HClO_4$ = strong; $HClO_4(aq) \rightarrow H^+(aq) + ClO_4^-(aq)$

Arrhenius Bases

Lesson Objectives

- Define an Arrhenius base and know some examples of bases.
- State the properties of bases.
- Describe the neutralization reaction that bases undergo.

Introduction

Arrhenius broke ground in our understanding of acids and bases. He was the first to provide us with a definition from which we could identify an acid from a base. We have learned earlier the definition of an acid and now we will extend this definition to include bases. Keep in mind that Arrhenius came up with these theories in the late 1800s so his definitions came with some limitations. These limitations will be expanded upon later on in the unit. For now we will focus on his definitions.

Bases Release OH^- in Solution

Arrhenius defined an acid as a substance that releases H^+ ions in solution. In contrast, he defined a base as a substance that releases OH^- ions in solution. Bases are ionic substances made up of a cation and an anion, of which the anion is the OH^- ion. It should be noted that very few of the hydroxides are actually soluble. If you recall from a previous chapter, only the alkali metals and Ba^{2+} ions are soluble. Therefore, few of the basic solids will result in solutions when dissolved in water. One of the metal hydroxides that is very soluble is NaOH. The dissolving equation for NaOH is shown in Equation 1.

$NaOH_{(s)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$ (Equation 1)

Barium hydroxide produces a similar reaction when dissociating in water (Equation 2).

$Ba(OH)_{2\,(s)} \rightarrow Ba^{2+}_{(aq)} + 2\,OH^-_{(aq)}$ Equation 2)

The production of OH^- ions is part of the conceptual definition of bases according to the Arrhenius definition of bases.

Sample question: Write the chemical equation for the reaction of the following bases in water.

(a) Lithium hydroxide (LiOH)

(b) Sodium hydroxide (NaOH)

(c) Potassium hydroxide (KOH)

Solutions:

(a) $LiOH_{(s)} \longrightarrow Li^{+}_{(aq)} + OH^{-}_{(aq)}$

(b) $NaOH_{(s)} \longrightarrow Na^{+}_{(aq)} + OH^{-}_{(aq)}$

(c) $KOH_{(s)} \longrightarrow K^{+}_{(aq)} + OH^{-}_{(aq)}$

Properties of Bases

There is one common base that some may have had the opportunity to taste: milk of magnesia is a slightly soluble solution of magnesium hydroxide. This substance is used for acid indigestion. Flavorings have been added to improve the taste, otherwise it would have a bitter taste when you drink it. Other common bases include substances like Windex, Drano, oven cleaner, soaps and many cleaning other products. **Please note**: do not taste any of these substances. A bitter taste is one property you will have to take for granted.

If you notice, one of the common bases is soap. This is an interesting example because another property of bases is that they are slippery to the touch. When you are washing dishes, you have probably noticed that the soapy water gets quite slippery. In fact, there may have been times when you dropped a dish or a glass or a cup because it was too slippery to hold on to. Now you know it isn't your fault – it's the soap's fault!

As with acids, bases have properties that allow us to identify them from other substances. We have learned that acids turn blue litmus paper red. It stands to reason then that bases would turn red litmus paper blue; see figure 3. Notice that the effect of the indicator is the opposite of that of acids.

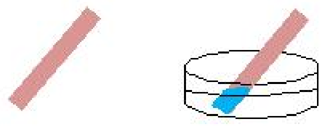


Figure 3: Red Litmus Paper and its Reaction With Bases.

(*Created by:* Therese Forsythe, *License:* CC-BY-SA)

As mentioned previously, bases have the ability to neutralize acids. Take for example the reaction between magnesium hydroxide (milk of magnesia) and HCl (stomach acid) shown in Equation 3.

$Mg(OH)_{2(s)} + 2\ HCl_{(aq)} \longrightarrow MgCl_{2(aq)} + 2H_2O_{(L)}$ (Equation 3)

You see in Equation 3 that here again we have an acid and a base producing a salt and water. This is a similar reaction to the reaction between sodium hydroxide and hydrochloric acid. We will learn more about these reactions in the next section as well.

Sample question: Write the balanced neutralization reaction between the following acids and bases.

(a) $HClO_4 + LiOH$

(b) $HNO_3 + Ba(OH)_2$

(c) H_2SO_4 + KOH

Solution:

(a) $HClO_{4(aq)} + LiOH_{(aq)} \rightarrow LiClO_{4(aq)} + H_2O_{(L)}$

(b) $2\ HNO_{3\ (aq)} + Ba(OH)_{2\ (aq)} \rightarrow Ba(NO_3)_{2\ (aq)} + 2\ H_2O_{(L)}$

(c) $H_2SO_{4\ (aq)} + 2\ KOH_{(aq)} \rightarrow K_2SO_{4\ (aq)} + 2\ H_2O_{(L)}$

Common Bases

We mentioned above that bases are common to our everyday lives. If you do any of the cleaning in your home, you would use bases quite frequently. Drano©, used to unclog drains, is a solution of sodium hydroxide; sodium hydroxide, NaOH, is also used to make some soap; soft soap is often prepared with potassium hydroxide, KOH. We have already mentioned that magnesium hydroxide, $Mg(OH)_2$, is used to make milk of magnesia. Windex is a water solution containing ammonium hydroxide, NH_4OH.

Soaps, as we know, have the ability to dissolve in water but also dissolve oil substances as well. The reason soap is able to do this is because of its structure. Soaps have long chains of carbon atoms, which make that part of the molecule nonpolar. This allows it to dissolve other nonpolar substances such as oils. And then on one end of the molecule is a sodium ion which makes that part of the molecule ionic. This ionic end of the molecule will be attracted to polar water molecules. This nonpolar-ionic molecule can attach any nonpolar particles to water molecules, and wash them away.

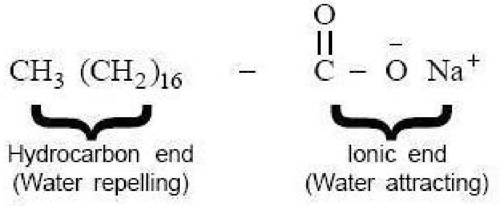


Figure 2: The Structure of Soap.

Lesson Summary

- An Arrhenius base is a substance that releases OH^- ions in solution. Bases turn red litmus paper blue, have a bitter taste, are slippery to the touch, and can neutralize acids.
- A neutralization reaction between an acid and a base will produce a salt and water. Example: $Mg(OH)_{2(aq)} + 2\ HCl_{(aq)} \rightarrow MgCl_{2(aq)} + 2\ H_2O_{(L)}$.
- Common bases include soap (NaOH) and Drano (NaOH), soft soap (KOH), milk of magnesia ($Mg(OH)_2$) and Windex (NH_4OH).

Review Questions

1. What is the role of litmus paper for acids and base chemistry? **(Beginning)**

2. What are the properties of bases? Give a common example. **(Beginning)**

3. Which statement best describes a characteristic of a base solutions? **(Beginning)**

(a) They taste bitter.

(b) They turn red litmus paper red.

(c) They react with some metals to form hydrogen gas.

(d) They are weak electrolytes.

4. Which of the following is the Arrhenius definition of a base? **(Beginning)**

(a) A base is a substance that donates protons.

(b) A base is a substance that accepts protons.

(c) A base is a substance that dissolves in water to form OH^- ions.

(d) A base is a substance that reacts with water to form H^+ ions.

5. Which of the following bases would be a weak electrolyte? **(Intermediate)**

(a) NaOH

(b) $Ba(OH)_2$

(c) $Ca(OH)_2$

(d) $Al(OH)_3$

6. Write the balanced neutralization reaction between the following acids and bases. **(Intermediate)**

(a) potassium hydroxide + hypochlorous acid

(b) hydrobromic acid + calcium hydroxide

(c) hydrochloric acid + sodium hydroxide

(d) potassium hydroxide + sulfuric acid

7. Write the net ionic equation for each of the neutralizations reactions in #4. **(Intermediate)**

Further Reading / Supplemental Links

http://en.wikipedia.org/wiki

Vocabulary

Arrhenius base	A substance that produces OH^- ions in a solution.

Review Answers

1. Litmus paper is an indicator meaning that it is used to indicate, in this case, whether the solution is an acid or a base. There are many indicators and most change color at a specific pH. Litmus is known as a general indicator. It simply changes from red to blue if it is an acid and blue to red if it is a base.

2. Bases taste bitter, turn red litmus paper blue, neutralize acids, and are slippery. A common example is soap (although answers will vary).

3. (a) They taste bitter.

4. (c) A base is a substance that dissolves in water to form OH^- ions.

5. (d) $Al(OH)_3$

6.

(a) $KOH_{(aq)} + HClO_{(aq)} \rightarrow KClO_{(aq)} + H_2O_{(L)}$

(b) $2HBr_{(aq)} + Ca(OH)_{2\ (aq)} \rightarrow Ca(Br)_{2\ (aq)} + 2H_2O_{(L)}$

(c) $HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(L)}$

(d) $H_2SO_{4\ (aq)} + 2\ KOH_{(aq)} \rightarrow K_2SO_{4\ (aq)} + H_2O_{(L)}$

7. (a) - (d) $H^+{}_{(aq)} + OH^{1-}{}_{(aq)} \rightarrow H_2O_{(L)}$

Salts

Lesson Objectives

- Describe the formation of salts in neutralization reactions in terms of Arrhenius theory.
- Identify acidic, basic, and neutral salts from neutralization reaction.

Introduction

Neutralization is a reaction between an acid and a base which produces water and a salt. The general reaction for the neutralization reaction is shown below.

$$\text{acid} + \text{base} \rightarrow \text{salt} + \text{water}$$

In this lesson, after reviewing the concept of ionic compounds, we will examine neutralization reactions and then look at the different type of salts that can be formed from acids and bases as they react in neutralization reactions.

Ionic Compounds

Ionic compounds are those formed between metal cations and nonmetal anions. When you take a look at the periodic table, the compounds with the most ionic character are those that are at opposite sides of the table. For example, sodium chloride will have more ionic character than zinc chloride. Look at the table below to see the positions of sodium, Na, zinc, Zn, and chlorine, Cl.

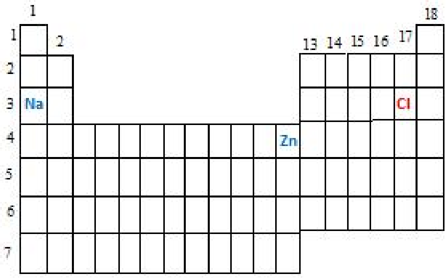


Figure 1: The positions of sodium, zinc, and chlorine in the periodic table.

(*Created by:* Theresa Forsythe, *License:* CC-BY-SA)

When ionic compounds form between metal cations and nonmetal anions they transfer electrons and form charged particles and are capable of forming electrolyte solutions. If you notice, this is all similar to the descriptions of acids and bases. Acids are a combination of a hydrogen cation and a nonmetal anion. Examples include HCl, HNO_3, and $HC_2H_3O_2$. Bases can be a combination of metal cations and nonmetal anions. Examples include NaOH, KOH, and $Mg(OH)_2$.

Salts

Salts that are ionic compounds result when an acid and a base react in a neutralization reaction.

$$\text{Acid} + \text{Base} \longrightarrow \text{Salt} + \text{Water}$$

It is this salt that is formed that is the ionic compound. Let us examine some examples of the reactions we have looked at to see some of the salts and their ionic character. Take a look at Equations 1, 2, and 3. Each of these equations has an acid and a base producing a salt and water.

$$HCl_{(aq)} + LiOH_{(aq)} \longrightarrow LiCl_{(aq)} + H_2O_{(L)} \qquad \text{(Equation 1)}$$

$$2\ HBr_{(aq)} + Ba(OH)_{2\ (aq)} \longrightarrow BaBr_{2\ (aq)} + 2\ H_2O_{(L)} \qquad \text{(Equation 2)}$$

$$2\ HF_{(aq)} + Mg(OH)_{2\ (aq)} \longrightarrow MgF_{2\ (aq)} + 2\ H_2O_{(L)} \qquad \text{(Equation 3)}$$

Notice that in Equation 1, lithium chloride (LiCl) shows Li^+ ions and the Cl^- ions are the furthest away from each other on the periodic table so, generalizing, they will produce the salt with the most ionic character. Magnesium fluoride in Equation 3 has Mg^{2+} ions and F- ion, which are closer to each other on the Periodic Table and therefore will have a little bit less ionic character.

All acid-base reactions produce salts. According to the conceptual definition of the Arrhenius acid and base, the acid will contribute the H^+ ion that will react to neutralize the OH^- ion, contributed by the base, to produce neutral water molecules. The anion from the acid will combine with the cation from the base to form the ionic salt. Look at Equations 4 and 5 below to see the conceptual definition in action.

$$HClO_{4\ (aq)} + NaOH_{(aq)} \longrightarrow NaClO_{4\ (aq)} + HOH_{(L)} \qquad \text{(Equation 4)}$$

$$H_2SO_{4\ (aq)} + 2\ KOH_{(aq)} \longrightarrow K_2SO_{4\ (aq)} + 2\ HOH_{(L)} \qquad \text{(Equation 5)}$$

(Note: HOH = H_2O)

No matter what the acid or the base may be, the products of this type of reaction will always be a salt and water. Aside from the fact that Arrhenius said that the H^+ ion will neutralize the OH^- ion to form water, we also know that these reactions are double displacement reactions and will therefore have their cations exchanging anions.

To write this with a **total ionic equation**:

$$H^+_{(aq)} + ClO_4{}^-_{(aq)} + Na^+_{(aq)} + OH^-_{(aq)} \rightarrow Na^+_{(aq)} + ClO_4{}^-_{(aq)} + H_2O_{(L)}$$

Or, since Na^+ and $ClO_4{}^-$ are spectator ions, the **net ionic equation** is:

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(L)}$$

This is the net ionic equation for **all** neutralization reactions.

The Hydrolysis of Salts

The Hydrolysis Reaction

When a salt is dissolved in water, it is possible for the solution to be neutral, acidic, or basic. If a solution is to be acidic, it must contain more hydrogen ions than hydroxide ions and for the solution to be basic, it must contain more hydroxide ions than hydrogen ions. The reason that a dissolving salt may produce non-neutral solutions is that the cation or anion from the salt may not dissociate 100% when in the presence of hydrogen or hydroxide ions. Water, itself, dissociates very slightly into hydrogen and hydroxide ions. Therefore, when a salt is dissolved in water, there are some hydrogen and hydroxide ions available in the solution. Consider, first, the solution produced when the salt KBr dissolves in water. There will be four ions present in the solution.

$$K^+ + Br^- + H^+ + OH^- \leftrightarrows \ ?$$

When potassium ions in the solution come into contact with hydroxide ions, if the ions were to join together, the molecule formed would be KOH, which is a strong base, and would, therefore, immediately dissociate back into ions. Similarly, if the bromide ions come into contact with hydrogen ions, the molecule formed would be HBr, which is a strong acid, and would immediately dissociate back into ions. Having sodium and chloride ions in a water solution would not cause a reaction.

Consider, now, the solution produced when the salt NH_4Cl is dissolved in water. There will be four ions present in the solution.

$$NH_4{}^+ + Cl^- + H^+ + OH^- \leftrightarrows \ ?$$

When hydrogen ions come into contact with chloride ions, if they join together, the resultant molecule would be HCl, which is a strong acid, and therefore the HCl would immediately dissociate back into the ions. When $NH_4{}^+$ ions come into contact with OH^- ions, however, the resultant molecule would be NH_4OH, which is a weak base and therefore, does not dissociate very much. Therefore, when ammonium chloride is dissolved in water, a reaction occurs.

$$NH_4{}^+ + Cl^- + H^+ + OH^- \leftrightarrows NH_4OH_{(aq)} + Cl^- + H^+$$

The ammonium hydroxide dissociates very little, so we would have mostly un-dissociated ammonium hydroxide molecules in solution with hydrogen and chloride ions. The hydrogen ions in this final solution would cause the solution to be acidic. Thus, dissolving ammonium chloride in water produces an *acidic* solution.

By a similar process, dissolving sodium acetate, $NaC_2H_3O_2$, in water will produce a basic solution. When the sodium acetate is dissolved in water, four ions will be present in the solution.

$$Na^+ + C_2H_3O_2{}^- + H^+ + OH^- \rightleftarrows \ ?$$

If sodium ions contact hydroxide ions, the substance formed would be a strong base which would immediately dissociate. If hydrogen ions contact acetate ions, however, the molecule formed would be acetic acid, which is a weak acid and the ions would NOT dissociate. Therefore, when sodium acetate is dissolved in water, a reaction will occur as shown below.

$$Na^+ + C_2H_3O_2{}^- + H^+ + OH^- \rightleftarrows HC_2H_3O_{2(aq)} + Na^+ + OH^-$$

The resultant solution has excess hydroxide ions and therefore, is basic. The dissolving of sodium acetate salt in water produces a basic solution.

The reactions between some of the ions in the salts and water are called **hydrolysis** reactions.

Neutral, Acidic, and Basic Salts

We have talked a little already about the fact that there are not just strong acids but there are also weak acids as well. The difference between them is the percent ionization. The same is true for bases. Strong bases dissociate 100% and weak bases do not. The table below shows all of the strong acids and bases, all of the rest of the acids and bases are weak.

Table 1: Strong Acids and Bases

Strong Acid	**Formula**	**Strong Base**	**Formula**
Hydrochloric Acid	HCl	Lithium hydroxide	LiOH
Hydrobromic Acid	HBr	Sodium hydroxide	NaOH
Hydroiodic Acid	HI	Potassium hydroxide	KOH
Nitric Acid	HNO_3	Rubidium hydroxide	RbOH
Perchloric Acid	$HClO_4$	Cesium hydroxide	CsOH
Sulfuric Acid	H_2SO_4	Calcium hydroxide	$Ca(OH)_2$
		Strontium hydroxide	$Sr(OH)_2$
		Barium hydroxide	$Ba(OH)_2$

So why is this important to us here? The information in the table helps us to determine what type of salt is formed in an acid-base reaction. For example if we have a reaction between a strong acid and a strong base we form a neutral salt. It is like a power struggle between the acid and the base. Since both are strong, there is no compound with more power and thus the salt ends up being neutral. If, however, we have a reaction between a weak acid and a strong base (Equation 6), the result would be a ***basic salt***.

$HC_2H_3O_{2(aq)}$	$+NaOH_{(aq)}$	$\rightarrow$	$NaC_2H_3O_{2(aq)}$	$+H_2O_{(L)}$	(Equation 6)
Acetic acid	sodium hydroxide		sodium acetate	water	
(weak acid)	(strong base)		(basic salt)		

When the basic salt is dissolved in water, a reaction called **hydrolysis** takes places in which extra hydroxide ions, OH^{1-}, are produced from the salt and the water molecules. Since the hydroxide ions come from a salt, it is called a basic salt.

A similar situation will occur when we have a strong acid reacting with a weak base. When a strong acid reacts with a weak base, an ***acidic salt*** is formed.

$HCl_{(aq)}$	$+NH_4OH_{(aq)}$	$\rightarrow$ $NH_4Cl_{(aq)}$	$+H_2O_{(L)}$	(Equation 7)
Hydrochloric acid	ammoniun hydroxide	ammonium chloride	water	
(strong acid)	(weak base)	(acidic salt)		

Again, a **hydrolysis** reaction takes place. The salt will react with water molecules and produce excess hydrogen ions, H^+, in solution and is therefore referred to as **an acidic salt**.

Sample question: Complete the following neutralization reactions and identify the type of salt produced.

(a) $H_2SO_{4\ (aq)} + Ba(OH)_{2\ (aq)} \rightarrow$?

(b) $HCOOH_{(aq)} + Ca(OH)_2(aq) \rightarrow$?

Solution:

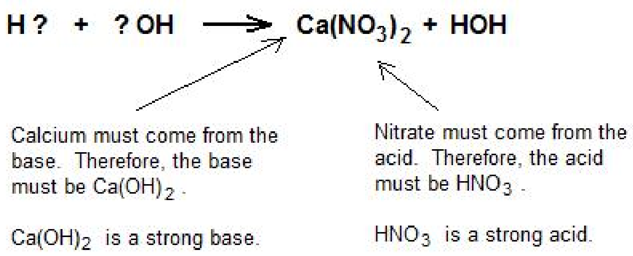
(a) $H_2SO_{4\ (aq)} + Ba(OH)_{2\ (aq)} \rightarrow BaSO_{4\ (aq)} + 2\ H_2O_{(L)}$

Strong acid + strong base = ***neutral salt***

(b) $2\ HCOOH_{(aq)} + Ca(OH)_{2\ (aq)} \rightarrow Ca(HCOO)_{2\ (aq)} + 2\ H_2O_{(L)}$

Weak acid + strong base = basic salt

It can also be determined which acid and base was used to form the salt and from this you could determine if your starting reaction was a strong acid or a weak acid, a strong base or a weak base. Watch how this works. You were given that the product salt was calcium nitrate, $Ca(NO_3)_2$. Remember that there is a double displacement reaction that forms the salt so we can write parts of the reaction:



Calcium must come from the base. Therefore, the base must be $Ca(OH)_2$.

$Ca(OH)_2$ is a strong base.

Nitrate must come from the acid. Therefore, the acid must be HNO_3 .

HNO_3 is a strong acid.

Therefore, the neutralization reaction would have been:

$2\ HNO_3 + Ca(OH)_2 \rightarrow Ca(NO_3)_2 + 2\ HOH$ (Equation 8)

So this salt would have been produced from a strong acid-strong base reaction!

Let's try another. Consider the salt copper (II) chloride ($CuCl_2$).

The copper would have come from the base, $Cu(OH)_2$, which is a weak base. The chloride would have come from the acid, HCl, which is a strong acid.

$2\ HCl + Cu(OH)_2 \rightarrow CuCl_2 + 2\ HOH$ (Equation 9)

Therefore the reaction is a strong acid weak base reaction!

Lesson Summary

- Ionic compounds are those formed between metal cations and nonmetal anions. Acids are a combination of hydrogen and a nonmetal anion. Bases can be a combination of metal cations and nonmetal anions. Ionic compounds result when an acid and a base react in a neutralization reaction (Acid + Base → Salt + Water).
- According to the conceptual definition of the Arrhenius acid and base, the acid will produce the H^+ ion, which will react to neutralize the OH^- ion produced by the base to produce the neutral water. The other product will be the ionic salt. A strong acid + a strong base in an acid/base neutralization reaction will form a neutral salt.
- A strong acid + a weak base in an acid/base neutralization reaction will form an acidic salt. A weak acid + a strong base in an acid/base neutralization reaction will form a basic salt.

Review Questions

1. How do an acid and a base fit the definition of an ionic compound? Use examples in your answer. **(Intermediate)**

2. Explain neutralization reactions in terms of Arrhenius theory. Use an example in your answer. **(Intermediate)**

3. Which salt will form a basic solution when dissolved in water? **(Challenging)**

(a) KNO_3

(b) $CaCl_2$

(c) $NaClO_4$

(d) $NaNO_2$

4. Which salt will form an acidic solution when dissolved in water? **(Challenging)**

(a) copper(II) sulfate

(b) sodium acetate

(c) potassium chloride

(d) sodium cyanide

5. Milk of magnesia is a common over- the - counter antacid that has, as its main ingredient, magnesium hydroxide. It is used by the public to relieve acid indigestion. Acid indigestion is caused by excess stomach acid being present. Since a stomach upset is caused by excess hydrochloric acid, this tends to be a quite painful affliction for people. Write the balanced chemical equation for the reaction between milk of magnesia and hydrochloric acid. What type of reaction is this? What type of salt is formed? **(Intermediate)**

6. Complete the following neutralization reactions and identify the type of salt produced. **(Intermediate)**

(a) $H_2SO_4(aq)$ and $NaOH(aq) \rightarrow$

(b) $HNO_3(aq)$ and $NH_4OH(aq) \rightarrow$

(c) $HF(aq)$ and $NH_4OH(aq) \rightarrow$

(d) $CH_3COOH(aq)$ and $KOH(aq) \rightarrow$

(e) $HCl(aq)$ and $KOH(aq) \rightarrow$

Further Reading / Supplemental Links

http://en.wikipedia.org/wiki/Salts

Vocabulary

basic salt	A salt formed in a neutralization reaction between a weak acid and a strong base.
acidic salt	A salt formed in a neutralization reaction between a strong acid and a weak base.
neutral salt	A salt formed in a neutralization reaction between a strong acid and a strong base or a weak acid and a weak base.

Review Answers

1. Answers will vary but answers should include the fact that an ionic compound includes a positive cation and a negative anion. Acids include the positive H^+ cation and then the negative anion (example HCl) and bases include a metal cation and a nonmetal anion (example NaOH). A neutralization reaction is one where an acid + a base yield a salt and water. According to the conceptual definition of the Arrhenius acid and base, the acid will produce the H^+ ion which will react to neutralize the OH^- ion produced by the base to in turn produce the neutral water. The anion from the acid will combine with the cation from the base to produce the salt.

Ex: Acid + Base → Salt + Water

2. $HClO_4(aq) + NaOH(aq) \rightarrow NaClO_4(aq) + H_2O(l)$

3. (d) $NaNO_2$

4. (a) copper(II) sulfate

5. $Mg(OH)_2(aq) + 2HCl(aq) \rightarrow MgCl_2(aq) + 2H_2O(l)$

6.

(a) $H_2SO_4(aq)$ and $NaOH(aq) \rightarrow Na_2SO_4(aq) + H_2O(l)$

Strong acid + strong base = neutral salt

(b) $HNO_3(aq)$ and $NH_4OH(aq) \rightarrow NH_4NO_3(aq) + H_2O(l)$

Strong acid + weak base = acidic salt

(c) $HF(aq)$ and $NH_4OH(aq) \rightarrow NH_4F(aq) + H_2O(l)$

Weak acid + weak base = neutral salt

(d) $CH_3COOH(aq)$ and $KOH(aq) \longrightarrow KCH_3COO(aq) + H_2O(l)$

Weak acid + strong base = basic salt

(e) $HCl(aq)$ and $KOH(aq) \longrightarrow KCl(aq) + H_2O(l)$

Strong acid + strong base = neutral salt

pH

Lesson Objectives

- Calculate $[H^+]$ for strong acids and $[OH^-]$ for strong bases.
- Define autoionization and use it to find $[H^+]$ from $[OH^-]$ or to find $[OH^-]$ from $[H^+]$.
- Describe the pH scale.
- Define pH.
- Calculate pH from $[H^+]$ or vice versa.

Introduction

A few very concentrated acid and base solutions are used in industrial chemistry and occasionally in inorganic laboratory situations. For the most part, however, acid and base solutions that occur in nature, those used in cleaning, and those used in organic or biochemistry applications are relatively dilute. Most of the acids and bases dealt with in laboratory situations have hydrogen ion concentrations between 1.0 M and 1.0×10^{-14} M.

Expressing hydrogen ion concentrations in exponential numbers becomes tedious and is difficult for those not trained in chemistry. A Danish chemist named Soren Sorenson developed a shorter method for expressing acid strength or hydrogen ion concentration with a non-exponential number. He named his method **pH** and while the exact definition of pH has changed over the years, the name has remained.

pH, today, is defined as the negative logarithm of the hydrogen ion concentration.

$$pH = -\log [H^+]$$

If the hydrogen ion concentration is between 1.0 M and 1.0×10^{-14} M, the value of the pH will be between 0 and 14.

Concentrations of Ions

We have said that a strong acid completely ionizes in solution and therefore in solution there are no intact acid molecules remaining but only the H^+ cations and the anions from the acid. Look at Equation 1 as an example.

$$HCl_{(aq)} \longrightarrow H^+_{(aq)} + Cl^-_{(aq)} \qquad \text{(Equation 1)}$$

100% ionized

We can extend this concept to give actual concentrations of the hydronium ion for strong acid solutions. If we had a 0.10 mol/L solution of hydrochloric acid and it completely ionizes, then the concentration of H^+ ions that are produced are also 0.10 mol/L. Look at the balancing coefficients for Equation 1. The balancing coefficients are all ones (1). Therefore the concentrations will all be the following:

$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$ (Equation 2)

0.10 mol/L 0.10 mol/L 0.10 mol/L

For strong bases, the same calculation can be performed. Since strong bases are 100% dissociated, when we are given the concentration of the strong base we can then conclude the concentration of the hydroxide ion. Let's look at the following example. What would be the $[OH^-]$ for a solution of $Ba(OH)_2$, knowing the concentration of $Ba(OH)_2$ is 0.24 mol/L?

$Ba(OH)_{2(aq)} \rightarrow Ba^{2+}_{(aq)} + 2\ OH^-_{(aq)}$ (Equation 3)

100% dissociated

Notice both the 100% dissociation and the balancing coefficients. Now let's fill in the coefficients. Take a look at Equation 4 to see how the balancing coefficients have helped determine the $[OH^-]$ in the same manner as they did for finding the $[H^+]$.

$Ba(OH)_{2(aq)} \rightarrow Ba^{2+}_{(aq)} + 2\ OH^-_{(aq)}$ ((Equation 4)

0.24 mol/L 0.24 mol/L 0.48 mol/L

Sample question: What would the $[H^+]$ be for the ionization of a 0.35 mol/L solution of nitric acid?

Solution:

$HNO_{3(aq)} \rightarrow H^+_{(aq)} + NO_3^-{}_{(aq)}$

0.35 mol/L 0.35 mol/L 0.35 mol/L

Relationship Between $[H^+]$ and $[OH^-]$

Concentrated hydrochloric acid is found in most high school chemistry labs. This acid is 12.0 mol/L or 12 mol of HCl dissolved in enough water to make 1 L. It is the presence of the water molecules that allows that hydrogen chloride to ionize and produce the hydrogen ions that end up in solution. Water also undergoes ionization. Actually, water undergoes autoionization. **Autoionization** is when the same reactant acts as both the acid and the base. Look at the reaction below.

$H_2O_{(L)} + H_2O_{(L)} \leftrightarrows H_3O^+_{(aq)} + OH^-_{(aq)}$

From experimentation, chemists have determined that in pure water $[H^+] = 1 \times 10^{-7}$ mol/L and $[OH^{-1}] = 1 \times 10^{-7}$ mol/L. In other words, $H_2O_{(L)}$ is autoionizing and so the $[H^+] = [OH^-] = 1 \times 10^{-7}$ mol/L.

The ionization of water is frequently written as $H_2O_{(L)} \leftrightarrows H^+ + OH^-$

The equilibrium constant expression for this dissociation would be:

$K_w = [H^+][OH^-]$

Like other equilibrium constants that are for special reactions, this K is given its own subscript. Since this equilibrium constant is for the dissociation of water, it is designated as K_w. The ***ion product constant for water***, K_w is the product of the hydronium ion and the hydroxide ion concentrations in the autoionization of water.

We can the calculate K_w because we know the value of $[H^+]$ and $[OH^-]$ for pure water at 25°C.

$K_w = [H^+]\ [OH^-]$

$K_w = (1 \times 10^{-7})\ (1 \times 10^{-7})$

$K_w = 1 \times 10^{-14}$

A further definition of acids and bases can now be made:

when

$[H_3O^+] = [OH^{-1}]$ (as in water), the solution is **neutral**

$[H_3O^+] > [OH^{-1}]$ the solution is an **acid**

$[H_3O^+] < [OH^{-1}]$ the solution is a **base**

To continue with these ideas:

an **acid** has a $[H_3O^+]$ that is greater than 1×10^{-7} and the $[OH^{-1}]$ is less than 1×10^{-7}

a **base** has a $[OH^{1-}]$ that is greater than 1×10^{-7} and the $[H_3O^+]$ is less than 1×10^{-7}

The equilibrium between the water molecules and the H^+ and OH^- ions will exist in all water solutions regardless of anything else that may be present in the solution. Some of the other substances that are placed in water solution may become involved with either the hydrogen or hydroxide ions and alter the equilibrium state. In all cases, as long as the temperature is 25°C, the equilibrium, $H_2O_{(L)} \leftrightarrows H^+ + OH^-$, will shift and maintain the equilibrium constant, K_w, at exactly 1×10^{-14}.

For example, a sample of pure water at 25°C, has a $[H^+]$ equal to 1×10^{-7} M and a $[OH^-] = 1 \times 10^{-7}$ M. The K_w for this solution, of course, will be 1×10^{-14}. Suppose some HCl gas is added to this solution so that the H^+ concentration increases. This is a stress to the equilibrium condition. Since the concentration of a product is increased, the reverse reaction rate will increase and the equilibrium will shift toward the reactants. The concentrations of both ions will be reduced until equilibrium is re-established. If the final $[H^+] = 1 \times 10^{-4}$ M, we can calculate the $[OH^-]$ because we know that the product of $[H^+]$ and $[OH^-]$ at equilibrium is always 1×10^{-14}.

$K_w = [H^+][OH^-] = 1 \times 10^{-14}$

$$[OH^-] = \frac{1 \times 10^{-14}}{[H^+]} = \frac{1 \times 10^{-14}}{1 \times 10^{-4}} = 1 \times 10^{-10}\ M$$

Suppose, on the other hand, something is added to the solution that reduces the hydrogen ion concentration. As soon as the hydrogen ion concentration begins to decrease, the reverse rate decreases and the forward rate will shift the equilibrium toward the products. The concentrations of both ions will be increased until equilibrium is re-established. If the final hydrogen ion concentration is 1 x 10^{-12} M, we can calculate the final hydroxide ion concentration.

$$K_w = [H^+][OH^-] = 1 \times 10^{-14}$$

$$[OH^-] = \frac{1 \times 10^{-14}}{[H^+]} = \frac{1 \times 10^{-14}}{1 \times 10^{-12}} = 1 \times 10^{-2}\ M$$

Using the K_2 expression and our knowledge of the K_2 value, anytime we know either the $[H^+]$ or the $[OH^-]$ in a water solution, we can always calculate the other one.

Sample question: What would be the $[H^+]$ for a grapefruit found to have a $[OH^-]$ of 1.26 x 10^{-11} mol/L? Is the solution acidic, basic, or neutral?

Solution:

$$K_w = [H^+][OH^-] = 1.00 \times 10^{-14}$$

$$[H^+] = \frac{1.00 \times 10^{-14}}{[OH^-]} = \frac{1.00 \times 10^{-14}}{1.26 \times 10^{-11}} = 7.94 \times 10^{-4}\ M$$

The pH Scale

Introduction to pH

The pH scale developed by Sorensen is a logarithmic scale. Not only is the pH scale a logarithmic scale but by defining the pH as the **negative** log of the hydrogen ion concentration, the numbers on the scale get smaller as the hydrogen ion concentration gets larger. For example, pH = 1 is a stronger acid than pH = 2 **and**, it is stronger by a factor of **10**. A solution whose pH = 1 has a hydrogen ion concentration of 0.10 M while a solution whose pH = 2 has a hydrogen ion concentration of 0.010 M. You should note the relationship between 0.10 and 0.010, 0.10 is 10 times 0.010. This is a very important point when using the pH scale.

As was pointed out earlier, when the $[H_3O^+]$ is greater than 1 x 10^{-7}, a solution is considered to be an acid. However, there are a great number of possibilities when you consider that an acid can have a hydrogen ion concentration that is *anything* greater than 1 x 10^{-7}. The same can be seen to be true for bases – just the opposite direction.

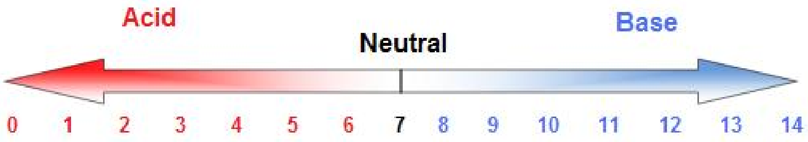


Figure 1: The pH Scale.

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There are a couple of important points to note here. First, all the numbers on the pH scale represent numbers with negative exponents and exponential numbers with negative exponents are small numbers; so all of these numbers represent $[H^+]$ that are less than one. Second, there are acids and bases whose H^+ concentrations do not fit within this range and therefore, not all acid or base strengths can be represented on the pH scale.

The pH scale found in Figure 1 shows that acidic solutions have a pH within the range of 0 up to but not including 7. The closer the pH is to 0 the greater the concentration of H_3O^+ ions and therefore the more acidic the solution. The basic solutions have a pH with the range from 7 to 14. The closer the pH is to 14, the higher the concentration of OH^- ion and the stronger the base. For 25°C, a pH of 7 is neutral which means that $[H_3O^+] = [OH^-] = 1 \times 10^{-7}$ M.

pH level	Solution
pH < 7	acidic
pH = 7	neutral
pH > 7	basic

pH = -log[H$^+$]

Sørensen's idea that the pH would be a simpler number to deal with in terms of discussing acidity level led him to a formula that relates pH and $[H^+]$. This formula is:

$$pH = -\log [H^+]$$

where p = – ***log*** and ***H*** refers to the hydrogen ion concentration. The ***p*** from pH comes from the German word *potenz* meaning power or the exponent of. In this case the exponent is 10. Therefore, $[H^+] = 10^{-pH}$.

When the $[H^+] = 0.01$ mol/L, the pH will be

$$pH = -\log (0.01)$$
$$pH = -\log (1 \times 10^{-2})$$
$$pH = 2$$

Since we are talking about negative logarithms (-log), the more hydrogen ions that are in solution, the more acidic the solution and the lower the pH.

The Mathematics of pH

pH measures the level of acidity in solution within a certain range and has the definition, **pH = -log [H$^+$]**. pH is a logarithmic scale which means that a difference of 1 in pH units indicates a difference of a factor of 10 in the hydrogen ion concentrations. If we have the pH of a solution and are asked to find the $[H^+]$, the formula for pH can be converted to a formula for $[H^+]$ by taking the inverse log of both sides of the equation. That process yields:

$[H^+] = 10^{-pH}$.

Example 1: Determine the pH of a solution that has a $[H^+] = 1 \times 10^{-8}$.

Solution:

pH = -log $[H^+]$ = -log (1 x 10^{-8})

The log of 1 is 0 and the log of 10^{-8} is -8.

pH = - (0 - 8) = 8

Sample question 2: Calculate the $[H^+]$ given that the pH is 4.

Solution:

$[H^+] = 10^{-pH}$

$[H^+] = 10^{-4}$

$[H^+]$ = 1 x 10^{-4} mol/L

Sometimes you will need to use a calculator.

Sample question 3: Calculate the pH of saliva with $[H^+]$ = 1.58 x 10^{-6} mol/L.

Solution:

pH = -log $[H^+]$ = -log (1.58 x 10^{-6})

pH = 5.8

Sample Question 4: Fill in the rest of the table below.

Table 1: pH = -log$[H^+]$

$[H^+]$ (mol/L)	-log$[H^+]$	pH
0.1	1.00	1.00
0.2	0.70	0.70
1.00 x 10^{-5}	?	?
?	?	6.00
0.065	?	?
?	?	9.00

Solution:

Table 1: pH = -log$[H^+]$

$[H^+]$ (mol/L)	-log$[H^+]$	pH
0.1	1.00	1.00
0.2	0.70	0.70
1.00 x 10^{-5}	5.00	5.00

1.00×10^{-6}	6.00	6.00
0.065	1.19	1.19
1.00×10^{-9}	9.00	9.00

We said that the pH scale was one that showed the pH becoming lower as the strength of the acid becomes larger. Let's think about this for a second. Stomach acid is HCl, a strong acid. Strong acids are powerful, we can assume because they completely ionize and therefore would have all of their H^+ ions present in the solution when the reaction is complete. Vinegar (that we may put on our salad, cook with, make those neat science fair volcanoes with!) is a weak acid. It only partially ionizes and only allows some of its H^+ ions to come into solution. Therefore, the pH of HCl, according to this observation would be lower than that of vinegar. Look at Figure 2. What does the pH scale diagram tell us about the pH of 0.1M HCl and 5% vinegar? Sure enough, the pH for HCl is 1.0 and that of 5% vinegar is around 2.8.

Have you ever cut an onion and had your eyes water up? This is because of a compound with the formula C_3H_6OS that is found in onions. When you cut the onion, a variety of reactions occur that release a gas. This gas can diffuse into the air and eventfully mix with the water found in your eyes to produce a dilute solution of sulfuric acid. This is what irritates your eyes and causes them to water. There are many common examples of acids and bases in our everyday lives. Look at the pH scale in Figure 2 to see how these common examples relate in terms of their pH.

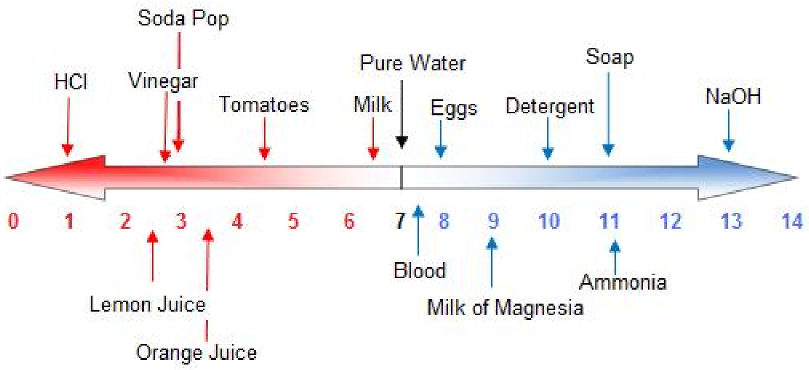


Figure 2: pH Scale for Common Substances.

You can see that pH definitely does play a role in our everyday lives as we come in contact with many substances that have varying degrees of acidity. We may not necessarily think about the pH of eggs as we eat them or think about how acidic orange juice is when we enjoy a glass, but maybe next time we have breakfast we may ponder for a second about the work of Sørensen … just maybe!

Summary

- Water dissociates to a very slight degree according to the equation $H_2O_{(L)} \leftrightarrows [H^+] + [OH^-]$.
- In pure water at 25°C, $[H^+] = [OH^-] = 1.00 \times 10^{-7}$ M.
- The equilibrium constant for the dissociation of water, called K_w, at 25°C is equal to 1.00×10^{-14}.

- The definition of pH is pH = -log [H^+].

Review Questions

1. Why is it necessary to balance the chemical equation before determining the [H^+] or [OH^-] for strong acids and bases? **(Intermediate)**

2. Why can't you determine the [H^+] or [OH^-] for weak acids and bases the same way you can determine the [H^+] or [OH^-] for strong acids and bases? **(Intermediate)**

3. What is the [H^+] ion concentration in a solution of 0.350 mol/L H_2SO_4? **(Intermediate)**

(a) 0.175 mol/L

(b) 0.350 mol/L

(c) 0.700 mol/L

(d) 1.42×10^{-14} mol/L

4. A solution has a pH of 6.54. What is the concentration of hydronium ions in the solution? **(Intermediate)**

(a) 2.88×10^{-7} mol/L

(b) 3.46×10^{-8} mol/L

(c) 6.54 mol/L

(d) 7.46 mol/L

5. A solution has a pH of 3.34. What is the concentration of hydroxide ions in the solution? **(Intermediate)**

(a) 4.57×10^{-4} mol/L

(b) 2.19×10^{-11} mol/L

(c) 3.34 mol/L

(d) 10.66 mol/L

6. A solution contains 4.33×10^{-8} M hydroxide ions. What is the pH of the solution? **(Intermediate)**

(a) 4.33

(b) 6.64

(c) 7.36

(d) 9.67

7. Fill in the table below and rank the solutions in terms of increasing acidity. **(Intermediate)**

Table 2: pH = -log[H^+]

Solutions	$[H^+]$ (mol/L)	$-\log[H^+]$	pH
A	0.25	0.60	0.60
B	?	2.90	?
C	1.25×10^{-8}	?	?
D	0.45×10^{-3}	?	?
E	?	1.26	?

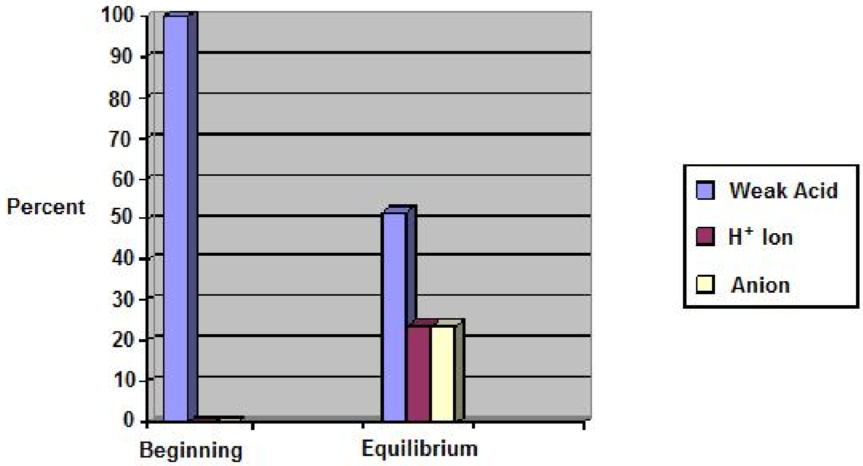
8. A bottle of calcium hydroxide is found in the lab with a label reading: 0.014 mol/L. **(Intermediate)**

(a) What are the concentrations of all of the ions present in the solution?

(b) What is the pH of the solution?

9. It has long been advocated that red wine is good for the heart. However, wine is also considered to be an acidic compound. Determine the concentration of hydronium ions in wine with pH 3.81. **(Challenging)**

10. The diagram that follows represents a weak acid before ionization and when the reaction comes to equilibrium. If the acid were weaker than the one represented in the diagram, how would the diagram change? Draw a new diagram to represent your answer. If the acid were a strong acid, how would the diagram change? Draw a new diagram to represent your answer. **(Intermediate)**



Further Reading / Supplemental Links

http://en.wikipedia.org

Vocabulary

pH scale	A scale measuring the $[H^+]$ with values from 0 to 14.
$pH = -\log [H^+]$	Formula used to calculate the power of the hydronium ion.
autoionization	Autoionization is when the same reactant acts as both the acid and the base.

ion product constant for water K_w, is the product of the hydronium ion and the hydroxide ion concentrations in the autoionization of water.

Review Answers

1. For strong acids and bases, the $[H^+]$ or $[OH^-]$ can be determined straight from the balanced chemical equation because the acids are completely ionized and the bases are completed dissociated. However, some acids are not monoprotic (have one H+ ion) but are diprotic (have 2 H^+ ions) or are polyprotic (have many H^+ ions). The same is true for bases. Bases can be monobasic (have one OH^- ion), dibasic (have two OH^- ions), or polybasic (have many OH^- ions). This fact must be kept into consideration when calculating the $[H^+]$ or $[OH^-]$ from the [acid] or [base].

2. Strong acids completely ionize and strong bases completely dissociate. What this means is that all of the H^+ ions from the acid are in solution when the reaction is complete and all of the OH^- ions are in solution when the base reaction is complete. This is not the case for weak acids and bases. For weak acids and bases, these substances only partially ionize or dissociate. Therefore in a weak acid solution, for example, when the reaction is complete, only a portion of the H^+ ions are in solution, the remainder are still associated with the acid molecule. The $[H^+]$ cannot be determined from the equation but must be determined some other way. Using the equation method assumes all of the H^+ has been released from the acid molecule.

3. (c) 0.700 mol/L

4. (a) 2.88×10^{-7} mol/L

5. (b) 2.19×10^{-11} mol/L

6. (b) 6.64

7.

Solutions	$[H^+]$ (mol/L)	$-\log[H^+]$	pH
A	0.25	0.60	0.60
B	1.25×10^{-3}	2.90	2.90
C	1.25×10^{-8}	7.90	7.90
D	0.45×10^{-3}	3.35	3.35
E	0.055	1.26	1.26

A > E > B > D > C in terms of $[H^+]$

8.

(a) $Ca(OH)_{2\,(aq)} \rightarrow Ca^{2+}_{(aq)} + 2\,OH^-_{(aq)}$

$[Ca(OH)_2] = 0.014$ mol/L $[Ca^{2+}] = 0.014$ mol/L $[OH^-] = 2(0.014$ mol/L$) = 0.028$ mol/L

(b) $K_w = [H^+][OH^-] = 1.00 \times 10^{-14}$

$[H^+] = \frac{1.00 \times 10^{-14}}{[OH^-]} = \frac{1.00 \times 10^{-14}}{0.028} = 3.57 \times 10^{-13}$ M

pH = 12.59

9.

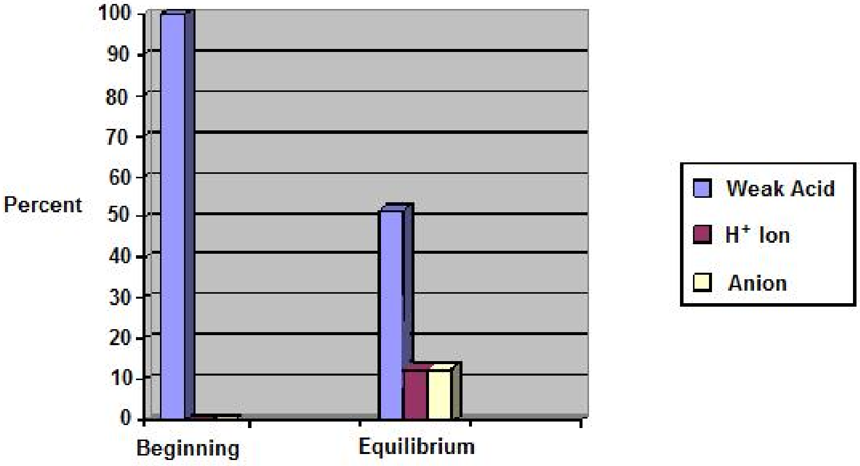
pH = -log[H^+]

[H^+] = 10^{-pH}

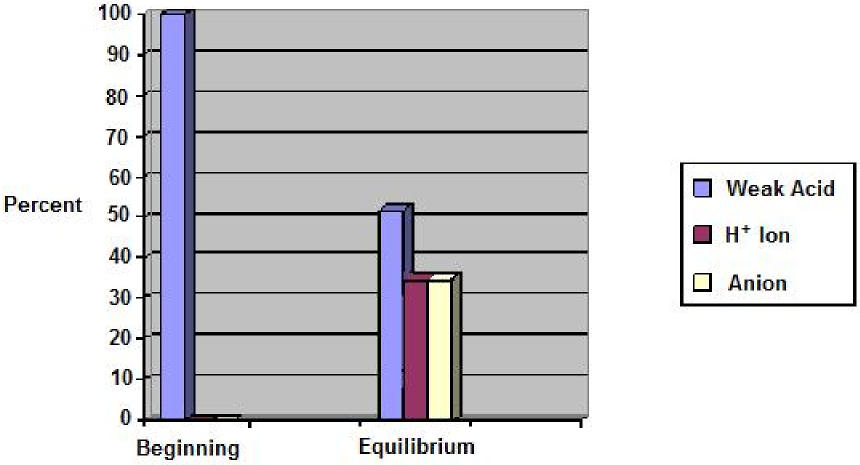
[H^+] = $10^{-3.81}$

[H^+] = 1.54×10^{-4} mol/L

10. (a) With a weaker acid there would be more weak acid at equilibrium and less H^+ ion (and less anion)



(b) If the acid was a strong acid, there would be no blue acid bar at the end and only H^+ ions and anions because the acid completely ionizes.



Weak Acid/Base Equilibria

Lesson Objectives

- Define weak acids and weak bases in terms of equilibrium.
- Define K_a and K_b.
- Use K_a and K_b to determine acid and base strength.
- Use K_a and K_b in acid/base equilibrium problems.

Introduction

Acid and base equilibria are another form of equilibrium reactions that deserve special mention. In prior learning we had discussed that weak acids and bases do not completely ionize or dissociate in solution. Thus, their reactions also possess an equilibrium state where their forward reaction rates equal their reverse reaction rates. Since this is the case, equilibrium constant expressions and equilibrium calculations can be completed for these reactions as was done for all other equilibria. When there are a group of reactions that are similar in appearance and function, the equilibrium constant for those reactions are often given a subscript denoting them as belonging to the group. Such was the case for solubility product constants which were given the designation K_{sp}. The dissociation of weak acids are also a special group of reactions and their equilibrium constant is designated K_a. The equilibrium constants for the dissociation of weak bases are designated K_b. In this section, we will focus our attention to a special case of equilibrium reactions, the acid - base equilibria.

Weak Acids and Weak Bases are Equilibrium Systems

Strong acids are defined as acids that completely ionize in water solution; strong bases as those that completely dissociate in water solution. Look at Equation 1 and Equation 2 for an example of a strong acid ionization reaction and a strong base dissociation reaction, respectively.

$$HCl_{(aq)} \longrightarrow H^+_{(aq)} + Cl^-_{(aq)}$$ (Equation 1)

$$NaOH_{(s)} \longrightarrow Na^+_{(aq)} + OH^-_{(aq)}$$ (Equation 2)

Weak acids and bases, however, do not completely ionize or dissociate in solution. In the chapter on weak acids and bases, we learned that solutions of weak acids and bases ionize or dissociate much less than 100%. Ammonia is a weak base, for example. Look at Equation 3, the dissociation reaction for ammonia.

$$NH_{3(aq)} + H_2O_{(L)} \leftrightarrows NH_4{}^+_{(aq)} + OH^-_{(aq)}$$ (Equation 3)

Ammonia has an equilibrium constant, K_b, of 1.8×10^{-5}. This value is less than 1. This means that the equilibrium position favors the reactants and that there is not very much reaction of ammonia to form the protonated ammonium ion. Said another way, at equilibrium, there are many more ammonia molecules present in solution than there are ammonium ions or hydroxide ions.

The same is true for weak acids. Vinegar is a common weak acid and represents an approximately 5% acetic acid solution. Equation 4 shows the ionization of acetic acid or vinegar.

$HC_2H_3O_{2(aq)} \leftrightarrows H^+_{(aq)} + C_2H_3O_2^-{}_{(aq)}$ (Equation 4)

The equilibrium constant, K_a, for acetic acid is 1.8×10^{-5}. Again, this value is small indicating that the equilibrium position lies more to the left than to the right. In other words, there are more acetic acid molecules at equilibrium than there are acetate ions or hydronium ions. Since K_a is less than 1, we know that $[HC_2H_3O_2] > [C_2H_3O_2^-]$ or $[H^+]$ at equilibrium.

Sample question 1: Put the following acids in order of decreasing acid strength. Write equilibrium reactions for each. Remember K_a is the equilibrium constant for the acid ionization which increases with increasing acid strength (or decreasing pH).

Formic acid, HCOOH, $K_a = 6.3 \times 10^{-4}$

Phosphoric acid, H_3PO_4, $K_a = 7.2 \times 10^{-3}$

Oxalic Acid, HCOOCOOH, $K_a = 5.6 \times 10^{-2}$

Arsenic acid, H_3AsO_4, $K_a = 6.0 \times 10^{-3}$.

Solution:

Order of decreasing acid strength: Oxalic acid > Phosphoric acid > Arsenic acid > Formic acid

Equilibrium Reactions:

1. Oxalic acid: $HCOOCOOH_{(aq)} \leftrightarrows H^+_{(aq)} + HCOOCOO^-_{(aq)}$
2. Phosphoric acid: $H_3PO_{4(aq)} \leftrightarrows H^+_{(aq)} + H_2PO_4^-{}_{(aq)}$
3. Arsenic acid: $H_3AsO_{4(aq)} \leftrightarrows H^+_{(aq)} + H_2AsO_4^-{}_{(aq)}$
4. Formic acid: $HCOOH_{(aq)} \leftrightarrows H^+_{(aq)} + COOH^-_{(aq)}$

K_a and K_b

The pH of solutions of strong acids and strong bases can be calculated simply by knowing the concentration of the strong acid and, of course, knowing that these acids and bases dissociate in solution 100%. Consider a solution that is 0.010 M HCl. HCl is a strong acid and therefore, the acid molecules dissociate 100% and this 0.010 M solution of HCl will be 0.010 M in H^+ ion and 0.010 M in Cl^- ion. Plugging the value of the hydrogen ion concentration into the pH formula, we can determine that this solution has a pH = 2.

Consider a solution that is 0.0010 M NaOH. NaOH is a strong base and therefore, this solution will be 0.0010 M in sodium ions and also in hydroxide ions. Since the solution is 1.0×10^{-3} M in hydroxide ions, it will be 1.0×10^{-11} M in hydrogen ions. Therefore, this solution will have a pH = 11.

A diatomic strong acid such as H_2SO_4 is only slightly more complicated. Suppose we wish to determine the pH of a 0.00010 M solution of H_2SO_4.

$H_2SO_{4(aq)} \rightarrow 2\ H^+ + SO_4{}^{2-}$

Since the original solution was 0.00010 M in the acid molecules and sulfuric acid is a strong acid, then the 100% dissociation will produce a solution that contains $[H^+]$ = 0.00020 M. Substituting this hydrogen ion concentration in the pH formula yields:

$\text{pH} = -\log (2.0 \times 10^{-4})$

$\text{pH} = -(0.30 - 4) = -(-3.7) = 3.7$

Let's now consider the process for finding the pH of weak acids and bases. In these cases, you need more information than you need for strong acids and bases. Not only do you need to know the concentration of the original acid or base solution, but you also must know the K_a or K_b.

Suppose we wish to know the pH of a 1.0 M solution of ascorbic acid, $H_2C_6H_6O_{6(aq)}$, whose $K_a = 1.8 \times 10^{-5}$.

$H_2C_6H_6O_{6(aq)} \rightleftarrows H^+{}_{(aq)} + HC_6H_6O_6{}^-{}_{(aq)} \qquad K_a = 1.8 \times 10^{-5}$

The K_a for this reaction would be written

$$K_a = \frac{[H^+][HC_6H_6O_6^-]}{[H_2C_6H_6O_6]}$$

To find the hydrogen ion concentration from this K_a expression and the original concentration of the acid, we need a little algebra. We need to assign some variables.

Let the molarity of the acid that dissociated be represented by x. Then the molarity of the hydrogen ions and ascorbate ions in solution will also be represented by x. The molarity of the undissociated acid remaining would be represented by 1.0 - x. We can now substitute these variables into the K_a expression and set it equal to the given K_a value.

$$K_a = \frac{(x)(x)}{(1.0-x)} = 1.8 \times 10^{-5} \qquad \text{Expression 1}$$

When this equation is simplified, we find that it is a quadratic equation . . . which, of course, can be solved by the quadratic formula.

$x^2 + (1.8 \times 10^{-5})x - 1.8 \times 10^{-5} = 0$ and $x = 4.2 \times 10^{-3}$ M

However, there is a shortcut available to solve this problem that simplifies the math greatly. It involves significant figures and adding or subtracting extremely small numbers from large numbers. If you are working to 3 significant figures and you are required to subtract 0.00005 from 1.00, when you carry out the subtraction and round to 3 significant figures, you discover that you get the original number before you subtracted.

1.00 - 0.00005 = 0.99995 which to 3 significant figures is 1.00

In the problem we solved above about ascorbic acid, the K_a value is very small, 1.8×10^{-5}. This indicates that the amount of ascorbic acid that dissociates, represented by x, is tiny. When we assigned the variables in that problem, we see that the molarity of ascorbic acid remaining after dissociation is represented by 1.0 - x. Since this x is very tiny, the result of this subtraction will be 1.0 M. Therefore, the K_a expression from above,

$K_a = \frac{(x)(x)}{(1.0-x)} = 1.8 \times 10^{-5}$ Expression 1

can quite safely be written as

$K_a = \frac{(x)(x)}{(1.0)} = 1.8 \times 10^{-5}$ Expression 2

You should notice that the variable 1.0 - x has been replaced simply by 1.0 . We are assuming that the x is so small, it will not alter the value 1.0 when we subtract and then round to proper significant figures. This is a safe assumption when the value of the K_a is very small (less than 1×10^{-3}).

When we solve this second expression

$\frac{(x)(x)}{(1.0)} = 1.8 \times 10^{-5}$

$x^2 = 1.8 \times 10^{-5}$ and

$x = 4.2 \times 10^{-3}$ M

We no longer need to use the quadratic formula and you **must** note that the answer to the proper number of significant figures is exactly the same as when Expression 1 was solved by the quadratic formula.

Let's go through another of these problems finding the pH of a weak acid given the initial concentration of the acid and its K_a. This time we will use a hypothetical weak acid, 0.10 M HA, whose $K_a = 4.0 \times 10^{-7}$.

$HA_{(aq)} \leftrightarrows H^+ + A^-$ $K_a = 4.0 \times 10^{-7}$

$K_a = \frac{[H^+][A^-]}{[HA]} = 4.0 \times 10^{-7}$

Let x represent the molarity of HA that dissociates, then $[H^+] = [A^-] = x$, and $[HA] = 0.10 - x$.

$K_a = \frac{[x][x]}{[0.10-x]} = 4.0 \times 10^{-7}$

Once again, since the K_a value is very small, the x subtracted in the denominator can be neglected and the equation becomes

$\frac{[x][x]}{[0.10]} = 4.0 \times 10^{-7}$

so, $x^2 = 4.0 \times 10^{-8}$ and $x = 2.0 \times 10^{-4}$ M.

Therefore, the hydrogen ion concentration in this solution is 2.0×10^{-4} M and substituting this value into the pH formula yields

$pH = -\log(2.0 \times 10^{-4}) = -(0.3 - 4) = -(-3.7) = 3.7$

The same process is used for weak bases. There is one additional step when working with weak bases because once the hydroxide ion concentration is determined, you must then find the hydrogen ion concentration before substituting into the pH formula. K_b represents the equilibrium constant for the dissociation of a weak base. Look at the dissociation of dimethylamine (a weak base used in making detergents). We will calculate the pH of a 1.0 M solution of this weak base.

$$(CH_3)_2NH_{(aq)} + H_2O_{(L)} \leftrightarrows (CH_3)_2NH_2{}^{+}{}_{(aq)} + OH^{-}{}_{(aq)} \qquad K_b = 5.9 \times 10^{-4}$$

$$K_b = \frac{[(CH_3)_2NH_2^{+}][OH^{-}]}{[(CH_3)_2NH]} = 4.0 \times 10^{-7}$$

Allowing x to represent the molarity of $(CH_3)_2NH$ that dissociates results in $[(CH_3)_2NH_2{}^{+}] = x$ and $[OH-] = x$. The molarity of undissociated $(CH_3)_2NH$ will be 1.0 - x.

Substituting the variables into the K_b expression yields

$$\frac{[x][x]}{[1.0-x]} = 4.0 \times 10^{-7},$$

and neglecting the x subtracted in the denominator because it is beyond the significant figures of the problem yields

$$\frac{[x][x]}{[1.0]} = 4.0 \times 10^{-7}.$$

Therefore, $x^2 = 4.0 \times 10^{-7}$ and $x = 6.3 \times 10^{-4}$ M.

Now that we know the hydroxide ion concentration in the solution, we calculate the hydrogen ion concentration by dividing the $[OH^-]$ into the K_w. This will yield $[H^+] = 1.6 \times 10^{-11}$ M. The final step is to plug the hydrogen ion concentration into the pH formula.

$$pH = -\log (1.6 \times 10^{-11}) = 10.8$$

Sample question 2: Acetic acid is mixed with water to form a 0.10 mol/L $HC_2H_3O_{2(aq)}$ solution at 25°C. If the equilibrium concentrations of $H_3O^{+}{}_{(aq)}$ and $C_2H_3O_2{}^{-}{}_{(aq)}$ are both 1.34×10^{-3} mol/L and the equilibrium concentration of $HC_2H_3O_{2(aq)}$ is 0.0999 mol/L, determine the

(a) K_a and

(b) the pH of the solution at equilibrium.

Solution:

$$HC_2H_3O_{2(aq)} \leftrightarrows H^{+}{}_{(aq)} + C_2H_3O_2{}^{-}{}_{(aq)}$$

(a) $K_a = \dfrac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = \dfrac{(1.34 \times 10^{-3})(1.34 \times 10^{-3})}{(0.0999)} = 1.80 \times 10^{-5}$

(b)

$$pH = -\log [H^+]$$

$$pH = -\log (1.34 \times 10^{-3})$$

pH = 2.87

Lesson Summary

- Weak acids only partially ionize in solution and therefore represent equilibrium reactions. Weak bases only partially dissociate in solution and therefore represent equilibrium reactions. K_a represents the equilibrium constant for the ionization of a weak acid.
- K_b represents the equilibrium constant for the dissociation of a weak base. Equilibrium calculations are the same for weak acids and bases as they were for all other equilibrium reactions.

Review Questions

1. What makes weak acids and bases a special case for equilibrium reactions? **(Intermediate)**

2. What do the constants K_a and K_b represent? **(Beginning)**

3. Oxalic acid is a weak acid. Its ionization reaction is represented below. **(Intermediate)**

$$H_2C_2O_{4(aq)} + H_2O_{(L)} \leftrightarrows H_3O^+_{\ (aq)} + HC_2O_4^{\ -}{}_{(aq)}$$

Which of the following best represents the acid ionization constant expression, K_a?

(a) $K_a = \dfrac{[H_3O^+][HC_2O_4^-]}{[H_2C_2O_4][H_2O]}$

(b) $K_a = \dfrac{[H_2C_2O_4][H_2O]}{[H_3O^+][HC_2O_4^-]}$

(c) $K_a = \dfrac{[H_3O^+][HC_2O_4^-]}{[H_2C_2O_4]}$

(d) $K_a = \dfrac{[H_2C_2O_4]}{[H_3O^+][HC_2O_4^-]}$

4. Choose the weakest acid from the list below. **(Beginning)**

(a) $HNO_{2(aq)}$; $K_a = 5.6 \times 10^{-3}$

(b) $HF_{(aq)}$; $K_a = 6.6 \times 10^{-4}$

(b) $H_3PO_{4(aq)}$; $K_a = 6.9 \times 10^{-3}$

(c) $HCOOH_{(aq)}$; $K_a = 1.8 \times 10^{-4}$

5. Choose one of the following reactions that would best represent a reaction that has an equilibrium constant best described as a base dissociation constant, K_b. **(Intermediate)**

(a) $H_2PO_4^{\ -}{}_{(aq)} + H_2O_{(L)} \leftrightarrows HPO_4^{\ -2}{}_{(aq)} + H_3O^+_{\ (aq)}$

(b) $NH_4^{\ +}{}_{(aq)} + H_2O_{(L)} \leftrightarrows NH_{3(aq)} + H_3O^+_{\ (aq)}$

(c) $NH_4{}^-{}_{(aq)} + OH^-{}_{(aq)} \leftrightarrows NH_{3(aq)} + H_2O_{(L)}$

(d) $F^-{}_{(aq)} + H_2O_{(L)} \leftrightarrows HF_{(aq)} + OH^-{}_{(aq)}$

6. A 0.150 mol/L solution of a weak acid having the general formula HA is 15.0% ionized in aqueous solution. Which expression best represents the calculation of the acid ionization constant K_a for this acid? **(Intermediate)**

(a) $K_a = \frac{(0.150)(0.150)}{(0.150)}$

(b) $K_a = \frac{(0.0225)(0.0225)}{(0.128)}$

(c) Not enough information is given.

7. Put the following bases in order of increasing base strength. Write equilibrium reactions for each. **(Intermediate)**

ethanolamine ($HOCH_2CH_2NH_2$), $K_b = 3.2 \times 10^{-5}$, piperidine ($C_5H_{10}NH$), $K_b = 1.3 \times 10^{-3}$, triethylamine ($(CH_3CH_2)_3N$), $K_b = 5.2 \times 10^{-4}$, and ethylenediamine ($H_2NCH_2CH_2NH_2$), $K_b = 8.5 \times 10^{-5}$.

Further Reading / Supplemental Links

http://en.wikipedia.org/wiki

Vocabulary

acid ionization constant	K_a represents the equilibrium constant for the ionization of a weak acid.
base dissociation constant	K_b represents the equilibrium constant for the dissociation of a weak base.

Review Answers

1. Weak acids and bases do not completely ionize or dissociate in solution. Solutions of weak acids and bases ionize or dissociate very little in some cases. Therefore when a solution of a weak acid is ionized or a weak base is dissociated, there is mostly the acid molecule (or base formula) in solution and some of the ions that have been ionized (dissociated). It is also a special case because we use the constants K_a and K_b rather than just K.

2. K_a represents the acid ionization constant; K_b represents the base dissociation constant.

3. (c)

4. (b)

5. (d)

6. (b)

7. Order of increasing base strength: piperidine > triethylamine > ethanolamine > ethylenediamine

Equilibrium Reactions:

1. piperidine: $C_5H_{10}NH_{(aq)} + H_2O_{(L)} \leftrightarrows OH^-_{(aq)} + C_5H_{10}NH_2{}^+_{(aq)}$

2. triethylamine: $(CH_3CH_2)_3N_{(aq)} + H_2O_{(L)} \leftrightarrows OH^-_{(aq)} + (CH_3CH_2)_3NH^+_{(aq)}$

3. ethanolamine: $HOCH_2CH_2NH_{2(aq)} + H_2O_{(L)} \leftrightarrows OH^-_{(aq)} + HOCH_2CH_2NH_3{}^+_{(aq)}$

4. ethylenediamine: $H_2NCH_2CH_2NH_{2(aq)} + H_2O_{(L)} \leftrightarrows OH^-_{(aq)} + H_2NCH_2CH_2NH_3{}^+_{(aq)}$

Brønsted Lowry Acids-Bases

Lesson Objectives

- Define a Brønsted-Lowry acid and base.
- Identify Brønsted-Lowry acids and bases from balanced chemical equations.
- Define conjugate acid and conjugate base.
- Identify conjugate acids-bases in balanced chemical equations.
- Identify the strength of the conjugate acids and bases from strengths of the acids and bases.

Introduction

Arrhenius provided chemistry with the first definition of acids and bases but like a lot of theories, this model tended to be refined over time. This is exactly what happened in the area of acid/base chemistry. Two chemists, named Brønsted and Lowry, working on similar experiments as Arrhenius, derived a more generalized definition for acids and bases that we use in conjunction with the Arrhenius theory. The Brønsted-Lowry theory is the focus of this lesson. As the Brønsted-Lowry definition unfolded, the number of acids and bases that were able to fit into each category increased. Thus, the definitions were broader for each.

Brønsted-Lowry Acids and Bases

Bronsted-Lowry Definitions

Arrhenius made great in-roads into the understanding of acids and bases and how they behaved in chemical reactions. Brønsted and Lowry slightly altered the Arrhenius definition and greatly enlarged the number of compounds that qualify as bases. The Brønsted-Lowry theory defines an acid as a substance that is a proton donor and a base as a proton accepter. Look at equation 1 in which hydrochloric acid is reacting with water:

$HCl_{(g)} + H_2O_{(L)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$ (Equation 1)

What is happening is that the acid, HCl is losing a H^+ ion to form Cl^- and the H_2O is gaining a H^+ ion to form H_3O^+. The Brønsted-Lowry concept of acids and bases states that the ***acid*** donates a proton and the ***base*** accepts a proton. Therefore HCl is donating an H^+ ion to H_2O to form Cl^- and the H_2O is accepting an H^+ ion from HCl to form H_3O^+; HCl is acting as the acid and $H_2O(aq)$ is acting as the base. Look at equation 2 to see another example of the Brønsted-Lowry Theory in action.

$H_2PO_4{}^-_{(aq)} + OH^-_{(aq)} \leftrightarrows HPO_4{}^{2-}_{(aq)} + H_2O_{(L)}$ (Equation 2)

We can see that again, the equation shows $H_2PO_4^-$ is donating a proton to OH^- to form HPO_4^{2-} and OH^- is accepting the proton to form H_2O. Thus $H_2PO_4^-(aq)$ is acting as the acid and $OH^-(aq)$ is acting as the base.

Sample question: Identify the Brønsted Lowry Acids and Bases from each of the following equations:

(a) $HC_2H_3O_{2(aq)} + H_2O_{(L)} \leftrightarrows C_2H_3O_2^-{}_{(aq)} + H_3O^+{}_{(aq)}$

(b) $HCN_{(aq)} + H_2O_{(L)} \leftrightarrows CN^-{}_{(aq)} + H_3O^+{}_{(aq)}$

Solution:

(a) $HC_2H_3O_2{}_{(aq)} + H_2O_{(L)} \leftrightarrows C_2H_3O_2^-{}_{(aq)} + H_3O^+{}_{(aq)}$

Acid base

(b) $HCN_{(aq)} + H_2O_{(L)} \leftrightarrows CN^-{}_{(aq)} + H_3O^+{}_{(aq)}$

Acid base

Brønsted–Lowry Acids/Bases Definitions Includes More Compounds

If you think about the definition of an Arrhenius acid, it includes substances such as HCl, HNO_3, $HC_2H_3O_2$, in essence all substances that contain H^+ ions. This is because according to Arrhenius, the acid ionizes in water to produce H^+ ions. This definition limits what can fit under the umbrella of the definition of acid. The Brønsted-Lowry definition of the acid is broader in that it defines the acid as a proton donor. With this broader definition there is the ability to include more compounds in the category of acid. Consider the reaction Equation 3:

$HSO_4^-{}_{(aq)} + OH^-{}_{(aq)} \leftrightarrows H_2O_{(L)} + SO_4^{2-}{}_{(aq)}$ (Equation 3)

It needs to be pointed out that if a substance is an acid in the Arrhenius definition, it will be an acid in the Brønsted–Lowry definition. However, the reverse is not true. Nor, do Brønsted–Lowry acids now have the properties of an Arrhenius acid. The same is true for bases. In equation 3, the hydroxide ion, OH^-, is both an Arrhenius base and in the reaction a Brønsted–Lowry base. In other words, the Brønsted-Lowry definition can be viewed as an extension to the Arrhenius definition rather than a replacement for it.

May or May Not be in Water Solution

With the Arrhenius theory, one aspect that is consistent, is that water was part of the equation. Arrhenius said that an acid must produce H^+ ions in a water solution. Therefore, according to Arrhenius, the following equation would be representative of an Arrhenius acid.

$HCl_{(g)} + H_2O_{(L)} \rightarrow H_3O^+{}_{(aq)} + OH^-{}_{(aq)}$ (Equation 4)

If you look at all of the equations we have used thus far for Arrhenius, and even the definitions in Arrhenius theory, one commonality shows through: water must be in the equation. Here is where the Brønsted-Lowry definition again varies from Arrhenius theory. Look at the equation below.

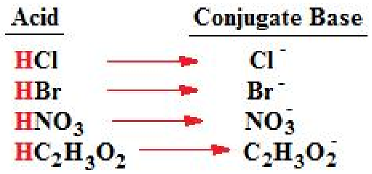
$NH_{3(aq)} + NH_{3(aq)} \leftrightarrows NH_4^+{}_{(aq)} + NH_2^-{}_{(aq)}$ (Equation 5)

When you look at Equation 5, the first NH_3 molecule is accepting a proton to form NH_4^+ and is therefore a Brønsted-Lowry base, the second $NH_3(aq)$ molecule is donating a proton to form NH_2^- and is therefore a Brønsted-Lowry acid. Ammonia molecules, however, do not donate hydrogen ions in water and therefore, do not qualify as Arrhenius acids. The Brønsted-Lowry theory has provided a broader theory for acid-base chemistry.

It should be noted that NH_3 is an example of an ***amphoteric*** species. Amphoteric species are those that in different situations can act as either an acid or a base. That is, in some circumstances, they donate a proton and in other circumstances, they accept a proton. Here in Equation 5, NH_3 is doing just this. Water is also an amphoteric species.

Acid-Base Conjugate Pairs Definition

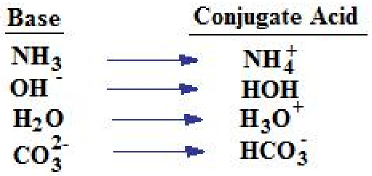
There is one more aspect of the Brønsted-Lowry theory that was a significant breakthrough to acid-base chemistry. Brønsted and Lowry said that in acid-base reactions, there are actually pairs of acids and bases in the reaction itself. According to Brønsted-Lowry, for every acid there is a conjugate base associated with that acid. The ***conjugate base*** is the result of the acid losing (or donating) a proton. Therefore, if you look at Figure 1, you can see on the left, the acid and on the right the conjugate base.



Acid		Conjugate Base
HCl	→	Cl^-
HBr	→	Br^-
HNO_3	→	NO_3^-
$HC_2H_3O_2$	→	$C_2H_3O_2^-$

Figure 1: Acids and Their Conjugate Bases

Notice that the difference between the acid and its conjugate base is simply a difference of a proton. The conjugate base has one less proton (or H^+). Conjugate acids work the same way. For every base in the acid-base reaction, there must be a corresponding conjugate acid. The ***conjugate acid*** is the result of the base gaining (or accepting) the proton. Look at Figure 2 and see the difference between the base and the corresponding conjugate acid.



Base		Conjugate Acid
NH_3	→	NH_4^+
OH^-	→	HOH
H_2O	→	H_3O^+
CO_3^{2-}	→	HCO_3^-

Figure 2: Bases and Their Conjugate Acids

Now that we know what a conjugate acid and base is, let's now try to identify them in acid-base reactions. Look at Equation 6 below, a reaction between acetic acid and water.

$$HC_2H_3O_{2(aq)} + H_2O_{(L)} \leftrightarrows C_2H_3O_2{}^-{}_{(aq)} + H_3O^+{}_{(aq)} \qquad \text{(Equation 6)}$$

Acetic Acid Water

Step 1: Identify the acid and base.

$HC_2H_3O_{2(aq)} + H_2O_{(L)} \leftrightarrows C_2H_3O_2{}^-{}_{(aq)} + H_3O^+{}_{(aq)}$

Acid Base

Step 2: Identify the conjugate acid and base on the product side of the equation. Look at the product side to see what product has gained a proton (this is the conjugate base) and which product has lost a proton (this is the conjugate acid).

$HC_2H_3O_{2(aq)} + H_2O_{(L)} \leftrightarrows C_2H_3O_2{}^-{}_{(aq)} + H_3O^+{}_{(aq)}$

Acid Base Conjugate Base Conjugate Acid

As a result, the conjugate acid/base pairs are $HC_2H_3O_2{}_{(aq)}$/ $C_2H_3O_2{}^-{}_{(aq)}$ and $H_2O_{(L)}/H_3O^+{}_{(aq)}$.

Now you try. Identify the conjugate acid-base pairs in the following equation.

$CH_3NH_2{}_{(aq)} + HClO_{(aq)} \leftrightarrows ClO^-{}_{(aq)} + CH_3NH_3{}^+{}_{(aq)}$ (Equation 7)

First, identify the acid and base on the reactant side.

Step 1: $CH_3NH_2{}_{(aq)} + HClO_{(aq)} \leftrightarrows ClO^-{}_{(aq)} + CH_3NH_3{}^+{}_{(aq)}$

Base Acid

Then identify the conjugate acid and base in the products.

Step 2: $CH_3NH_2{}_{(aq)} + HClO_{(aq)} \leftrightarrows ClO^-{}_{(aq)} + CH_3NH_3{}^+{}_{(aq)}$

Base Acid Conjugate Base Conjugate Acid

Hence, the conjugate acid/base pairs are CH_3NH_2 / $CH_3NH_3{}^+$ and HClO / ClO^-.

Sample Problem: Identify the conjugate acid-base conjugate pairs in each of the following equations:

(a) $NH_3{}_{(aq)} + HCN_{(aq)} \leftrightarrows NH_4{}^+{}_{(aq)} + CN^-{}_{(aq)}$

(b) $CO_3{}^{2-}{}_{(aq)} + H_2O_{(L)} \leftrightarrows HCO_3{}^-{}_{(aq)} + OH^-{}_{(aq)}$

Solution:

(a)NH_3/ $NH_4{}^+$ and HCN/ CN^-

(b)$CO_3{}^{2-}$/ $HCO_3{}^-$ and H_2O/ OH^-

The Strength of Conjugate Acids and Bases

The definition of a Bronsted-Lowry acid is that it donates a proton (hydrogen ion). In order to be a strong Bronsted-Lowry acid, it must donate the proton readily. That is, the bond between the hydrogen ion and the cation is weak so that the proton is released easily. The definition of a Bronsted-Lowry base is that it accepts a proton. In order to be a strong base, it must take on that proton readily. Therefore, a Bronsted-Lowry strong base would hold onto the proton tightly.

If we consider a strong acid, such as HCl, we know that the acid releases its proton readily . . . does that tell us anything about the Cl^- ion as a base? If the chloride ion does not hold onto the proton tightly, we know HCl will be a strong acid, and therefore, because the chloride ion releases the proton easily, it cannot be a strong base. The same behavior that qualifies an anion attached to a hydrogen ion as a strong acid also qualifies the anion alone as a weak base.

The reverse of this situation would also be true. Consider a weak acid such as acetic acid, $HC_2H_3O_2$. This is a weak acid because the acetate ion does not release the hydrogen ion readily; it holds it tightly, hence only ionizes to a slight degree. That tells us that the acetate ion takes on a proton readily and holds it and that qualifies the acetate ion as a strong base.

Strong acids produce conjugate bases that are weak bases and weak acids produce conjugate bases that are strong bases.

In this same way, a strong base such as OH^- ion takes on hydrogen ions readily and holds them tightly. Therefore, the conjugate base of OH^- ion, which is H_2O, will be a weak acid. A weak base such as ammonia, NH_3, does not take on a hydrogen ion readily and that causes it to be a weak base. Therefore, the conjugate acid of NH_3, NH_4^+, will be a strong acid.

Strong bases produce conjugate acids that are weak acids and weak bases produce conjugate acids that are strong acids.

Which conjugate bases would be strong and which would be weak?

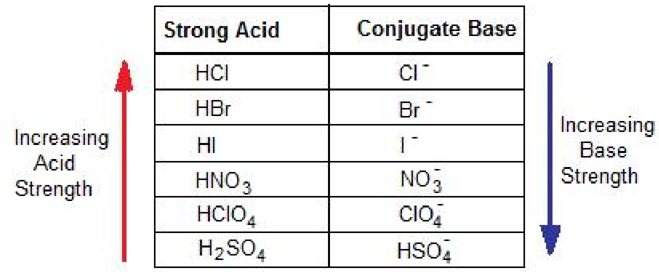
Table 1: Strong Acids

Name	**Symbol**	**Conjugate Base**	**Strength of Conjugate Base**
Hydrochloric Acid	HCl	Cl^-	Weak
Hydrobromic Acid	HBr	Br^-	Weak
Hydroiodic Acid	HI	I^-	Weak
Nitric Acid	HNO_3	NO_3^-	Weak
Perchloric Acid	$HClO_4$	ClO_4^-	Weak
Sulfuric Acid	H_2SO_4	HSO_4^-	Weak

All of the strong acids will have weak conjugate bases. All other acids are weak and will therefore have conjugate bases that are strong.

The stronger the acid, the weaker the conjugate base. This means that the conjugate bases will follow a similar trend as the acids only in the reverse. Look at the Table 2. See how the acid strength trend compares with the conjugate base strength trend.

Table 2: Strong Acids and Their Conjugate Bases



Strong Acid	Conjugate Base
HCl	Cl^-
HBr	Br^-
HI	I^-
HNO_3	NO_3^-
$HClO_4$	ClO_4^-
H_2SO_4	HSO_4^-

As we have seen with the strong acids-weak conjugate bases and weak acids-strong conjugate bases, the same concept can be applied to bases. Strong bases have weak conjugate acids and weak bases have strong conjugate acids. Which conjugate acids would be strong and which would be weak?

Only the OH- ion represents a strong base and therefore only H_2O represents a weak conjugate acid. All of the other bases are weak. Therefore all of the other conjugate acids are strong. The strong bases are LiOH, NaOH, KOH, RbOH, CsOH, $Ca(OH)_2$, $Sr(OH)_2$, and $Ba(OH)_2$. All of these strong bases contain OH^- and therefore their weak conjugate acid will be H_2O. The remaining bases are weak and so would have strong conjugate acids.

Lesson Summary

- The Brønsted-Lowry concept of acids and bases states that the acid donates a proton and the base accepts a proton.
- The Brønsted-Lowry definition includes more substances because the definition is not confined to substances containing hydroxides or to be in water. A conjugate acid is a substance that results when a base gains (or accepts) a proton.
- A conjugate base is a substance that results when an acid loses (or donates) a proton.
- Strong acids result in weak conjugate bases when they lose a proton and weak acids result in strong conjugate bases when they lose a proton.
- Strong bases result in weak conjugate acids when they gain a proton and weak bases result in strong conjugate acids when they gain a proton.

Review Questions

1. What improvements did Bronsted-Lowry make over the Arrhenius definition for acids-bases? **(Intermediate)**

2. If you were to use HCl(aq) as an example, how would you compare the Arrhenius definition of an acid to the Bronsted-Lowry definition? **(Intermediate)**

3. What is the Bronsted-Lowry definition of an acid? **(Beginning)**

(a) a substance that donates protons

(b) a substance that accepts protons

(c) a substance that dissolves in water to form OH^- ions

(d) a substance that dissolves in water to form H^+ ions

4. If H_3O^+ is an acid according to the Bronsted-Lowry theory, what is the conjugate base of this acid? **(Intermediate)**

(a) $H_4O^{2+}{}_{(aq)}$

(b) $H^+{}_{(aq)}$

(c) $H_2O_{(L)}$

(d) $OH^-{}_{(aq)}$

5. What is the conjugate base of $H_2PO_4^-$? **(Intermediate)**

(a) $H_3O^+{}_{(aq)}$

(b) $H_3PO4_{(aq)}$

(c) $HPO_4^{2-}{}_{(aq)}$

(d) $PO_4^{3-}{}_{(aq)}$

6. In the following reactions, which are the Bronsted-Lowry acids? **(Intermediate)**

i) $H_3PO_{4\,(aq)} + H_2O_{(L)} \leftrightarrows H_3O^+{}_{(aq)} + H_2PO_4^-{}_{(aq)}$

ii) $H_2PO_4^-{}_{(aq)} + H_2O_{(L)} \leftrightarrows H_3O^+{}_{(aq)} + HPO_4^{2-}{}_{(aq)}$

(a) $H_2PO_4^-$, H_2O, HPO_4^{2-}

(b) H_3PO^4, H_2O, $H_2PO_4^-$

(c) H_3O^+, H_2O, HPO_4^{2-}

(d) H_3PO4, H_3O^+, $H_2PO_4^-$

7. Label the conjugate acid-base pairs in each reaction. **(Intermediate)**

(a) $HCO_3^- + H_2O \leftrightarrows H_2CO_3 + OH^-$

(b) $H_2PO_4^- + H_2O \leftrightarrows H_3O^+ + HPO_4^{2-}$

(c) $CN^- + H_2O \leftrightarrows HCN + OH^-$

(d) $HF(aq) + H_2O(l)\ \Omega\ H_3O^+(aq) + F^-(aq)$

8. Complete the following reactions. When done, label the conjugate acid/base pairs. **(Intermediate)**

(a) $BrO_3^- + H_2O \leftrightarrows$

(b) $HNO_3 + H_2O \rightarrow$

(c) $HSO_4^- + C_2O_4^{2-} \leftrightarrows$

9. For the reactions in question 7, which are the weak conjugate bases and which are the strong conjugate bases? **(Intermediate)**

Further Reading / Supplemental Links

http://learner.org/resources/series61.html'''

The ***learner.org*** website allows users to view streaming videos of the Annenberg series of chemistry videos. You are required to register before you can watch the videos but there is no charge. The website has one video that relates to this lesson called ***The Proton in Chemistry*** .

Vocabulary

Bronsted-Lowry acid	A substance that donates a proton (H^+).
Bronsted-Lowry base	A substance that accepts a proton (H^+).
amphoteric substances	Substances that act as both acids and bases in reactions (i.e. NH_3).
conjugate acid	The substance that results when a base gains (or accepts) a proton.
conjugate base	The substance that results when an acid loses (or donates) a proton.

Review Answers

1. The Bronsted-Lowry theory was much more general than the Arrhenius theory of the time. Arrhenius said that acids produced H^+ ions in solution and bases produced OH^- ions in solution. This, of course, meant that acids must have H^+ ions in them and bases OH^-. Bronsted-Lowry recognized that compounds such as NH_3 were bases but did not contain OH^- and therefore did not fit the Arrhenius definition. They therefore came up with the improved definition of an acid as a substance that donates a proton (H^+) and a base as a substance that accepts a proton.

2. Arrhenius defined an acid as a substance that produces H^+ ions when dissolved in water. Using $HCl_{(aq)}$ as an example, we could write the equation for the ionization of $HCl_{(aq)}$ as follows: $HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$. Bronsted-Lowry defined an acid as a substance that donates a proton. Using $HCl_{(aq)}$ as an example, we could write the equation for the ionization of $HCl_{(aq)}$ as follows: $HCl_{(aq)} + H_2O_{(L)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$. Technically the hydronium ion is a term given to the H_3O^+ ion.

3. (a) a substance that donates protons

4. (c) H_2O

5. (c) HPO_4^{2-}

6. (d) H_3PO_4, H_3O^+, $H_2PO_4^+$

7. Answers: Let A = Acid, B = Base, CA = Conjugate Acid and CB = Conjugate Base

a) $HCO_3^-{}_{(aq)} + H_2O_{(L)} \leftrightarrows H_2CO_{3\,(aq)} + OH^-{}_{(aq)}$

B A CA CB

Therefore the conjugate acid base pairs are: HCO_3^-/H_2CO_3 and H_2O/OH^-

(b) $H_2PO_4^-{}_{(aq)} + H_2O_{(L)} \leftrightarrows H_3O^+{}_{(aq)} + HPO_4^{2-}{}_{(aq)}$

A B CA CB

Therefore the conjugate acid base pairs are: $H_2PO_4^-/ HPO_4^{2-}$ and H_2O/ H_3O^+

(c) $CN^-{}_{(aq)} + H_2O_{(L)} \leftrightarrows HCN_{(aq)} + OH^-{}_{(aq)}$

B A CA CB

Therefore the conjugate acid base pairs are: CN^-/ HCN and H_2O/OH^-

(d) $HF_{(aq)} + H_2O_{(L)} \leftrightarrows H_3O^+{}_{(aq)} + F^-{}_{(aq)}$

A B CA CB

Therefore the conjugate acid base pairs are: HF/ F^- and H_2O/ H_3O^+

8. Again, let A = Acid, B = Base, CA = Conjugate Acid and CB = Conjugate Base

(a) $BrO_3^-{}_{(aq)} + H_2O_{(L)} \leftrightarrows HBrO_{3\,(aq)} + OH^-{}_{(aq)}$

B A CA CB

Therefore the conjugate acid base pairs are: $BrO_3^-/HBrO_3$ and H_2O/OH^-

b) $HNO_{3\,(aq)} + H_2O_{(L)} \longrightarrow H_3O^+{}_{(aq)} + NO_3^-{}_{(aq)}$

A B CA CB

Therefore the conjugate acid base pairs are: HNO_3/NO_3^- and H_2O/ H_3O^+

(c) $HSO_4^-{}_{(aq)} + C_2O_4^{2-}{}_{(aq)} \leftrightarrows SO_4^{2-}{}_{(aq)} + HC_2O_4^-{}_{(aq)}$

A B CB CA

Therefore the conjugate acid base pairs are: HSO_4^-/ SO_4^{2-} and $C_2O_4^{2-}/ HC_2O_4^-$

9. (a) CB = OH^- from H_2O (a weak acid) therefore is a strong conjugate base

(b) CB = NO_3^- from HNO_3 (a strong acid) therefore is a weak conjugate base

(c) CB = SO_4^{2-} from HSO_4^- (a weak acid) therefore is a strong conjugate base

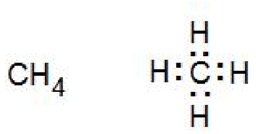
Lewis Acids and Bases

Lesson Objectives

- Define a Lewis acid and a Lewis base.
- Understand and define a coordinate covalent bond.
- Identify a Lewis acid and a base in reactions.

Introduction

Lewis is known for the shared-pair chemical bond and his work with electrons. We will be concentrating on his work with electrons. You may recall working with Lewis electron dot diagrams from an earlier chapter. Look at the example below for a quick refresher.

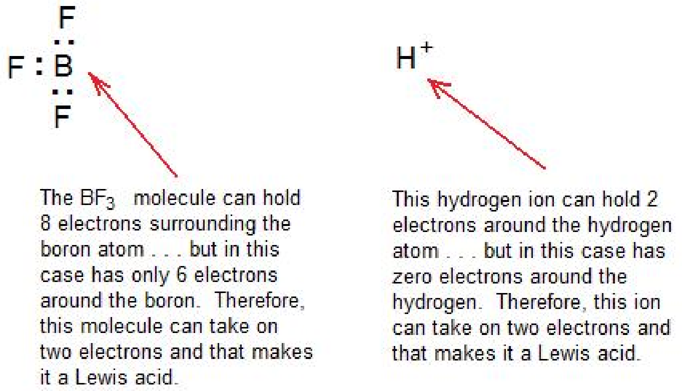


In the early 1930s, Gilbert Lewis saw the need for a more general definition for acids and bases that involved the use of electrons. Using the work of Bronsted and Lowry, he saw that in some cases the acids may not have protons to donate, but may have electron pairs to donate. We will give a look at the contribution of Lewis to the theory of acids and bases. It should be noted that most chemists today use the Bronsted-Lowry definitions of acids-bases and the Lewis definitions are used in more specialized situations.

Lewis Acids

Lewis defined an acid as a substance that accepts a pair of electrons from another substance. Therefore, ***Lewis acids*** must have room in their structure to accept a pair of electrons. Remember that each central atom can hold eight electrons. What this means is that if the atom does not have eight electrons, but six electrons, then it can accept one more pair. Look at the structure in Figure 1. Notice how, in each case, there is room to accept a pair of electrons.

The Lewis acid will accept the electron pair in order to form a bond. The bond that forms between the two atoms will be covalent bonds. Covalent bonds are formed when electrons are shared between two atoms.



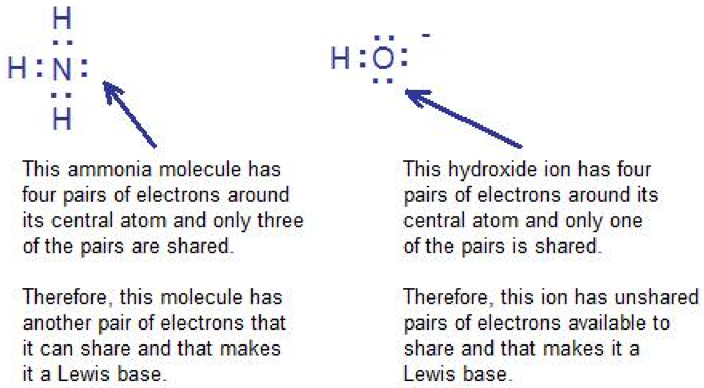
The BF_3 molecule can hold 8 electrons surrounding the boron atom . . . but in this case has only 6 electrons around the boron. Therefore, this molecule can take on two electrons and that makes it a Lewis acid.

This hydrogen ion can hold 2 electrons around the hydrogen atom . . . but in this case has zero electrons around the hydrogen. Therefore, this ion can take on two electrons and that makes it a Lewis acid.

Figure 1: Examples of Lewis Acids.

Lewis Bases

Lewis defined a base as a substance that donates a pair of electrons to a substance. Lewis bases have a lone pair of electrons that they can share with another species when they donate them as part of their performance as a base. If we look at the example of bases in the Diagram 2, we can see that each of them has a lone pair of electrons available to donate.



This ammonia molecule has four pairs of electrons around its central atom and only three of the pairs are shared.

Therefore, this molecule has another pair of electrons that it can share and that makes it a Lewis base.

This hydroxide ion has four pairs of electrons around its central atom and only one of the pairs is shared.

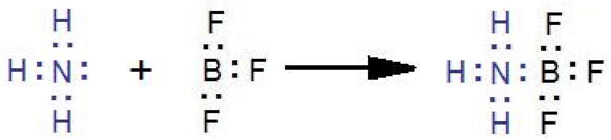
Therefore, this ion has unshared pairs of electrons available to share and that makes it a Lewis base.

Figure 2: Examples of Lewis Bases.

Again, since the base will share the electrons with the corresponding acid when it donates this pair, the resulting bond that forms between the acid and the base will be a covalent bond.

Lewis Acid-Base Neutralization

We have said already that the Lewis acid accepts a pair of electrons from a Lewis base that donates the pair of electrons. The resulting bond that forms is a covalent bond. In a regular covalent bond, each of the bonded atoms contributes one of the shared pair of electrons. In certain cases, it is possible for one of the bonded atoms to contribute both of the shared electrons and the other atom contributes no electrons. ***Coordinate covalent bond*** is the term given to bonds formed when both electrons come from the same atom. Look at the equation below.



This is a Lewis acid combining with a Lewis base and therefore, this reaction represents a Lewis acid-base neutralization reaction. Since both of the electrons that participate in the bond between N and B have come from the Lewis base NH_3, the N—B bond is a coordinate covalent bond.

Sample question: Identify the Lewis acid and Lewis base in each of the following reactions. Then write the reactions to show that these reactions involve coordinate covalent bonds.

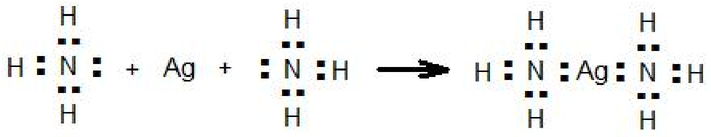
(a) $Ag^+_{(aq)} + 2\ NH_{3\ (aq)} \rightarrow Ag(NH_3)_{2\ (aq)}$

(b) $H_2O_{(L)} + NH_{3\ (aq)} \rightarrow NH_4OH_{(aq)}$

Solution:

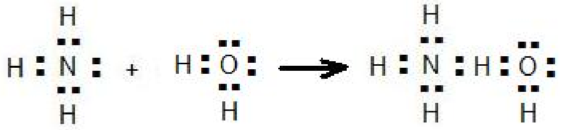
(a) $Ag^+_{(aq)}$ $+2\ NH_{3\ (aq)} \rightarrow Ag(NH_3)_{2\ (aq)}$

Acid Base



(a) $H_2O_{(L)}$ $+NH_{3\ (aq)} \rightarrow NH_4OH_{(aq)}$

Acid Base



Lesson Summary

- Lewis defined an acid as a substance that accepts a pair of electrons from a substance to form a bond. Lewis defined a base as a substance that donates a pair of electrons to a substance to form a bond.
- Coordinate covalent bond is the term given to bonds formed when both electrons come from the same atom.

Review Questions

1. How do the Lewis definitions of acids and bases compare to the Bronsted-Lowry definitions of acids and bases? **(Intermediate)**

2. In the following reversible reaction, which of the reactants is acting as a Lewis base? **(Intermediate)**

$Cd^{2+}{}_{(aq)} + 4I^{-}{}_{(aq)} \leftrightarrows CdI_4{}^{2-}{}_{(aq)}$

(a) Cd^{2+}

(b) I^{-}

(c) $CdI_4{}^{2-}$

(d) none of the above, this is not an acid-base reaction.

3. Which of the following statements are false? **(Intermediate)**

(a) NH_3 is a Lewis base.

(b) $B(OH)_3$ is a Lewis acid.

(c) CO_2 is a Lewis base.

(d) Ag^{+} Is a Lewis acid.

4. Which of the following statements are true? **(Intermediate)**

(a) NH_3 is a Lewis base.

(b) $B(OH)_3$ is a Lewis acid.

(c) CO_2 is a Lewis base.

(d) Ag^{+} Is a Lewis acid.

5. Classify each of the following as a Lewis acid or base. (a) H_2O (b) BF_3 (c) S^{2-} (d) Cu^{2+} (e) O^{2-} **(Intermediate)**

6. Write the balanced chemical equation between $SO_3{}^{2-}$ and H_2O and label the Lewis acids and bases. **(Intermediate)**

7. Identify the Lewis acid and Lewis base in each of the following reactions. Then write the reactions. **(Intermediate)**

(a) $Cu^{2+}{}_{(aq)} + 6\ H_2O_{(L)} \longrightarrow Cu(H_2O)_6{}^{2+}{}_{(aq)}$

(b) $(CH_3CH_2)_2O_{(aq)} + AlCl_{3\,(aq)} \longrightarrow (CH_3CH_2)_2O\ AlCl_{3\,(aq)}$

Further Reading / Supplemental Links

http://en.wikipedia.org

Vocabulary

Lewis acid	A substance that accepts a pair of electrons from a substance (i.e. BF_3).
Lewis base	A substance that donates a pair of electrons from a substance (i.e. NH_3).
coordinate covalent bond	A covalent bond formed where both electrons that are being shared come from the same atom.

Review Answers

1.

	Arrhenius	Bronsted-Lowry	Lewis
Acids	Produces H^+ ions in water	Donates a proton (H^+) to a base	Accepts an electron pair from a base
Bases	Produces OH^- ions in water	Accepts a proton (H^+) from and acid	Donates an electron pair to an acid.

2. (b) I^-

3. (c) CO_2 is a Lewis base.

4. All are true.

5.

(a) H_2 has a pair of electrons to donate, therefore is a Lewis base.

(b) BF_3 has no unshared pairs of electrons but it has a space to accept a pair of electrons and therefore, it is a Lewis acid.

(c) S^{2-} has pairs of electrons to share so it is a Lewis base.

(d) Cu^{2+} has no pairs to share but has space to accept a pair of electrons so it is a Lewis acid.

(e) O^{2-} has pairs of electrons to share so it is a Lewis base.

6. $SO_3{}^{2-}{}_{(aq)} + H_2O_{(L)} \longrightarrow HSO_3{}^{-}{}_{(aq)} + OH^-{}_{(aq)}$

Lewis base = $SO_3{}^{2-}$; the -2 charge on the ion means there lone pairs of electrons on the central atom, and therefore, $SO_3{}^{2-}$ would tend to donate these electrons (or share in a covalent bond) to H_2O in solution. Lewis acid = H_2O

7. (a) $Cu^{2+}{}_{(aq)} + 6\ H_2O_{(L)} \longrightarrow Cu(H_2O)_6{}^{2+}{}_{(aq)}$

Lewis acid   Lewis base

(b) $(CH_3CH_2)_2O_{(aq)} + AlCl_{3\ (aq)} \longrightarrow (CH_3CH_2)_2O\ AlCl_{3\ (aq)}$

Lewis base   Lewis acid

Both of these products involve coordinate covalent bonds because in each case the electron pairs participating in the bonding came from the same atom.

26. Water, pH and Titration

Water Ionizes

Lesson Objectives

- The student will write the equation for the autoionization of water and express the concentration of hydrogen and hydroxide ion in a neutral solution at 25°C.
- The student will express the value of K_w in a water solution at 25°C.
- The student will write the formulas for pH and pOH and show the relationship between these values and K_w.
- The student will express the relationship that exists between pH, pOH, and K_w.
- Given the value of any one of the following values in a water solution at 25°C, the student will calculate all the other values; $[H^+]$, $[OH^+]$, pH, and pOH.
- The student will state the range of values for pH that indicate a water solution at 25°C is acidic.
- The student will state the range of values for pH that indicate a water solution at 25°C is basic.
- The student will state the range of values for pH that indicate a water solution at 25°C is neutral.

Introduction

There are many properties of water that we have learned. We know, for example, that water is called the universal solvent because of its ability to dissolve both polar substances as well as most ionic ones. We also know that pure water does not conduct electricity. The reason pure water does not conduct electricity is because of the small concentration of ions present when water ionizes. In this lesson, we will look a little closer at the uniqueness of autoionization. We will expand on the effect other added substances have on the $[H_3O^+]$ and $[OH^-]$ in water. Thus, we need to have formulas readily available to calculate the pH, the pOH, the $[H_3O^+]$, and/or the $[OH^-]$. Much of what you will learn may be review.

Water Ionization is Small But Significant

Autoionization, as we learned in a previous lesson, is the process where the same molecule acts as both an acid and a base. Water is one of the compounds that can exhibit this unique property. When speaking about the autoionization of water, another term that is also used is the self-ionization of water. The reaction for the autoionization of water is shown in Equation 1 and its net ionic equation in Equation 2.

$$H_2O_{(L)} + H_2O_{(L)} \leftrightarrows H_3O^+{}_{(aq)} + OH^-{}_{(aq)} \qquad \text{(Equation 1)}$$

$$H^+ + OH^- + H_2O \leftrightarrows H_3O^+{}_{(aq)} + OH^-{}_{(aq)} \qquad \text{(Equation 2)}$$

If you notice in Equation 1, one $H_2O_{(L)}$ molecule donates a proton and is therefore a Brønsted-Lowry acid; the second $H_2O_{(L)}$ molecule accepts a proton and is therefore a Brønsted-Lowry base.

While this does indeed occur, it only happens to about 2 molecules for every billion! This is the reason that pure – or what can also be referred to as distilled or deionized water – will not conduct electricity. In contrast, water that comes into our houses and we get from turning on the tap, is not pure water and *can* conduct electricity. You may have seen hair dryers with warnings labels attached that remind you not to use them while in the bath. Tap water has various ions dissolved in it, which makes it an electrolyte and an electrical current that could pass through tap water and into you, could be dangerous. Some of the ions that are dissolved in tap water are Na^+, Cl^-, Mg^{2+}, Ca^{2+} and various others. When tap water boils away it often leaves a residue in the pan or kettle.

The Mathematics of pH and pOH

Water ionizes to a very slight degree.

$$H_2O_{(L)} \leftrightarrows H^+ + OH^-$$

At 25°C, the ionization equation above reaches equilibrium when $[H^+] = [OH^-] = 1 \times 10^{-7}$ M. Therefore, the equilibrium constant for this reaction, at 25°C, will be:

$$K_w = [H^+][OH^-] = (1 \times 10^{-7})(1 \times 10^{-7}) = 1 \times 10^{-14}$$

When the concentrations of the hydrogen and hydroxide ions are equal, we say the solution is neutral. When some substance is added to the water and alters the hydrogen and hydroxide ion concentrations so that they are no longer equal, the solution will become either acidic or basic. The hydrogen and hydroxide ions will return to an equilibrium position but the concentrations of the ions may not be equal.

If, at equilibrium, $[H^+] > [OH^-]$, the solution is acidic.

If, at equilibrium, $[H^+] = [OH^-]$, the solution is neutral.

If, at equilibrium, $[H^+] < [OH^-]$, the solution is basic.

pH is used to express the acid strength of water solutions.

$$pH = -\log [H^+]$$

For acid solutions, the pH will be less than 7. For basic solutions, the pH will be greater than 7. For solutions that are neutral, the pH will be equal to 7.

The pH equation can also be used to find the hydrogen ion concentration when the pH is given.

$$[H^+] = 10^{-pH}$$

Even though both acidic and basic solutions can be expressed by pH, someone decided to create an equivalent set of expressions for the concentration of the hydroxide ion in water; hence pOH.

$$pOH = -\log [OH^-]$$

If the pOH is greater than 7, the solution is acidic. If the pOH is equal to 7, the solution is neutral. If the pOH is less than 7, the solution is basic.

If we take the negative log of the complete K_w expression:

$$K_w = [H^+][OH^-]$$

$-\log K_w = (-\log [H^+]) + (-\log [OH^-])$

$-\log (1 \times 10^{-14}) = (-\log [H^+]) + (-\log [OH^-])$

$14 = pH + pOH.$

We can determine that the sum of the pH and the pOH is always equal to 14 (at 25°C).

Remember that the pH scale is written with values from 0 to 14 because many useful acid and base solutions fall within this range. We can use this formula to carry many different types of calculations. Before moving on to these, one more deduction can be made from all that we have done so far. If p( ) = -log( ) such that $pH = -\log [H^+]$ and $pOH = -\log [OH^-]$ and we know that $K_w = 1.00 \times 10^{-14}$, then we can calculate pK_w using the formula $pK_w = -\log K_w$.

Now let's go through a few examples to see how this calculation works for problem-solving in solutions other than water.

Sample question 1: What is the $[H^+]$ for a solution of NH_3 whose $[OH^-] = 8.23 \times 10^{-6}$ mol/L?

Solution:

$[H_3O^+][OH^-] = 1.00 \times 10^{-14}$

$$[H_3O^+] = \frac{1.00 \times 10^{-14}}{[OH^-]} = \frac{1.00 \times 10^{-14}}{[8.23 \times 10^{-6}]} = 1.26 \times 10^{-9} \text{ M}$$

Sample question 2: Black coffee has a $[H_3O^+] = 1.26 \times 10^{-5}$ mol/L. What is the pOH?

Solution:

$pH = -\log [H^+] = -\log 1.26 \times 10^{-5} = 4.90$

$pH + pOH = 14$

$pOH = 14 - pH = 14 - 4.90 = 9.10$

Lesson Summary

- Autoionization is the process where the same molecule acts as both an acid and a base:
- $pK_w = -\log K_w$
- $pH + pOH = pK_w = 14.0$
- $pH + pOH = 14.0$ is a formula used to find a number of different pieces of information from an acid-base equation including $[H^+]$, $[OH^-]$, pH, and pOH. Only one of these four pieces must be known to find the other three.

Review Questions

1. How do pH and pOH relate to the pH scale? **(Intermediate)**

2. What does the value of K_w tell you about the autoionization of water? **(Intermediate)**

3. If the pH of an unknown solution is 4.25, what is the pOH? **(Intermediate)**

(a) $10^{-4.25}$

(b) $10^{-9.75}$

(c) 9.75

(d) 14.0 - $10^{-9.75}$

4. A solution contains a hydronium ion concentration of 3.36 x 10^{-4} mol/L. What is the pH of the solution? **(Intermediate)**

(a) 3.36

(b) 3.47

(c) 10.53

(d) none of the above

5. A solution contains a hydroxide ion concentration of 6.43 x 10^{-9} mol/L. What is the pH of the solution? **(Intermediate)**

(a) 5.80

(b) 6.48

(c) 7.52

(d) 8.19

6. An unknown solution was found in the lab. The pH of the solution was tested and found to be 3.98. What is the concentration of hydroxide ion in this solution? **(Intermediate)**

(a) 3.98 mol/L

(b) 0.67 mol/L

(c) 1.05 x 10^{-4} mol/L

(d) 9.55 x 10^{-11} mol/L

7. If a solution is known to have a hydroxide ion concentration of 2.5 x 10^{-5} mol/L, then the pH of the solution is ___________ and it is ___________. **(Intermediate)**

(a) 2.5, acidic

(b) 4.6, basic

(c) 4.6, acidic

(d) 9.4, basic

8. K_w is the ionization product constant for water but is also the equilibrium constant for the acid-base autoionization reaction for water. When dealing with equilibrium constants, such as K_w, it is important to take

into account the temperature as temperature affects the value of the equilibrium constant. The value of 1.0 x 10^{-14} for K_w is for a temperature of 25°C. If the temperature was raised to 60°C, the value of K_w changes to 1.0 x 10^{-13}. How does this effect $[H^+]$,$[OH^-]$, pH, and pOH? **(Challenging)**

Further Reading / Supplemental Links

http://en.wikipedia.org

Vocabulary

autoionization The process where the same molecule acts as both an acid and a base.

Review Answers

1. The pH scale is typically a scale from 0 to 14 because most acids and bases fall within these values. A pH scale measures the level of H^+ ions, decreasing as the pH increases. The pOH scale measures the level of OH^- which would also decrease as pOH increases. For acids and bases dissolved in water, there is always present some form level of H^+ and OH^- in the solution. We can then calculate the pH and the pOH for these solutions. pH + pOH = 14.0.

2. Since $K_w = 1.0 \times 10^{-14}$ which is a very small number, it means that there are very few products and a large number of reactants.

3. (c) 9.75

4. (b) 3.47

5. (a) 5.80

6. (d) 9.55 x 10^{-11} mol/L

7. (d) 9.4, basic

8. $K_w = [OH^-][H_3O^+]$

$[H_3O^+] = [OH^-]$

$K_w = [H_3O^+]^2$

$1.0 \times 10^{-13} = [H_3O^+]^2$

$[H_3O^+] = \sqrt{1.0 \times 10^{-13}}$

$[H_3O^+] = 3.16 \times 10^{-7}$ mol/L

$[OH^-] = 3.16 \times 10^{-7}$ mol/L

$pH = -\log [H_3O^+]$

$\text{pH} = -\log (3.16 \times 10^{-7})$

$\text{pH} = 6.50$

$\text{pOH} = -\log [\text{OH}^-]$

$\text{pOH} = -\log (3.16 \times 10^{-7})$

$\text{pOH} = 6.50$

Indicators

Lesson Objectives

- Define an acid-base indicator.
- Explain the difference between natural and synthetic indicators.
- List examples of natural and synthetic indicators.
- Explain how indicators work.
- Explain the usefulness of indicators in the lab.

Introduction

Indicators are used everyday both in our lives and in our laboratories. We make a cup of tea, we work in the garden, we have a bowl of cereal and throw some blueberries on it, or we may go to chemistry class and do an experiment to identify some of the properties of household substances using indicator solutions. All of these situations involve the use of indicators; the only difference is that some indicators are natural and some are synthetic (well, maybe – depending what you use in your chemistry class!) In this lesson you are going to examine the concept of natural and synthetic indicators and the use of these in the modern chemistry lab.

Substances That Change Color Due to pH Change

Litmus paper is a paper that has been dipped in a substance that will undergo a color change when it is dipped in either an acid or a base. The litmus paper is called an indicator because it is used to indicate whether the solution is an acid or a base. If the red litmus paper turns blue, the solution is basic (pH > 7), if the blue litmus turns red the solution is acidic (pH < 7).

Figure 1: Hydrangeas

(*Source:* http://www.publicdomainpictures.net/view-image.php?image=1254, *License:* Public Domain)

An indicator is a substance that changes color at a specific pH and is used to indicate the pH of the solution. The juice from red cabbage, for example, can be used to prepare an indicator paper. It contains the chemical anthrocyanin which is the active ingredient in the indicator. Did you know that there are actually indicator fish in the world? It's true! In Singapore there are fish that have been genetically altered with the indicator in hopes of detecting pollutants in the water. These rainbow fish turn color from green to red depending on the amounts of heavy metals and are thus given their name. (You may see, in news articles, these fish referred to as "litmus fish" but, of course, the color changes in these fish have nothing to do with the substance litmus.) Another example of a natural indicator is flowers. Hydrangea is a common garden plant with flowers that come in many colors depending on the pH of the soil. If you are travelling around and see a hydrangea plant with blue flowers, the soil is acidic, the creamy white flowers indicate the soil is neutral, and the pink flowers mean the soil is basic.

A ***natural indicator*** is an indicator that is produced from a substance that is naturally occurring or is itself a naturally occurring substance. Red beets, blueberries, and cranberries are other great examples of a naturally occurring indicator. These are all due to the same active ingredient anthocyanin found in the red cabbage.

So how do naturally occurring indicators differ from synthetic indicators? ***Synthetic indicators*** are compounds created in a chemistry lab rather than compounds found in nature. Both naturally occurring indicators and synthetic indicators are weak organic acids or bases. For example, a common synthetic indicator used in most chemistry laboratories is phenolphthalein (see Figure 1).

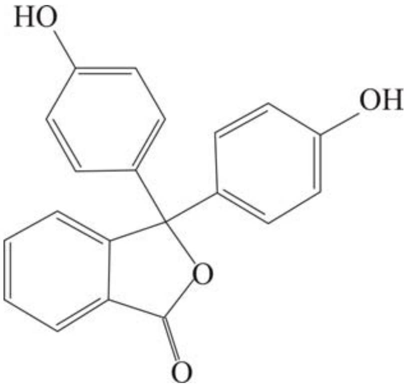


Figure 2: Structure of Phenolphthalein.

(*Source:* http://commons.wikimedia.org/wiki/File:Phenolphthalein, *Author:* Andel Fruh, *License:* Public Domain)

This indicator, in particular, changes color at pH of 8.2, before 8.2 it is colorless and after 8.2 it is pink. There are many common synthetic indicators that are useful in the chemistry laboratory. All of these have similar structures. In the acidic range, chemistry students may use methyl orange. The structure for methyl orange is shown in Figure 3.

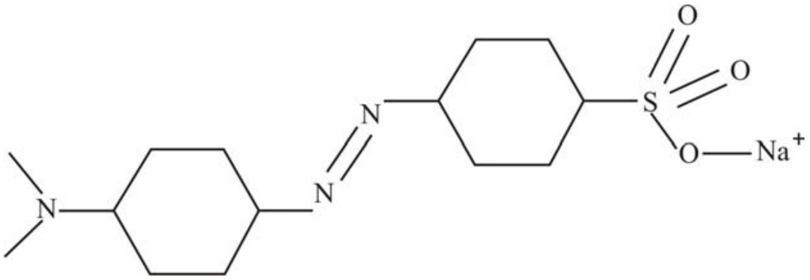


Figure 3: Structure of Methyl Orange (Yellow Form).

(*Source:* http://commons.wikimedia.org/wiki/File:Methyl-orange-skeletal, *License:* Public Domain)

Methyl Orange changes color from pH 3.2 to 4.4. Below 3.2, the color of the indicator is red. Above 4.4 the color of the indicator is yellow. In between 3.2 and 4.4, at 3.8, the color would be orange … hence the name.

What happens chemically when there is a color change is that the structure of the molecule donates or accepts a proton. Remember Bronsted-Lowry acids and bases? A Bronsted-Lowry acid donates a proton and a Bronsted-Lowry base accepts a proton. There are two requirements for a substance to function as an acid-base indicator; 1) the substance must have an equilibrium affected by hydrogen ion concentration, and 2) the two forms of the compound on opposite sides of the equilibrium must have different colors. Most indicators function in the same general manner and can be presented by a generic indicator equation. In the equation below, we represent in the indicator ion with a hydrogen ion attached as HIn and we represent the indicator ion without the hydrogen attached as In^-.

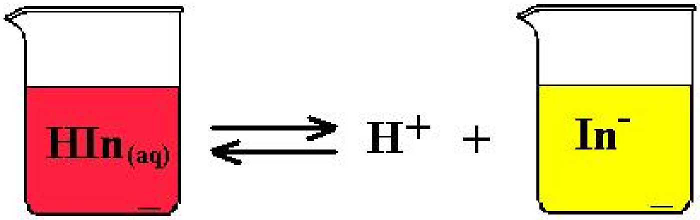


Figure 4: The color of an indicator depends on the pH of the solution.

(*Created by:* Richard Parsons, *License:* CC-BY-SA)

Since the indicator itself is a weak acid, the equilibrium between the protonated form and the anionic form is controlled by the hydrogen ion concentration. For the example above, the protonated form is colored red and the anionic form is colored yellow. If we add hydrogen ion to the solution, the equilibrium will be driven toward the reactants and the solution will turn red. If we add base to the solution (reduce hydrogen ion concentration), the equilibrium will shift toward the products and the solution will turn yellow. It is important to note that if this indicator changes color at pH = 5, then at all pH values less than 5, the solution will be red and at all pH values greater than 5, the solution will be yellow. Therefore, putting this indicator into a solution and having the solution turn yellow does NOT tell you the pH of the solution . . . it only tells you that the pH is greater than 5 . . . it could be 6, 7, 8, 9, etc. At pH values less than 5, the great majority of the indicator molecules are in the red form and the solution will be red. At pH's greater than 5, the great majority of the indicator particles will be in the yellow form and the solution will be yellow. The equilibrium between these indicator particles is such that the particles will be 50% red form and 50% yellow form at exactly pH = 5. Therefore, at pH = 5, the actual color of the solution will be a 50-50 mixture of red and yellow particles and the solution will be ORANGE.

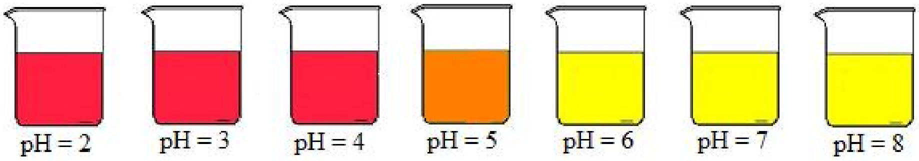


Figure 5: The color change of an indicator occurs over a very short range.

(*Created by:* Richard Parsons, *License:* CC-BY-SA)

You should recognize that an indicator will only indicate the actual pH at one particular pH and that is the color-change pH.

Laboratory Uses for pH Indicators

There are many indicators that are available to be used to help determine the pH of solutions. A list of the most common indicators is found in Table 1 along with their respective color change pHs and corresponding color changes.

Table 1: Colors and pH Ranges for Common Indicator

Indicator	pH range	Color Range
Methyl violet	0.0 - 1.6	Yellow - Blue
Thymol blue	1.2 - 2.8	Red – Yellow
Orange IV	1.3 – 3.0	Red – Yellow
Methyl orange	3.2 - 4.4	Red – Orange
Bromphenol Blue	3.0 – 4.7	Orange/Yellow – Violet
Congo Red	3.0 - 5.0	Blue – Red
Bromocresol green	3.8 - 5.4	Yellow – Blue
Methyl red	4.8 - 6.0	Red – Yellow
Litmus	5.0 - 8.0	Red – Blue
Chlorophenol Red	4.8 – 6.2	Yellow – Red
Bromothymol blue	6.0 - 7.6	Yellow – Blue
Phenol Red	6.4 – 8.2	Yellow –Red/Violet
Thymol blue	8.0 - 9.6	Yellow – Blue
Phenolphthalein	8.2 - 10.0	Colorless – Pink
Thymolphthalein	9.4 - 10.6	Colorless – Blue
Alizarin yellow R	10.1 - 12.0	Yellow – Red
Methyl Blue	10.6 – 13.4	Blue – Pale Violet
Indigo Carmine	11.4 – 13.0	Blue – Yellow

There are many more indicators than are shown in the table above. Those that are shown are ones that you may find in common chemistry classroom laboratories or in universities depending on where you are located or what your experimental needs are at the time. One that is not found in the table is known as the universal indicator. The universal indicator is a solution that has a different color for each pH from 0 – 14. Universal indicator is produced by creatively mixing many of the individual indicators together so that a different coor is achieved for each different pH. It is used for all types of experiments to determine if solutions are acids or bases and where on the pH scale the substance belongs. The chart below indicates the colors of universal indicator for different pH values.

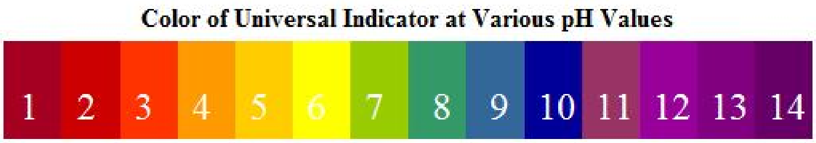


Figure 5: The color of Universal Indicator at various pH's.

(*Created by:* Richard Parsons, *License:* CC-BY-SA)

Why is this information be so important? If you look at Table 1, Thymol blue changes color from pH of 8.0 to pH = 9.6. What this means is that from pH of 0 to pH of 8.0, the color of the solution will stay yellow. At pH = 8.0 the color will begin to change from yellow to blue and from pH of 9.6 until pH = 14, the color of the solution will be blue. Around pH = 8.8 (the midway mark between 8.0 and 9.6) the color of the solution would be green.

Sample question: If the pH of the solution is 4.8, what would be the color of the solution if the following indicators were added?

(a) Universal indicator

(b) Bromocresol Green

(c) Phenol red

Solution:

(a) Universal indicator = Orange to orange-yellow (see table 2)

(b) Bromocresol Green = green (midway pH = 4.6)

(c) Phenol red = yellow

There is another important use for indicators in the lab and this is to determine the pH of an unknown solution. They are also used in titrations, a concept we will be exploring in the another lesson. For now, let's look at how we can use indicators to determine the pH of an unknown solution. For example, a solution has been found in the laboratory that was tested with a number of indicators. It was found that the following indicators showed these results:

Phenolphthalein was colorless

Bromocresol green was blue

Methyl red was yellow

Phenol red was yellow

What was the pH of the solution? Let's look at the data.

Phenolphthalein was colorless, pH < 8.0

Bromocresol green was blue, pH > 5.4

Methyl red was orange, pH > 6.2

Phenol red was yellow, pH < 6.4

Therefore the pH of the solution must be between 6.3 and 6.4.

Lesson Summary

- An indicator is a substance that changes color at a specific pH and is used to indicate the pH of the solution. A natural indicator is an indicator that is produced from a substance that is naturally occurring or is itself a naturally occurring substance.

- Synthetic indicators are normally an organic weak acid or base with usually a complicated structure. Universal indicator is a solution that has a different color for each pH from 0 – 14.

Review Questions

1. Describe the uses for litmus and universal indicator in the laboratory setting. **(Beginning)**

2. What is the difference between a natural and a synthetic indicator? **(Beginning)**

3. Describe how indicators work. **(Intermediate)**

4. If you had an acid-base neutralization reaction that turned phenolphthalein pink and Thymolphthalein blue, what is the pH of the solution? **(Intermediate)**

(a) 8.2

(b) 9.4

(c) 10

(d) Not enough information is available.

5. If you had an acid-base neutralization reaction that turned methyl violet blue and Thymol blue orange, what is the pH of the solution? **(Intermediate)**

a. 1.6

b. 2.0

c. 2.8

d. Not enough information is available.

6. Universal indicator is an indicator commonly used in the laboratory. At a pH of 6 it is pale yellow and at a pH of 4 it is pale orange. If the indicator was orange, which statement would be definitely true? **(Intermediate)**

(a) The solution is probably acidic.

(b) The pH is between 4 and 5.

(c) The solution is probably basic.

(d) The pH is less than 5.0.

7. Alizarin Yellow R is an indicator that changes color in the pH range from 10.1 to 12.0. Below 10.1 the color is Yellow, above 12.0 the color is red. If the color of the solution containing Alizarin Yellow R was orange, which statement about the solution would be true? **(Intermediate)**

(a) The pH is below 10.

(b) The pH is above 12.0.

(c) The solution is definitely acidic.

(d) The pH is between 10.1 and 12.0.

8. If the pH of the solution is 8.9, what would be the color of the solution if the following indicators were added? **(Intermediate)**

(a) Universal indicator

(b) Thymol blue

(c) Methyl blue

9. A solution has been found in the laboratory that was tested with a number of indicators. It was found that the following indicators showed these results: **(Intermediate)**

(a) Phenolphthalein was colorless

(b) Orange IV was yellow

(c) Universal indicator was orange

(d) Methyl orange was red

What was the pH of the solution?

Further Reading / Supplemental Links

http://en.wikipedia.org

Vocabulary

indicator	A substance that changes color at a specific pH and is used to indicate the pH of the solution.
natural indicator	An indicator that is produced from a substance that is naturally occurring or is itself a naturally occurring substance.
synthetic indicator	An indicator that is a complicated structure of an organic weak acid or base.

Review Answers

1. Litmus has a pH range of 5.0 to 8.0. Therefore it is good for distinguishing an acid solution from a base solution. The universal indicator shows a different color at each pH level from 1.0 through to 12.0. It is more useful than litmus and is indeed used more readily in classroom laboratories for titrations.

2. A natural indicator is produced naturally (i.e. Hydrangea plants change different colors depending on the pH of the soil) or occurs itself in nature (i.e. blueberries). Synthetic indicators are weak organic acids or bases that are prepared as indicators commercially (i.e. methyl orange).

3. Indicators work by donating or accepting protons and in so doing change colors.

4. d

5. b

6. (b) The pH is between 4 and 5.

7. (d) The pH is between 10.1 and 12.0.

8. (a) Universal indicator = dark green

(b) Thymol blue = green (midway pH = 8.8)

(c) Methyl blue = blue

9. (a) Phenolphthalein was colorless, pH < 8.0

(b) Orange IV was yellow, pH > 3.0

(c) Universal indicator was orange, pH = 3-4

(d) Methyl orange was red, pH < 3.2

Therefore the pH of the solution must be between 3.0 and 3.2, should be pH = 3.1 .

Titrations

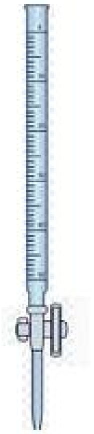
Lesson Objectives

- Define titrations and identify the different parts of the titration process.
- Explain the difference between the endpoint and the equivalence point.
- Describe the three types of titration curves.
- Identify points on the titration curves for the three types of titrations.
- Define a standard solution.
- Calculate the accurate concentration of an acid or base using a standard.
- Calculate unknown concentrations or volumes of acids or bases at equivalence.

Introduction

For acid-base neutralization reactions, the typical laboratory procedure for determining the stoichiometric amounts of acid and/or base in the reaction is to complete a titration. There are three main types of titration experiments and each of these has some similarities but also have some differences. A titration experiment can involve equipment from the simple (such as using an eyedropper) to the complex (such as using a burette, a pH meter, a magnetic stirrer). As we go through this lesson, we will use some of the prior knowledge we have obtained about acids and bases, about chemical reactions, molarity calculations, and about indicators to apply them to the concept of titrations.

Titration



One of the properties of acids and bases is that they neutralize each other. In the laboratory setting, an experimental procedure where an acid is neutralized by a base (or vice versa) is known as a titration. A ***titration,*** by definition, is the addition of a known concentration of base (or acid) (also called the ***titrant***) to a solution of acid (or base) of unknown concentration. Since both volumes of the acid and base are known, the concentration of the unknown solution is then mathematically determined. So what does one do in a titration? When doing a titration, you need to have a few pieces of equipment. A ***burette*** (see Figure 1) is used to accurately dispense the volume of the solution of known concentration (either the base or the acid). An ***Erlenmeyer flask*** is used to hold a known volume of the unknown concentration of the other solution (either the acid or the base). Also an indicator is used to determine the endpoint of the titration. A few drops of the indicator are added to the flask before you begin the titration. The ***endpoint*** is the point where the indicator changes color, which tells us that the acid is neutralized by the base. The ***equivalence point*** is the point where the number of moles of acid exactly equals the number of moles of base. The equivalence point is a calculated point in the neutralization of the acid and the base. Some laboratories have pH meters (see Figures 2A and 2B) that measures this point more accurately than the indicator although an indicator is much more visual! Diagram 2A shows a simplified version of a pH meter with the probe from the meter immersed in the liquid. Diagram 2B shows a typical electronic pH meter with the attached probes. The main purpose of a pH meter is to measure the changes in pH as the titration goes from start to finish.

Figure 1: Burette (*Created by:* Richard Parsons, *License:* CC-BY-SA)

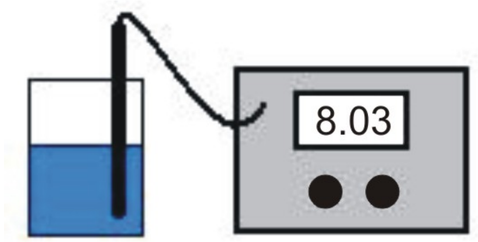


Figure 2A: A simple pH meter with its probe immersed in a mildly alkaline solution (pH = 8.03). The two knobs on the meter are used to calibrate the instrument. (*Created by:* Therese Forsythe, *License:* CC-BY-SA)

Figure 2B: An electronic pH meter (*Source:* http://commons.wikimedia.org/wiki/File:PH_meter.jpg, *Author:* Datamax, *License:* Public Domain)

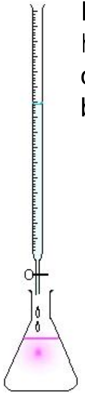


Figure 3 shows a typical titration setup. The burette is upright ready to drip the solution into the flask holding the solution of unknown concentration and the few drops of indicator. When the indicator changes color, the number of moles of acid equals the number of moles of base and the acid (or base) has been neutralized.

Figure 3: Typical Titration Setup.

(*Source:* http://commons.wikimedia.org/wiki/File:Titration.jpg, *Author:* Theresa Knott, *License:* GNU Free Documentation License)

There are three types of titrations that are normally performed in the laboratory in order to determine the unknown concentration of the acid or base. These three types are:

(1) Strong acid vs. Strong base

(2) Strong acid vs. Weak base

(3) Weak Acid vs. Strong base

In these titrations, a pH meter may be used to measure the changes in the pH as the titration goes to completion. If so, a titration curve can be constructed for each curve. A ***titration curve*** is a graph of the pH versus the volume of titrant added. Let's take a look at how each of these types of titrations differs in terms of their pH curves and their pH at the equivalence point.

(1) Strong Acid vs. Strong Base

For a strong acid vs. a strong base titration, let's assume the strong base is the titrant. Therefore, in the Erlenmeyer flask is the strong acid and a few drops of your indicator. Think about the pH of the solution in the flask. Do you think it will be high (around pH = 11.0), mildly basic (around pH = 8.0), mildly acidic (around pH = 6.0), or low (around pH = 1.0)? Probably the pH will be around 1.0 since the solution is a strong acid. As the base is added, the acid is slowly neutralized. At first the change in pH is minimal. This resistance is due to the fact that the flask has a much greater number of H_3O^+ ions than the OH^- ions available from the added titrant.

As more and more base is added, more OH^- ions are added and thus more H_3O^+ ions get neutralized. Let's stop here and look at the reaction. Equation 1 shows the total ionic equation of a reaction between a strong acid and a strong base.

$$H^+_{(aq)} + Cl^-_{(aq)} + Na^+_{(aq)} + OH^-_{(aq)} \rightarrow Na^+_{(aq)} + Cl^-_{(aq)} + H_2O_{(L)} \text{ (Equation 1)}$$

Equation 2 shows the net ionic equation for the reaction between the strong acid and the strong base.

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(L)} \text{ (Equation 2)}$$

So you see that as we add more OH^- ions, more H_3O^+ (or H^+) ions are being neutralized. Since these two ions react to form water, a neutral solution will be formed. For a strong acid and a strong base, this means the pH = 7.0 at the point of neutralization. If we continue to add the titrant (containing OH^- ions) after all of the H_3O^+ ions have been neutralized, the pH will continue to rise as more base is added and there are excess OH^- ions.

Now we know what happens in a strong acid/strong base titration, what does the titration curve look like? Look at Diagram 4. The main points of the titration curve described above are shown in the titration curve below.

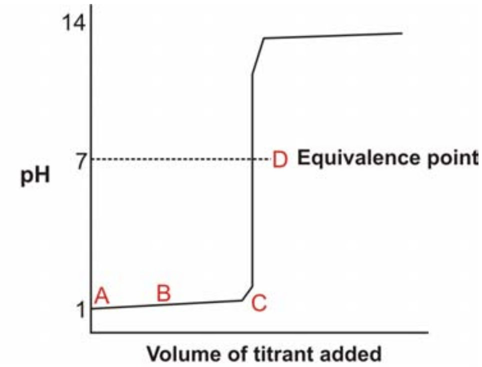


Figure 4: Titration Curve for a Strong Acid vs. Strong Base.

(*Created by:* Therese Forsythe, *License:* CC-BY-SA)

The points A through D sum up the description of the events that take place during the titration. Point A is the start of the titration. Point B is the midpoint, the point where half of the H^+ ions have been neutralized.

Point D is the equivalence point.

(2) Strong Acid vs. Weak Base

What would happen if we were to titrate a strong acid with a weak base or vice versa? Look at Diagram 5. Can you determine what is happening in the titration just by looking at the graph?

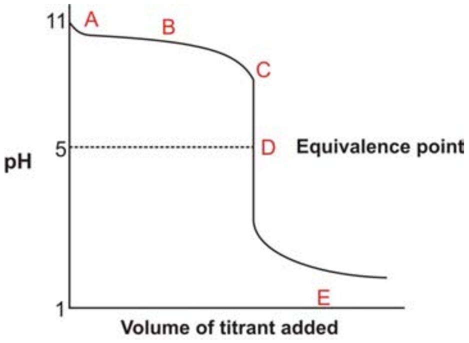


Figure 5: Titration Curve for a Strong Acid vs. Weak Base.

(*Created by:* Therese Forsythe, *License:* CC-BY-SA)

When you look at Point A, the pH is high but not too high (pH approx 11). This means that there is a weak base in the flask. As the acid (the titrant) is added, the pH decreases as the H_3O^+ ions being added and begin to neutralize the OH^- ions. Point C represents the point where the volume of acid necessary to neutralize the base is measured. Therefore, if we draw a line down to the x-axis, we can find the volume of titrant necessary for the neutralization reaction (same as before). Point D is the equivalence point. Notice that for a weak base and a strong acid titration, the pH at equivalence point is more acidic. Equation 3 is the reaction between $NH_{3(aq)}$, a weak base, and $HCl_{(aq)}$, a strong acid.

$NH_{3(aq)} + HCl_{(aq)} \rightarrow NH_4Cl_{(aq)} + H_2O_{(L)}$ (Equation 3)

The ionic equation is Equation 4.

$NH_{3(aq)} + H^+_{(aq)} + Cl^-_{(aq)} \rightarrow NH_4^+{}_{(aq)} + Cl^-_{(aq)} + H_2O_{(L)}$ (Equation 4)

(3) Weak Acid vs. Strong Base

The third type of titration is that of a weak acid with a strong base. When we follow through with the same procedure as was done with the previous two titrations, we can determine a great deal of information simply by looking at the pH curve. For example, let's consider the titration of a solution of acetic acid, $HC_2H_3O_2$, with a solution of potassium hydroxide, KOH. We can write the chemical reaction for this acid-base neutralization (see Equation 5) and begin to draw a rough sketch of a titration curve.

$H^+_{(aq)} + C_2H_3O_2^-{}_{(aq)} + K^+_{(aq)} + OH^-_{(aq)} \rightarrow K^+_{(aq)} + C_2H_3O_2^-{}_{(aq)} + H_2O_{(L)}$ (Equation 5)

Acetic acid is a weak acid and we know that the pH at the start of the titration will be around 2.8. Potassium hydroxide is a strong base so the curve will end high on the graph, around a pH = 12.

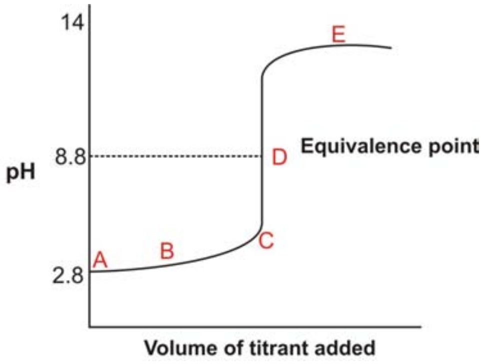


Figure 6: Titration Curve for a Weak Acid vs. Strong Base.

(*Created by:* Therese Forsythe, *License:* CC-BY-SA)

The points on the curve represent the same points as with the other two titration curves. Look, however, at the equivalence point. Notice how the pH for the equivalence point of the weak acid-strong base titration is above 7.0. Look at Equation 5.

Sample question: Draw a rough sketch of the titration curve between nitric acid and ethylamine, CH_3NH_2. Assume the acid is in the burette. What is the estimated pH at the equivalence point?

Solution:

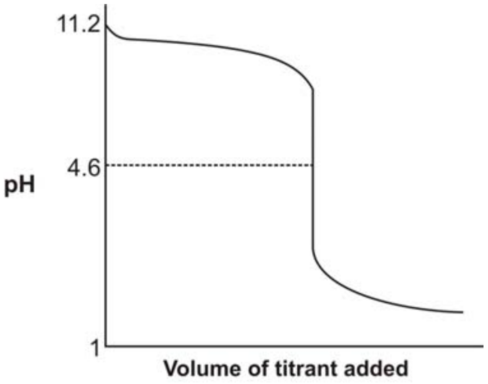


Figure 7: Titration Curve for a HNO_3 vs. CH_3NH_2.

(*Created by:* Therese Forsythe, *License:* CC-BY-SA)

The pH at the equivalence point is approximately 4.6 from this graph.

Standard Solutions

As was previously stated, when we do a titration the titrant is the solution of known concentration. For accuracy reasons, this titrant is normally titrated to find the exact concentration before beginning the acid-base titration. The purpose of this initial titration is to determine, with as much accuracy as possible, the exact concentration of the solution in the burette. To determine the exact concentration of the titrant, we use a standard solution. A ***standard solution*** is a solution whose concentration is known exactly. Standard solutions have this property because these chemicals are normally found in pure, stable forms. Examples of chemicals used to prepare standard solutions are the acidic potassium hydrogen phthalate, $KHC_7H_4O_4$ (sometimes referred to as KHP), and the basic sodium carbonate, Na_2CO_3.

When using a standard solution, the standard is first prepared by dissolving the solid in a known volume of water, add a few drops of indicator, and titrate with the solution that you want to standardize.

Sample question: What is the concentration of sodium hydroxide when 32.34 mL is required to neutralize a solution prepared by dissolving 1.12 g of $KHC_7H_4O_{4(s)}$ in 25.00 mL of $H_2O_{(L)}$?

Solution:

Step 1: Find the mols of $KHC_7H_4O_{4(s)}$.

$$\text{mols } KHC_7H_4O_4 = \frac{\text{mass}}{\text{molar mass}} = \frac{1.12\text{ g}}{192.2\text{ g/mol}} = 5.83 \times 10^{-3}\text{ mol}$$

Step 2: Use mol ratio from the reaction to find the moles of NaOH.

$$KHC_7H_4O_{4(aq)} + NaOH_{(aq)} \rightarrow KNaC_7H_4O_{4(aq)} + H_2O_{(L)}$$

Since the reaction is 1:1, or 1 mole of KHP reacts with every mole of NaOH, the number of moles of KHP = number of moles of NaOH.

$$\text{mol NaOH} = 5.83 \times 10^{-3}\text{ mol}$$

Step 3: Determine the concentration of NaOH.

$$[NaOH] = \frac{5.83 \times 10^{-3}\text{ mol}}{0.03234\text{ L}} = 0.180\text{ M}$$

Therefore, the exact concentration of the sodium hydroxide solution used in the titration is 0.180 mol/L.

Choosing an Appropriate Indicator

To choose an appropriate indicator for a titration, a titration curve is useful. Knowing the pH at equivalence for the different types of titrations (see Table 1) is also needed.

Table 1: pH at Equivalence for Titrations

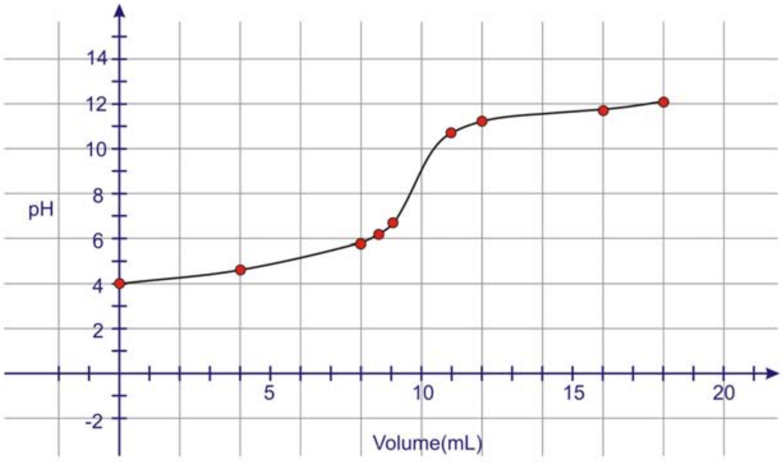
Type of Titration	**pH at Equivalence**
Strong Acid – Strong Base	pH = 7.0
Strong Acid – Weak Base	pH < 7.0
Weak Acid – Strong Base	pH > 7.0

Choosing an indicator close to the equivalence point is essential to see the point where all of the H^+ ions and OH^- ions have been neutralized. The color change should occur on or around the equivalence point. So, for example, with a strong acid, strong base titration, the pH at equivalence is 7.0. Indicators such as bromothymol blue (pH range = 6.0 - 7.6) and phenol red (pH range = 6.6 - 8.0) are common. If you notice the midpoint color (green) for bromothymol blue would appear at a pH = 6.8 which is close to 7.0. For phenol red, the midpoint color (orange) would appear at pH = 7.3, again close to 7.0.

The same process is used for other titration types. For a strong acid-weak base titration where the pH at equivalence is less than 7, the indicators normally chosen for these titrations are methyl red (pH range = 4.8 - 6.0) and chlorophenol red (pH range = 4.8 - 6.2). For a weak acid-strong base titration where the pH at equivalence is greater than 7, the indicators normally chosen for these titrations are phenolphthalein (pH range = 8.2 - 10) and thymol blue (pH range = 8.0 - 9.6). As with strong acid-strong base titration, the visual observation of the midpoint color should indicate close proximity to the equivalence point.

Sample question: Look at the graph below and determine the appropriate indicator.

Graph 1: Titration of a Weak Acid with a Strong Base

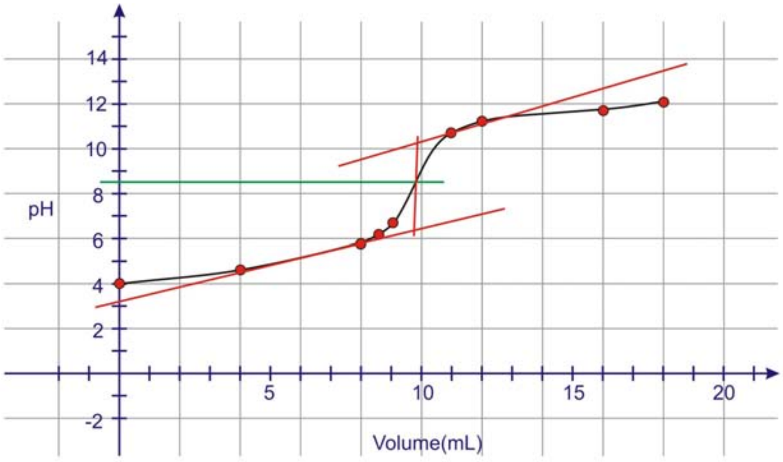


(*Created by:* Therese Forsythe, *License:* CC-BY-SA)

Solution:

We first look at the graph and mark the vertical stretch of the titration curve (red lines) in order to find the half-way mark on this vertical stretch (green line). Looking at the graph, when we follow this half-way mark over to the y-axis, we can see that the equivalence point occurs at approximately pH = 8.2. The indicator appropriate to use would be phenolphthalein (pH range = 8.2 - 10) and as soon as the pink color forms we are at the equivalence point.

Graph 2: Titration of a Weak Acid with a Strong Base



(*Created by:* Therese Forsythe, *License:* CC-BY-SA)

Reaction Continues to the End Point

There is an interesting observation about the endpoint that has yet to be mentioned. The endpoint was defined earlier as the point where the indicator changes color. In an acid-base neutralization reaction, this point may not be the point where all of the H^+ ions have been neutralized by OH^- ions, or vice versa. The experimenter continues titration until the indicator changes color, that is, the endpoint has been reached. The equivalence point is the point where the moles of hydrogen ion and the moles of hydroxide ion are equal. It requires knowledge by the experimenter to select an indicator that will make the endpoint as close as possible to the equivalent point.

Titration Calculations

For the calculations involved here, we will restrict our acid and base examples where the stoichiometric ratio of H^+ and OH^- is 1: 1. To determine the concentration or volume required to neutralize and acid or a base, in other words, to reach the equivalence point, we will use a formula similar to the dilution formula used in your prior learning. The formula has the structure:

$$M_a \times V_a = M_b \times V_b$$

where M_a = molarity of the acid
V_a = volume of the acid
M_b = molarity of the base
V_b = volume of the base

Sample question: When 10.0 mL of a 0.125 mol/L solution of hydrochloric acid, HCl, is titrated with a 0.100 mol/L solution of potassium hydroxide, KOH, what is the volume of the hydroxide solution required to neutralize the acid? What type of titration is this?

Solution:

Step 1: Write the balanced ionic chemical equation.

$$H^+_{(aq)} + Cl^-_{(aq)} + K^+_{(aq)} + OH^-_{(aq)} \longrightarrow K^+_{(aq)} + Cl^-_{(aq)} + H_2O_{(L)}$$

Step 2: Use the formula and fill in all of the given information.

$$M_a \times V_a = M_b \times V_b$$

M_a = 0.125 mol/L
V_a = 10.0 mL
M_b = 0.100 mol/L
V_b = ?

$$M_a \times V_a = M_b \times V_b$$

$$V_b = \frac{M_a \times V_a}{M_b} = \frac{(0.125\ \text{mol/L})(10.0\ \text{mL})}{0.100\ \text{mol/L}} = 12.5\ \text{mL}$$

Therefore, for this weak acid-strong base titration, the volume of base required for the titration is 12.5 mL.

Lesson Summary

- A titration is the addition of a known concentration of base (or acid) to a solution of acid (or base) of unknown concentration. The titrant in the titration is the solution of known concentration. This solution is normally in the burette. A burette is a piece of equipment used in a titration to accurately dispense the volume of the solution of known concentration (either the base or the acid). The endpoint is the point in the titration where the indicator changes color. The equivalence point is the point in the titration where the number of moles of acid equals the number of moles of base; pH meters are used in many laboratories for acid-base titrations. The main purpose of a pH meter is to measure the changes in pH as the titration goes from start to finish.
- The three types of titrations usually performed in the laboratory are: strong acid vs. strong base, strong acid vs. weak base, and weak acid vs. strong base. A titration curve is a graph of the pH versus the volume of titrant added. For a strong acid vs. strong base titration, the pH at equivalence is 7.0. For a strong acid vs. weak base titration, the pH at equivalence is less than 7.0. For a weak acid vs. strong base titration, the pH at equivalence is greater than 7.0. A standard solution is a solution whose concentration is known exactly and is used to find the exact concentration of the titrant. For titrations where the stoichiometric ratio of mol H^+: mol OH^- is 1:1, the formula $M_a \times V_a = M_b \times V_b$ can be used to calculate concentrations or volumes for the unknown acid or base.

Review Questions

1. Why do you think there would be more experimental error with using an indicator over using a pH meter in a titration? **(Intermediate)**

2. Why would there not be a weak acid-weak base titration? **(Intermediate)**

3. Which of the following definitions best suits that of an endpoint? **(Intermediate)**

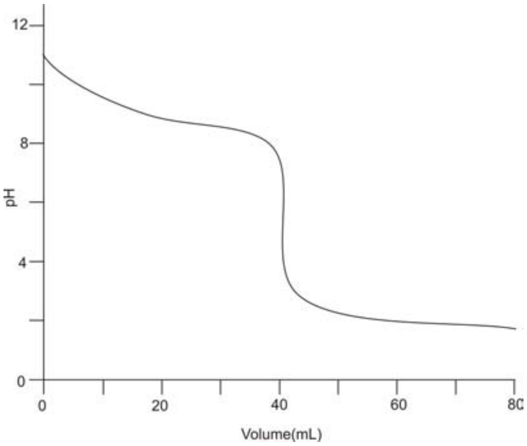
(a) The stoichiometric point where the number of moles of acid equals the number of moles of base.

(b) The visual stoichiometric point where the number of moles of acid equals the number of moles of base.

(c) The midpoint of the vertical stretch on the titration curve.

(d) None of the above

4. In the following titration curve, what pair of aqueous solutions would best represent what is shown to be happening in the curve? **(Intermediate)**



a. $HCOOH_{(aq)}$ + $NH_{3(aq)}$

b. $HCOOH_{(aq)}$ + $NaOH_{(aq)}$

c. $H_2SO_{4(aq)}$ + $Ba(OH)_{2(aq)}$

d. $HClO_{4(aq)}$ + $NH_{3(aq)}$

5. What would be the best indicator to choose for the pH curve shown in question 3? **(Intermediate)**

a. Methyl red

b. Litmus

c. Phenolphthalein

d. Phenol red

6. What is the best indicator to use in the titration of benzoic acid with barium hydroxide? **(Intermediate)**

Indicator	**pH Range**
Methyl violet	0.0 – 1.6
Bromothymol blue	3.0 – 4.7
Phenolphthalein	8.2 – 10.0
Methyl blue	10.6 – 13.4
Indigo carmine	11.4 – 13.0

(a) Methyl violet

(b) Bromothymol blue

(c) Phenolphthalein

(d) Methyl blue

(e) Indigo carmine

7. If 22.50 mL of a sodium hydroxide is necessary to neutralize 18.50 mL of a 0.1430 mol/L HNO_3 solution, what is the concentration of NaOH? **(Intermediate)**

(a) 0.1176 mol/L

(b) 0.1430 mol/L

(c) 0.1740 mol/L

(d) 2.64 mol/L

8. Plot the following titration data on a titration curve of pH vs. volume of base added. When complete, find the pH at equivalence and choose an appropriate indicator for the titration. What volume of base is necessary to neutralize all of the acid? **(Intermediate)**

Volume of base added (mL)	**pH**
0.00	1.0
2.00	1.2
4.00	1.4
6.00	1.6
8.00	1.9
9.00	2.3
9.50	2.6
9.90	3.3
9.99	4.3
10.00	7.0
10.01	9.7
10.50	10.7
12.00	11.4

14.00	121
16.00	121

9. Calculate the concentration of hypochlorous acid if 25.00 mL of HClO is used in a titration with 32.34 mL of a 0.1320 mol/L solution of sodium hydroxide. **(Intermediate)**

Further Reading / Supplemental Links

http://en.wikipedia.org

Vocabulary

titration	The lab process in which a known concentration of base (or acid) is added to a solution of acid (or base) of unknown concentration.
titrant	The solution in the titration of known concentration.
burette	A piece of equipment used in titrations to accurately dispense the volume of the solution of known concentration (either a base or an acid).
Erlenmeyer flask	A piece of equipment used in titrations (and other experiments) to hold a known volume of the unknown concentration of the other solution (either the acid or the base).
endpoint	The point in the titration where the indicator changes color.
equivalence point	The point in the titration where the number of moles of acid equals the number of moles of base.
pH meter	A device used to measure the changes in pH as the titration goes from start to finish.
titration curve	A graph of the pH versus the volume of titrant added.
standard solution	A solution whose concentration is known exactly and is used to find the exact concentration of the titrant.

Review Answers

1. Answers will vary but aside from the pH meters being mechanical in nature, students may discuss the fact that indicators change color over a pH range rather than a pH point. Therefore, skill is a key factor in determining an accurate endpoint; otherwise the endpoint would occur over a range of pHs.

2. You can do a weak acid-weak base titration; the graph ends up being more of a point of inflexion. The pH begins around 4 or 4.5 and end 8.5 or 9 with a slow sweeping curve. Because there is no steep part to the curve, the equivalence point is difficult to pick out as well.

3. (b) The visual stoichiometric point where the number of moles of acid equals the number of moles of base.

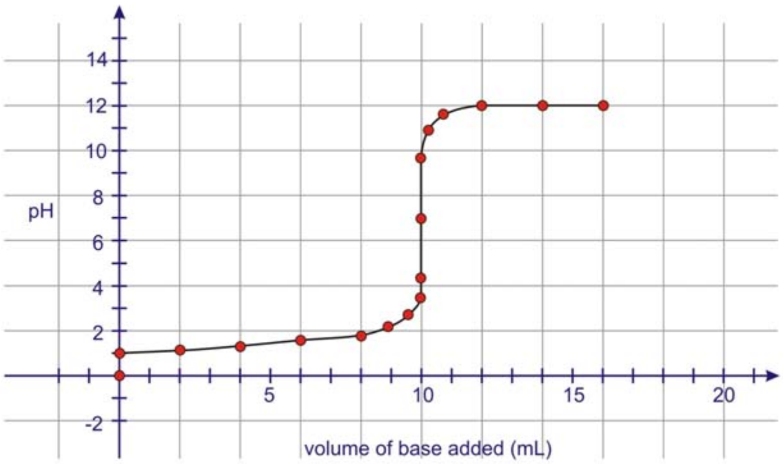
4. (d) $HClO_{4(aq)} + NH_{3(aq)}$

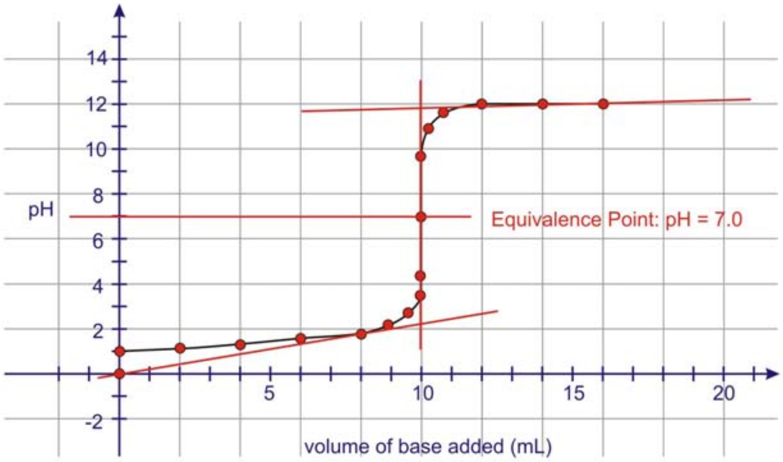
5. (a) Methyl red

6. (c) Phenolphthalein

7. (a) 0.1176 mol/L

8. Plotting the graph:





To find the equivalence point, find the half way mark for the vertical region.

With a pH at equivalence at 7.0, the most appropriate indicator would likely be bromothymol blue (pH range = 6.0 - 7.6).

9. $HClO_{(aq)} + NaOH_{(aq)} \rightarrow NaClO_{(aq)} + H_2O_{(L)}$

$M_a \times V_a = M_b \times V_b$

M_a = ?

V_a = 25.00 mL

M_b = 0.1320 mol/L

V_b = 32.34 mL

$(M_a)(25.00 \text{ mL}) = (0.1320 \text{ mol/L})(0.03234 \text{ L})$

$$M_a = \frac{(0.1320 \text{ mol/L})(0.03234 \text{ L})}{(0.02500 \text{ L})} = 0.1708 \text{ mol/L}$$

Therefore, for this weak acid-strong base titration, the [HClO] = 0.1708 mol/L.

Buffers

Lesson Objectives

- Define a buffer and give various examples of buffers.
- Explain the effect of a strong acid on the pH of a weak acid/conjugate base buffer.
- Explain the effect of a strong base on the pH of a weak base/conjugate acid buffer.

Introduction

There are many situations in which it is desirable to keep the pH of a solution close to a particular value even though quantities of acids and/or bases are added to the solution. Many organic and biochemical reactions require acids or bases in the reaction but if the pH goes too high or too low, the products will be destroyed. For these reactions, it is necessary to keep the pH within a very small range even while acids or bases are added to the reaction. Chemists use mixtures called ***buffers*** to keep the reaction solutions within the necessary pH range. Buffers are mixtures of chemicals that cause a solution to resist changes in pH.

Buffers are very important to many biological reactions. Human blood is a substance whose function is very dependent on the function of buffers. Human blood must maintain an almost constant pH between 7.3 and 7.5 . If a person's blood pH goes 0.2 outside the acceptable range, the person will become unconscious and the blood pH goes 0.4 outside the range, the person will die. The pH of human blood can change depending on foods we eat and the rate at which we inhale and exhale CO_2. Fortunately, the human blood stream has buffers which are able to resist pH changes due to food intake and breathing rates.

Buffers

A ***buffer*** is a solution that maintains the pH level when small amounts of acid or base are added to the system. Buffer solutions contain either a weak acid and the conjugate base of the weak acid or a weak base and the conjugate acid of the weak base. A common procedure for producing a buffer in the lab is to make a solution of a weak acid and a salt of that weak acid. For example, you could make a buffer by making a solution containing acetic acid and sodium acetate.

The common buffer mentioned above would contain acetic acid, CH_3COOH, and the acetate ion, CH_3COO^-. This buffer can keep a solution in the range of a pH of 3.7 – 5.8 even though small amounts of acids or bases are added to the solution. Another example is hydrogen phosphate ion, $HPO_4{}^{2-}$, and the phosphate ion, $PO_4{}^{3-}$ which will buffer a solution in the pH range of 11.3 – 13.3.

How is it possible that a solution will not change its pH when an acid or base is added? Let's examine the acetic acid/acetate ion buffer. The ionization equation for acetic acid is shown below.

$$HC_2H_3O_{2(aq)} \leftrightarrows H^+ + C_2H_3O_2{}^-$$

It is obvious that if acid (H^+ ions) is added to this solution, the equilibrium will shift toward the reactants to use up some of the added hydrogen ions. Equilibrium will be re-established in the solution with different concentrations of the three species in the reaction. It is also obvious that if a base is added to this solution, the base will remove hydrogen ions and the equilibrium will shift to the right to partially counteract the stress. Again, equilibrium will be re-established with new concentrations.

What is not obvious about this buffer solution is that acetic acid is a weak acid and therefore, most of the acid dissolved in the solution remain as acid molecules and do not dissociate. Therefore, there will a large quantity of undissociated $HC_2H_3O_2$. The fact that we also dissolved sodium acetate in this solution provides a large quantity of acetate ions, $C_2H_3O_2{}^-$, in the solution. The existence of large quantities of both undissociated acid molecules and acetate ions in the solution is what allows the buffer to consume quite a large amount of added acid or base without the pH changing significantly.

Examine what happens to 1.00 liter of pure water to which 0.100 mole of gaseous HCl is added.

The original concentration of hydrogen ion in the pure water is 1.00 x 10^{-7} M and therefore, the pH is 7.

After the 0.100 mole of HCl is added, the concentration of the hydrogen ion will be 0.100 M (plus the original 1.00 x 10^{-7} M which can be neglected as not significant). This new concentration of hydrogen ion will produce a pH = 1. So, the addition of the 0.100 mole of gaseous HCl caused the pH of the pure water to change from 7 to 1.

Let's now see what happens if this same amount of gaseous HCl is added to an acetic acid-acetate ion buffer. We'll the same amount of original solution, 1.00 liter, and let's say we made this solution to contain 0.50 M acetic acid and 0.50 M acetate ion (0.50 M sodium acetate which totally dissociated). The acetic acid dissociation equation will reach equilibrium and its K_a will be 1.8 x 10^{-5}.

$$K_a = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = 1.8 \times 10^{-5}$$

We know both the acetic acid and the acetate ion concentrations will be 0.50 M, so we can plug these values into the expression and solve for $[H^+]$.

$$[H^+] = \frac{(1.8 \times 10^{-5})[HC_2H_3O_2]}{[C_2H_3O_2^-]} = \frac{(1.8 \times 10^{-5})(0.50)}{(0.50)} = 1.8 \times 10^{-5}\ M$$

Then we can insert the hydrogen ion concentration into the pH formula and determine the original pH of the buffer solution.

$$pH = -\log(1.8 \times 10^{-5}) = 4.74$$

Next, we will add the same 0.100 mole of gaseous HCl to this buffer solution and calculate the pH of the solution after the acid has been added and equilibrium has been re-established.

When we add 0.100 mole HCl gas to this solution, the added hydrogen ion will combine with acetate ion to produce more undissociated acid. A small amount of the added hydrogen ions may remain as ions but the amount is, once again, beyond the significant figures of the problem and can be neglected. The new $[HC_2H_3O_2]$ will equal 0.60 M (the original 0.50 M plus the added 0.10 M) and the new $[C_2H_3O_2^-]$ will equal 0.40 M (the original 0.50 M minus the 0.10 M that reacted with the added hydrogen ions). We can now plug these values into the K_a expression, calculate the new $[H^+]$, and find the new pH.

$$K_a = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = 1.8 \times 10^{-5}$$

$$[H^+] = \frac{(1.8 \times 10^{-5})[HC_2H_3O_2]}{[C_2H_3O_2^-]} = \frac{(1.8 \times 10^{-5})(0.60)}{(0.40)} = 2.7 \times 10^{-5}\ M$$

$$pH = -\log(2.7 \times 10^{-5}) = 4.57$$

The same quantity of HCl gas that changed the pH of pure water from 7 to 1 has changed the pH of this buffer from 4.74 to 4.57 . . . only a change of 0.17 . . . that is the function of a buffer. Buffers resist change to pH. We could this same calculation but add a base instead of an acid and show that the pH increases by this same slight amount. Maybe that would be good practice for you.

Sample question: Which of the following combinations would you expect possible to make into buffer solutions:

(a) $HClO_4/ClO_4^-$

(b) $CH_3NH_2/CH_3NH_3^+$

Solution:

(a) $HClO_4/ClO_4^-$: $HClO_4$ is a strong acid and buffers are made from weak acids and their conjugate bases or weak bases and their conjugate acids. Therefore this cannot be made into a buffer solution.

(b) $CH_3NH_2/CH_3NH_3^+$: CH_3NH_2 is a weak base and $CH_3NH_3^+$ is the conjugate acid of this base. Therefore this can be made into a buffer solution.

The Buffer in Blood

The primary buffer found in your bloodstream is carbonic acid, H_2CO_3. The carbonic acid is present due to carbon dioxide from your respiratory system dissolving in water.

$CO_{2(g)} + H_2O_{(L)} \leftrightarrows H_2CO_{3(aq)}$ Equation 1

The amount of carbonic acid in your bloodstream is affected by the rate of your respiration. If you breathe rapidly, you reduce the amount of CO_2 in your bloodstream and the equilibrium shown in Equation 1 shifts toward the reactants thus lowering the amount of H_2CO_3. If you breathe slowly, the amount of CO_2 in your bloodstream increases and the equilibrium in Equation 1 shifts toward the products increasing the amount of H_2CO_3 in your system.

Once the H_2CO_3 is produced by dissolving carbon dioxide, the carbonic acid dissociates in your blood as shown in Equation 2.

$H_2CO_{3(aq)} \leftrightarrows H^+ + HCO_3^-$ Equation 2

This is the buffering reaction in your blood, composed of the weak acid, H_2CO_3, and its conjugate base, HCO_3^-.

Any changes in blood pH that could be caused by food intake, will be buffered by this equilibrium system. If acid is added to your blood, the equilibrium in Equation 2 will shift toward the reactants using up the hydrogen ions and if base were added to your blood thus reacting with hydrogen ions, the equilibrium will shift toward the products generating more hydrogen ions. This buffer in your blood is very efficient at keeping your blood pH in the necessary range.

A problem exists for a few people because their respiratory rate is highly affected by their emotional state. Some people, when they get nervous, begin breathing very fast or very slow. Breathing too fast is called hyperventilating and breathing too slow is called hypoventilating. Your respiratory rate is normally controlled by the amount of carbon dioxide in the blood. Your body receives instructions to breathe faster or slower to adjust the amount of carbon dioxide in your blood in order to properly regulate the buffer system. When people people breathe too fast or too slow because of other reasons, the CO_2 content of the blood becomes incorrect and the pH of the blood rises or lowers outside the acceptable range of 7.3 - 7.5 . When this happens, the person passes out or becomes unconscious. People who hyperventilate when excited or nervous are sometimes advised to carry a lunch sack or something similar to breathe into when they are feeling light-headed. Breathing into a sack returns air with the same concentration of carbon dioxide that was exhaled .

. . this keeps the amount of carbon dioxide in the blood up and avoids passing out.

Lesson Summary

- A buffer is a solution of a weak acid and its conjugate base or a weak base and its conjugate acid that resists changes in pH when an acid or base is added to it.
- Adding a strong acid to a weak acid/conjugate base buffer only decreases the pH by a small amount.
- Adding a strong base to a weak base/conjugate acid buffer only increases the pH by a small amount.

Review Questions

1. Define a buffer solution. **(Beginning)**

2. What are two different types of buffer solutions? **(Beginning)**

3. One of the following statements of buffers is incorrect. Which one? **(Intermediate)**

(a) A buffer may be prepared from a weak acid and its conjugate base salt.

(b) A buffer may be prepared from a weak base and its conjugate acid salt.

(c) A buffer is a solution that can resist changes in pH when any amount of acid or base is added to it.

(d) A buffer is a solution that can resist changes in pH when a small amount of acid or base is added to it.

4. Which pair of aqueous 1.0 mol/L solutions could be chosen to prepare a buffer? **(Intermediate)**

I. $NH_4HSO_{4(aq)}$ and $H_2SO_{4(aq)}$

II. $HNO_{2(aq)}$ and $NaNO_{2(aq)}$

III. $NH_4Cl_{(aq)}$ and $NH_{3(aq)}$

(a) I and III only

(b) II and III only

(c) I, II and III

(d) None of these solutions is a buffer.

5. Which of the following would form a buffer solution if combined in appropriate amounts? **(Intermediate)**

(a) HCl and NaCl

(b) HCN and NaCN

(c) H_2S and Na_2S

(d) HNO_3 and $NaNO_3$

6. A buffer is made up of a weak acid and a conjugate base. A small amount of acid is added to the buffer. What happens to the resulting solution? **(Intermediate)**

(a) The acid dissociation constant goes up.

(b) The concentration of the weak acid in the buffer goes down.

(c) The pH of the solution goes up.

(d) The pH remains almost the same.

7. Almonds from the wild have a very bitter taste because of hydrogen cyanide (and therefore are very dangerous to eat!!!). Interestingly if we think about HCN in a buffer situation, HCN and NaCN can be considered to act as a buffer solution. Sulfurous acid is used quite frequently as a cleansing agent. If we take the sodium salt, Na_2SO_3, of sulfurous acid, H_2SO_3 we do not make a buffer solution. Why is this so? Why would one make a buffer solution and not the other? **(Intermediate)**

Further Reading / Supplemental Links

http://en.wikipedia.org

Vocabulary

buffer A buffer is a solution of a weak acid and its conjugate base or a weak base and its conjugate acid that resists changes in pH when an acid or base is added to it.

Review Answers

1. A buffer is a solution of a weak acid and its conjugate base or a weak base and its conjugate acid that resists changes in pH when an acid or base is added to it.

2. The two different types (or two ways buffer solutions can be prepared) are by mixing a weak acid and its conjugate base salt, or by mixing a weak base and its conjugate acid salt.

3. (c) A buffer is a solution that can resist changes in pH when any amount of acid or base is added to it.

4. (b) II and III only

5. (b) HCN and NaCN

6. (d) The pH remains almost the same.

7. Na_2SO_3 and H_2SO_3 do not act as a buffer because the sulfite ion, SO_3^{2-}, is not the conjugate base of sulfurous acid, H_2SO_3. HSO_3^- would be the conjugate base of H_2SO_3. An aqueous mixture of NaCN (or more accurately CN^-) and HCN is a buffer because the cyanide acts as a weak base and hydrogen cyanide is a weak acid. HCN and CN^- is a conjugate pair, and each species will react with water.

27. Thermodynamics

Energy Change in Reactions

Lesson Objectives

- Define energy, potential energy, kinetic energy.
- Define endothermic and exothermic reactions.
- Describe how heat is transferred in endothermic and exothermic reactions.

Introduction

In physics, work is defined as the force exerted on an object multiplied by the distance the object moves due to that force. Energy is defined as the **ability to do work**. Therefore, energy is the ability to exert forces on objects and move them around due to that force. Energy is often divided into two types, kinetic energy and potential energy. Kinetic energy is the energy of motion . . . all moving objects have kinetic energy. It's fairly easy to see how a moving object can do work on another object simply by ramming into it. Potential energy is the energy of position. A stretched rubber band has potential energy. A rock held up above the earth has potential energy. This form of energy also has the ability to do work, all you have to do is release the object from its position and the resultant motion will exert forces on other objects.

Molecules contain potential energy in their physical states and in their chemical bonds. You will remember that when solid substances were changed into liquid, energy had to be added to provide the *heat of melting* (a/k/a heat of fusion). That energy was used to pull the molecules further apart . . . changing solid form into liquid form. That energy is stored in the liquid as potential energy due to the greater distances between attracting molecules. Energy also had to be added to a liquid substance to convert it to a gas. Again, the energy was used to pull the molecules further apart and again, the energy is stored in the gaseous molecules as potential energy. If a gaseous substance is changed back to liquid or a liquid to solid, those quantities of potential energy are released by the substances and can be used to do work.

Chemical bonds store potential energy in a slightly different way. To understand how chemical bonds store energy, we can view a substance as having maximum potential energy in bonds when all the atoms of the substance are separated from each other and are in atomic form (no bonds). The atoms can then form many different bonds and when bonds form, energy is released so the potential energy of the substance decreases. Each of the possible bonds the atoms may form will release a different amount of energy. The various bonded conditions of the atoms then, will be on different levels of potential energy . . . like the steps on a ladder. In order to get potential energy out of a bond, you must move the substance from one step on a ladder to a lower step. Generally, this requires that you break all the old bonds first (input energy to move to the top of the ladder) and then form new bonds **that are lower in potential energy that the original bonds**. If you understand this, then you can see that when a group of atoms are bonded in the lowest possible potential energy for those atoms, it is impossible to get energy out of the bonds - because there is no lower step to which you can move the material.

Sometimes, a chemical reaction forms new bonds that are higher in potential energy than the original bonds and when that happens, energy must be added to make the extra PE in the bonds. These reactions where the net change of energy is added into the bonds are called endothermic reactions. When a reaction forms bonds that contain less PE than the original bonds, the excess energy is released to the surroundings. Those reactions are called exothermic reactions.

All Chemical Reactions Involve Energy

Every system or sample of matter has energy stored in it. When chemical reactions occur, the new bonds formed never have exactly the same amount of potential energy as the bonds that were broken. Therefore, all chemical reactions involve energy changes. Energy is either given off by the reaction or energy is taken on by the reaction.

When you think about most events in life, they either require energy or release energy. The last time you went camping, you might have lit a campfire. The burning of the wood in the fire pit released energy into the environment. In the same way, all chemical reactions require energy or release energy as they proceed from reactants to products. But like lighting the fire at the camp, chemical reactions need a minimum amount of energy in order for a reaction to begin.

Think about it another way. If you were pitching a ball up to home plate, holding the ball in your hand, your arm has a certain amount of potential or stored energy to move that ball. If you want the ball to go to home plate, your arm has to give the ball an amount of energy that will carry it the 60 feet 6 inches to the home plate. There is a minimum amount of energy necessary to carry the ball to the plate.

The same is true for reactions. Before any reaction can occur, reactant bonds need to be broken. A minimum amount of energy, that is the activation energy, must be supplied before any reaction can take place. Sometimes this minimum energy might be in the form of heat or sometimes in the form of electrical current.

$NaCl_{(aq)} + AgNO_{3(aq)} \rightarrow AgCl_{(s)} + NaNO_{3(aq)} \qquad \Delta H = -166\ kJ$ (Equation 1)

Equation 1 represents a chemical reaction in which energy is produced. This means that there is less energy stored in the bonds of the products than there was in the bonds in the reactants. Therefore, extra energy was left over when the reactants become the products.

The decomposition of mercury(II) oxide requires a net input of energy (see Equation 2).

$2\ HgO_{(s)} \rightarrow 2\ Hg_{(L)} + O_{2(g)} \qquad \Delta H = 181.7\ kJ$ (Equation 2)

In this reaction, there is less energy stored in the bonds of the mercury (II) oxide than is stored in the bonds of the products. Therefore, extra energy had to be added to the reaction to form the products.

These two equations represent the two types of chemical reactions that involve energy transfer and illustrate that chemical reactions involve energy.

Bond Breaking and Bond Forming

In the previous section, we looked at two different types of reactions that involved energy. ΔH, or the heat of reaction, measures the change in the internal energy of the reaction. The internal energy is the sum of all the energy of the chemical system, that is, the potential and the kinetic. ΔH is also known as change in enthalpy. ***Enthalpy***, by definition, is the amount of energy a system or substance contains. Enthalpy cannot be measured directly. What can be measured is the change in enthalpy (or ΔH). For Equation 1, the bonds of the reactants contain more energy than the bonds of the products and thus the reaction is exothermic and ΔH is negative.

For Equation 2, the bond breaking required more energy input than bond formation produced and thus an energy input was required and the reaction is endothermic and ΔH is positive.

System and Surroundings

Many chemical reactions take place in an open system. Whether the reaction is exothermic or endothermic, there is energy transfer between the system and the surroundings. For example, you take an ice cube out of the refrigerator and place it on a counter. As the ice cube melts it requires a small amount of heat to be absorbed from the surroundings (the room) in order to produce the liquid (See Equation 3).

$H_2O_{(s)} \rightarrow H_2O_{(L)}$ $\Delta H = +6.01$ kJ/mol (Equation 3)

The **system** in this example is the ice cube melting to form the liquid water. The ***surroundings*** are the container, room and building in which the reaction is taking place. In other words, the "system" involves the reactants and products in the reaction. The "surroundings" are everything else.

Before moving any further in our discussion, it is important to distinguish between heat and temperature when talking about heat transfer. ***Heat*** is the total amount of energy that is transferred between the system (reactants and products) and the surroundings (the container, etc). ***Temperature*** is a the average kinetic energy of a substance and is measured using a thermometer. Temperature measures the kinetic energy of the reactant and/or product particles. For example a cup of water and a bucket of water boil at the same temperature (100°C) but it will require different amounts of heat to bring these two volumes of water to a boil.

An ***endothermic reaction*** absorbs heat from the surroundings. Notice in Equation 3 that the sign of ΔH is positive which indicates that it is endothermic. Phase changes from a solid → liquid → gas are all endothermic. Diagram 1 illustrates the transfer of heat energy from the surroundings to the system.

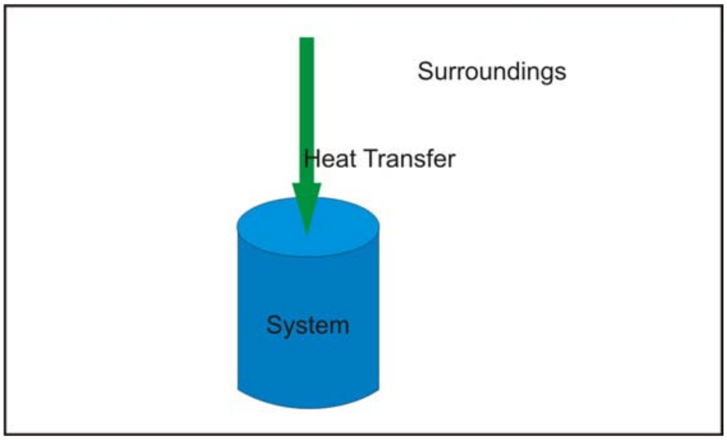


Figure 1: Illustration of Heat Transfer for Endothermic Reactions.

(*Created by:* Therese Forsythe, *License:* CC-BY-SA)

An ***exothermic reaction*** system releases heat to the surroundings. Diagram 2 illustrates the transfer of heat energy to the surroundings from the system.

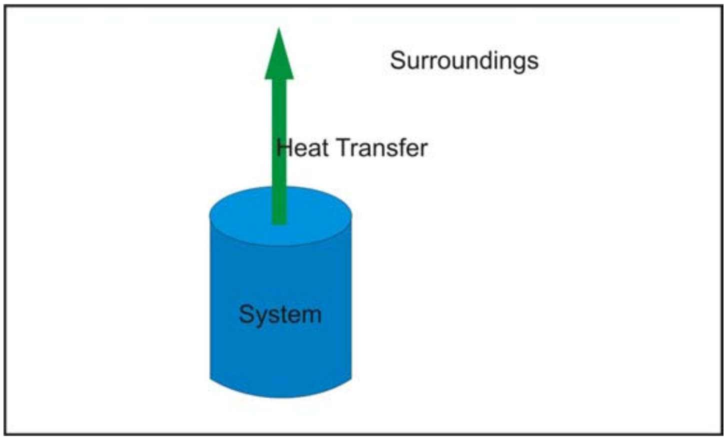


Figure 2: Illustration of Heat Transfer for Exothermic Reactions.

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An example of an exothermic reaction is shown in Equation 4. Notice the value of ΔH is negative. The negative value indicates an exothermic reaction and that there is a release of heat into the surroundings.

$2\ SO_{2(g)} + O_{2(g)} \longrightarrow 2\ SO_{3(g)} \qquad \Delta H = -46.8\ kJ/mol$ (Equation 4)

The reason that endothermic reactions have positive ΔHs and exothermic reactions have negative ΔHs is because the definition of ΔH is:

$\mathbf{\Delta H = H_{products} - H_{reactants}}$.

Therefore, when the reactants contain more PE in their bonds than do the products, energy is given off and mathematically in the equation, a larger number is subtracted from a smaller one, so the answer is negative.

Just as phase changes from a solid → liquid → gas are all endothermic, the reverse of these are exothermic. Other reactions that you know as exothermic may be the combustion of fuels. Fuels used to drive your car, heat your barbeque or your home all involve reactions that are exothermic in nature.

Sample question: Which of the following processes would be endothermic or exothermic?

(a) water boiling

(b) gasoline burning

(c) water vapor condensing

(d) iodine crystals subliming

(e) ice forming on a pond

Solution:

(a) Water boiling: endothermic – state change from liquid to a gas absorbs heat from the surroundings

(b) Gasoline burning: exothermic – combustion releases heat to the surroundings

(c) Water vapor condensing: exothermic – state change from gas to a liquid releases heat to the surroundings

(d) Iodine crystals subliming: endothermic – state change from solid to a liquid absorbs heat from the surroundings

(e) Ice forming on a pond: exothermic – state change from liquid to a solid releases heat to the surroundings

Lesson Summary

- Energy is the ability to do work. Potential energy is the energy of position. Kinetic energy is the energy of motion. ΔH, or the heat of reaction, measures the change in the internal energy of the reaction. The internal energy is the sum of all the energy of the chemical system. ΔH is also known as change in enthalpy. Enthalpy, by definition, is the amount of energy a system or substance contains.
- The "system" involves the reactants and products in the reaction. The "surroundings" are everything else. An endothermic reaction system absorbs heat from the surroundings. An exothermic reaction system releases heat to the surroundings. Heat is the energy that is transferred between the system (reactants and products) and the surroundings (the container). Temperature measures the average kinetic energy

of the reactant and/or product particles.

Review Questions

1. Define endothermic and exothermic reactions and give an example of each. **(Beginning)**

2. How does a campfire involve energy? **(Beginning)**

3. If a chemical reaction absorbs heat from the surroundings, it is said to be what? **(Beginning)**

(a) in equilibrium

(b) in a closed system

(c) an exothermic reaction

(d) an endothermic reaction

4. If a chemical reaction releases heat to the surroundings, it is said to be what? **(Beginning)**

(a) in equilibrium

(b) in a closed system

(c) an exothermic reaction

(d) an endothermic reaction

5. Symbolically, change in enthalpy is represented as: **(Beginning)**

a. H

b. ΔH

c. E

d. ΔE

6. Which of the following processes would be endothermic? **(Beginning)**

a. natural gas burning

b. melting chocolate

c. fireworks exploding

d. Steam condensing

7. Which of the following processes would be exothermic? **(Beginning)**

a. gasoline burning

b. evaporation of ether

c. melting butter

d. boiling water

Further Reading / Supplemental Links

http://en.wikipedia.org

Vocabulary

energy	The ability to do work.
potential energy	The energy of position or stored energy.
kinetic energy	The energy of motion.
enthalpy	The amount of energy a system or substance contains.
heat	The energy that is transferred between the system (reactants and products) and the surroundings.
temperature	The average kinetic energy of the molecules of a substance.

Review Answers

1. An endothermic reaction system absorbs heat from the surroundings (example: water boiling); an exothermic reaction system releases heat to the surroundings (example: steam condensing).

2. Activation energy (the match) is needed to begin a fire; once the fire is burning and energy is being released, some of that energy will be used as the activation energy so that the reactions will continue.

3. (d) an endothermic reaction

4. (c) an exothermic reaction

5. (b) ΔH

6. (b) melting chocolate

7. (a) gasoline burning

Enthalpy

Lesson Objectives

- Define and understand enthalpy of reaction.
- Calculate the enthalpy of reaction using $\Delta H_{rxn} = \Delta H_{products} - \Delta H_{reactants}$.
- Describe, interpret, and draw potential energy diagrams.
- Define and understand ΔH_f.
- Define Hess's Law.
- Calculate ΔH_{rxn} using Hess's Law.

Introduction

The change in enthalpy for a reaction can be determined by three methods. First, the enthalpy of the reaction is found by finding the difference between the enthalpies of the products and reactants in the lab using a calorimeter. Second, the change in enthalpy for a reaction can also be calculated using the heats of formation of all the reactants and products. Thirdly, the change in enthalpy can be calculated using the mathematical application of Hess's Law.

The Energy Content of a System

Enthalpy has been defined previously as the measure of the total internal energy of a system. The difference between the enthalpy of the reactants and the enthalpy of the products is called the change in enthalpy. When reactions take place in an open system, such as a beaker, or a container on a counter, the pressure in the system is constant because the pressure is the atmospheric pressure in the room. The change in enthalpy for reactions occurring under constant pressure is also called the ΔH or heat of reaction.

$$\Delta H_{rxn} = \Delta H_{products} - \Delta H_{reactants}$$

Remember that for an endothermic reaction, the value of ΔH is positive, therefore the $\Delta H_{products}$ must be greater than $\Delta H_{reactants}$. To illustrate this, look at Figure 1.

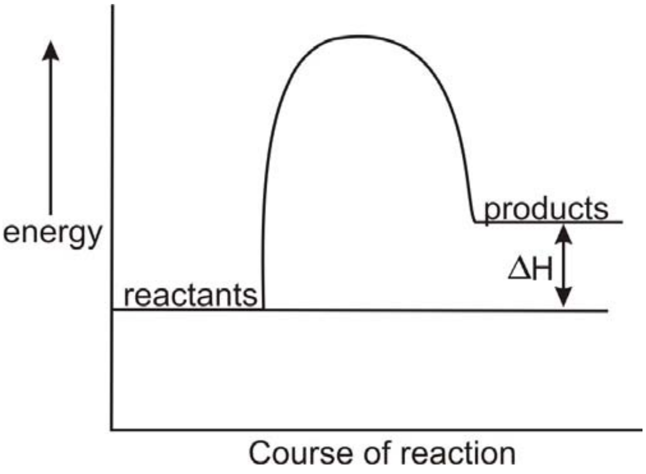


Figure 1: Illustration of an Endothermic Reaction.

(*Created by:* Therese Forsythe, *License:* CC-BY-SA)

In Figure 1, the enthalpy of the reactants is lower than the energy of the products. Therefore, energy must be input into the reaction and the value of the ΔH will be positive.

The opposite is true for exothermic reactions. For exothermic reactions the value of ΔH is negative and therefore the enthalpy of the products must be less than enthalpy of the reactants. Notice that for Figure 2, the energy of the reactants is higher than the energy of the products. Therefore the value of the ΔH will be negative.

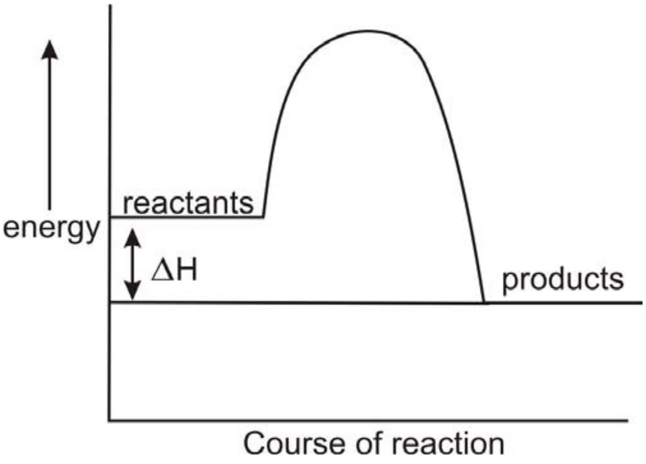
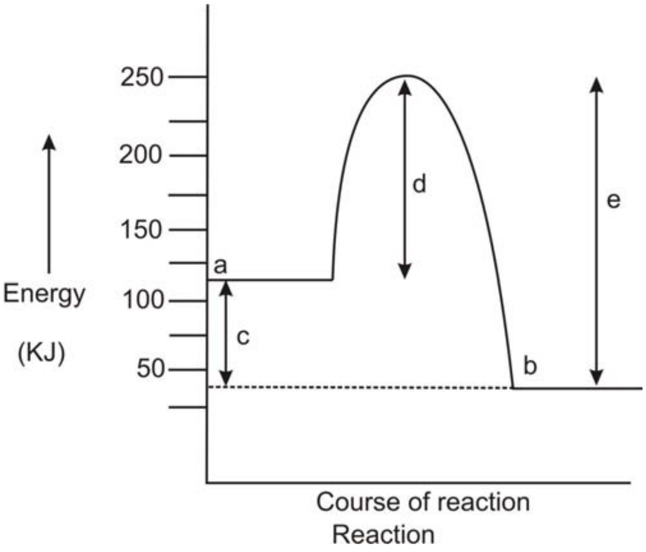


Figure 2: Illustration of an Exothermic Reaction.

(*Created by:* Therese Forsythe, *License:* CC-BY-SA)

The figures represented are referred to as ***potential energy diagrams*** . They are called this because they indicate the potential energy of the reactants and the products.

Sample question: Using the diagram below, answer questions (a) through (d).



(a) Which letter represents the activation energy for the reaction? What is its value?

(b) Which letter represents the change in enthalpy of the reaction or the ΔH? What is its value?

(c) Is the reaction endothermic or exothermic? How can you tell?

(d) What does the letter (e) represent?

Solution:

(a) The activation energy is represented by letter (d). It has a value of 250 – 100 = 150 kJ.

(b) The enthalpy change (ΔH) is represented by letter (c). It has a value of 50 – 100 = -50 kJ.

(c) The reaction is exothermic because ΔH is negative and the products are lower than the reactants on the potential energy diagram.

(d) Letter *e* represents the activation energy for the reverse reaction.

Enthalpy of Formation

A **formation reaction** is a reaction in which exactly one mole of a product is formed from its elements. The ***enthalpy of formation*** , ΔH_f, is the energy required to form one mole of a substance from its constituent elements at standard temperature and pressure. Equation 1 represents the ΔH_f for the formation of one mole of $NH_{3(g)}$.

$\frac{1}{2} N_{2(g)} + \frac{3}{2} H_{2(g)} \rightarrow NH_{3(g)}$ $\Delta H_f = -46.1$ kJ/mol (Equation 1)

We can find these values for enthalpies of formation using a table of standard molar enthalpies found in the *CRC Handbook of Chemistry and Physics*, online, or in most chemistry textbooks. The values found in these sources are the values of ΔH_f or the enthalpy of formation.

In Equation 1, exactly one mole of ammonia is formed from its elements and that qualifies the reaction as a formation reaction and its ΔH to be a ΔH_f. Equation 2 does not qualify to be a formation reaction.

$2\ H_{2(g)} + O_{2(g)} \rightarrow 2\ H_2O_{(L)}$ $\Delta H_f = -571.6$ kJ (Equation 2)

The enthalpy of formation is for the formation of one mole of a substance from its elements. Equation 2 shows the formation of two moles of water and therefore does not represent ΔH_f. In order to represent the ΔH_f for water, we must divide Equation 2 by two.

$H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2O_{(L)}$ $\Delta H_f = -285.8$ kJ (Equation 3)

If we were to reverse this reaction, look at what would happen to the value of ΔH.

$H_2O_{(L)} \rightarrow H_{2(g)} + \frac{1}{2} O_{2(g)}$ $\Delta H = 285.8$ kJ (Equation 4)

Equation 4 no longer represents the heat of formation because the equation represents a decomposition reaction. However, look at the value of ΔH. Since the equation was reversed, the sign of the value of ΔH was also reversed. It 285.8 kJ was given when one mole of water formed from its elements, then to decompose that mole of water back into its elements, an input of 285.8 kJ is required. The ΔH for the forward reaction will be exactly the opposite of the ΔH for the reverse reaction.

You can use the values of ΔH_f found in the table of standard heats of formation to find the enthalpy of a reaction (or $\Delta H_{rxn\}}$). Consider the following equation.

Table 1: Standard Enthalpy of Formation for some Selected Compounds

Name of Compound	**Formation Reaction**	**Standard Enthalpy of Formation, ΔH_f °** (kJ/mol of product)
aluminum oxide	$2\ Al_{(s)} + \frac{3}{2} O_{2(g)} \rightarrow Al_2O_{3(s)}$	-1669.8
ammonia	$\frac{1}{2} N_{2(g)} + \frac{3}{2} H_{2(g)} \rightarrow NH_{3(g)}$	-46.1
carbon dioxide	$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$	-393.5

carbon monoxide	$C_{(s)} + \frac{1}{2} O_{2(g)} \rightarrow CO_{(g)}$	-110.5
copper (I) oxide	$Cu_{(s)} + \frac{1}{2} O_{2(g)} \rightarrow CuO_{(s)}$	-156
iron (III) oxide	$2\ Fe_{(s)} + \frac{3}{2} O_{2(g)} \rightarrow Fe_2O_{3(s)}$	-822.2
magnesium oxide	$Mg_{(s)} + \frac{1}{2} O_{2(g)} \rightarrow MgO_{(s)}$	-602
methane	$C_{(s)} + 2\ H_{2(g)} \rightarrow CH_{4(g)}$	-74.8
nitrogen monoxoide	$\frac{1}{2} N_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow NO_{(g)}$	+90.
nitrogen dioxide	$\frac{1}{2} N_{2(s)} + O_{2(g)} \rightarrow NO_{2(g)}$	+34
sodium chloride	$Na_{(s)} + \frac{1}{2} Cl_{2(g)} \rightarrow NaCl_{(s)}$	-411
sulfur dioxide	$S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)}$	-297
sulfur trioxide	$S_{(s)} + \frac{3}{2} O_{2(g)} \rightarrow SO_{3(g)}$	-393.2
water (gaseous)	$H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2O_{(g)}$	-241.8
water (liquid)	$H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2O_{(L)}$	-285.8

$CH_{4(g)} + 2\ O_{2(g)} \rightarrow CO_{2(g)} + 2\ H_2O_{(g)} \qquad \Delta H = ?$

From the table of standard heats of formation we know that:

$\Delta H_f\ CH_{4(g)} = -74.8$ kJ/mol

$\Delta H_f\ O_{2(g)} = 0$ kJ/mol (Note: all elements in their natural state have a $\Delta H_f = 0$ kJ/mol)

$\Delta H_f\ CO_{2(g)} = -393.5$ kJ/mol

$\Delta H_f\ H_2O_{(g)} = -241.8$ kJ/mol

We also know that $\Delta H_{rxn} = \Delta H_{products} - \Delta H_{reactants}$

Therefore for this reaction, $\Delta H_{rxn} = [\Delta H_f\ (CO_{2(g)}) + 2\ \Delta H_f(H_2O_{(g)})] - [\Delta H_f(CH_{4(g)}) + 2\ \Delta H_f\ (O_{2(g)})]$

Note that the heat of formation for gaseous water and that for oxygen gas are to be multiplied by two because there are two moles of oxygen gas and two moles of gaseous water in the combustion reaction.

We can now calculate the value for ΔH_{rxn} because we have all of the required values for $\Delta H_{products}$ and $\Delta H_{reactants}$.

$\Delta H_{rxn} = [(-393.5 \text{ kJ/mol}) + (2)(-241.8 \text{ kJ/mol})] - [(-74.8 \text{ kJ/mol}) + (2)(0 \text{ kJ/mol})]$

$\Delta H_{rxn} = [-877.1 \text{ kJ/mol}] - [-74.8 \text{ kJ/mol}]$

$\Delta H_{rxn} = -802.3$ kJ/mol

Rewriting the equation we see:

$CH_{4(g)} + 2\ O_{2(g)} \longrightarrow CO_{2(g)} + 2\ H_2O_{(g)}$ $\Delta H = -802.3$ kJ/mol

Sample Question: Calculate the value of ΔH_{rxn} for the following reaction.

$2\ Al_{(s)} + Fe_2O_{3(s)} \longrightarrow Al_2O_{3(s)} + 2\ Fe_{(L)}$

Solution:

From the table of standard heats of formation we know that:

$\Delta H_f\ Al_{(s)} = 0$ kJ/mol (Note: all elements in their natural state have a $\Delta H_f = 0$ kJ/mol)

$\Delta H_f\ Fe_2O_{3(s)} = -822.2$ kJ/mol

$\Delta H_f\ Al_2O_{3(s)} = -1669.8$ kJ/mol

$\Delta H_f\ Fe_{(L)} = -12.4$ kJ/mol

$2\ Al_{(s)} + Fe_2O_{3(s)} \longrightarrow Al_2O_{3(s)} + 2\ Fe_{(L)}$

$\Delta H_{rxn} = [\Delta H_f\ (Al_2O_{3(s)}) + 2 \times \Delta H_f\ (Fe_{(L)})] - [2 \times \Delta H_f\ (Al_{(s)}) + \Delta H_f\ (Fe_2O_{3(s)})]$

$\Delta H_{rxn} = [-1669.8 \text{ kJ/mol} + (2)(-12.4 \text{ kJ/mol})] - [(2)(0 \text{ kJ/mol}) + -822.2 \text{ kJ/mol}]$

$\Delta H_{rxn} = [-1694.6 \text{ kJ/mol}] - [-822.2 \text{ kJ/mol}]$

$\Delta H_{rxn} = -872.4$ kJ/mol

Rewriting the equation: $2\ Al_{(s)} + Fe_2O_{3(s)} \longrightarrow Al_2O_{3(s)} + 2\ Fe_{(L)}$ $\Delta H_{rxn} = -872.4$ kJ/mol

Hess's Law of Heat Summation

The first method shown for finding the ΔH_{rxn} is to subtract the ΔH (reactants) from the ΔH (products.) Sometimes, however, this method is not always possible. Compounds may not be easily produced from their elements and, therefore, there is not an available value for the ΔH_f. Other times, there may be side reactions happening and, therefore, there is a need for a more indirect method for calculating the value of the ΔH_{rxn}. In the middle of the 1800s, Germain Hess developed a method for determining the ΔH_{rxn} indirectly. ***Hess's Law*** states in any series of reactions that start with the same reactants and end with the same products, the net change in energy must be the same. This means that if multiple reactions are combined, the enthalpy change, ΔH, of the combined reaction is equal to the sum of all the individual enthalpy changes. So how does this work? It can be as straight forward as multiplying a reaction by a number or rearranging the reactions. Consider the following example.

Given the following equation: $S(s) + \frac{3}{2}\ O_2(g) \longrightarrow SO_3(g),$ $\Delta H_f = -393.2$ kJ/mol.

Calculate ΔH for the reaction $2\ S_{(s)} + 3\ O_{2(g)} \longrightarrow 2\ SO_{3(g)}$.

Notice that the difference between the two equations is that the second equation is the first equation multiplied by two. Therefore we can simply multiply the ΔH by the same factor, that is, two.

$2\ S_{(s)} + 3\ O_{2(g)} \rightarrow 2\ SO_{3(g)} \qquad \Delta H_f = -786.4\ kJ$

If we were to reverse the direction of a reaction, then the sign of the ΔH must also be reversed. Look at the example below that illustrates this possibility.

Given the following equation: $2\ NO_{(g)} + O_{2(g)} \rightarrow 2\ NO_{2(g)} \quad \Delta H = -114\ kJ$

What is the value of ΔH for the reaction: $2\ NO_{2(g)} \rightarrow 2\ NO_{(g)} + O_{2(g)}$

Notice when looking at the two equations, the second equation is the reverse of the first equation; therefore the ΔH value will change signs (or be multiplied by -1).

$2\ NO_{2(g)} \rightarrow 2\ NO_{(g)} + O_{2(g)} \qquad \Delta H = +114\ kJ$

The most useful of Hess's law, and the critical part of his definition, is the ability to add multiple reactions to obtain a final reaction, and subsequently add the ΔH's. Consider Equation 1 below.

$CuO_{(s)} + H_{2(g)} \rightarrow Cu_{(s)} + H_2O_{(g)} \qquad$ (Reaction 1)

Suppose we wish to know the ΔH for this reaction but necessary ΔH_f values are not available. We do, however, have the following two equations available.

$CuO_{(s)} \rightarrow Cu_{(s)} + \frac{1}{2}\ O_{2(g)} \qquad \Delta H_2 = +155\ kJ \qquad$ (Reaction 2)

$H_{2(g)} + \frac{1}{2}\ O_{2(g)} \rightarrow H_2O_{(g)} \qquad \Delta H_3 = -242\ kJ \qquad$ (Reaction 3)

If we add equations 2 and 3 by the normal addition of equations process, the result is exactly the same as equation 1.

$CuO_{(s)} \rightarrow Cu_{(s)} + \frac{1}{2}\ O_{2(g)} \qquad \Delta H_2 = +155\ kJ \qquad$ (Equation 2)

$H_{2(g)} + \frac{1}{2}\ O_{2(g)} \rightarrow H_2O_{(g)} \qquad \Delta H_3 = -242\ kJ \qquad$ (Equation 3)

$CuO_{(s)} + H_{2(g)} \rightarrow Cu_{(s)} + H_2O_{(g)} \qquad \Delta H_1 = ?\ kJ \qquad$ (Equation 1)

Hess's Law tells us that since equations 2 and 3 add up to give equation 1, the sum of ΔH_2 and ΔH_3 will be equal to ΔH_1. (Note: Since one-half mol of oxygen gas appears on each side of the equation, it cancels out).

It is relatively easy to demonstrate the truth of this statement mathematically. We can express ΔH_1 as the heats of formation of its products minus the heats of formation of its reactants in the normal way.

$\Delta H_1 = [\Delta H_f\ (Cu_{(s)}) + \Delta H_f\ (H_2O_{(g)})] - [\Delta H_f\ (CuO_{(s)}) + \Delta H_f\ (H_{2(g)})]$

$\Delta H_1 = \Delta H_f\ (Cu_{(s)}) + \Delta H_f\ (H_2O_{(g)} - \Delta H_f\ (CuO_{(s)}) - \Delta H_f\ (H_{2(g)}) \qquad$ (Equation 1)

We can do the same for ΔH_2 and ΔH_3 and then add the expressions for ΔH_2 and ΔH_3 together.

$$\Delta H_2 = \Delta H_f\ (Cu_{(s)}) + \Delta H_f\ (\tfrac{1}{2}\ O_{2(g)}) - \Delta H_f\ (CuO_{(s)})$$

$$\Delta H_3 = \Delta H_f\ (H_2O_{(g)} - \Delta H_f\ (H_{2(g)}) + \Delta H_f\ (\tfrac{1}{2}\ O_{2(g)})$$

$$\Delta H_2 + \Delta H_3 = \Delta H_f\ (Cu_{(s)}) + \Delta H_f\ (\tfrac{1}{2}\ O_{2(g)}) - \Delta H_f\ (CuO_{(s)}) + \Delta H_f\ (H_2O_{(g)} - \Delta H_f\ (H_{2(g)}) + \Delta H_f\ (\tfrac{1}{2}\ O_{2(g)})$$

If you can sort through that mess of symbols, you will see that the heat of formation for one-half mole of oxygen gas is added in one place and subtracted in another place. Therefore, those cancel and can be removed from the equation.

$$\Delta H_2 + \Delta H_3 = \Delta H_f\ (Cu_{(s)}) - \Delta H_f\ (CuO_{(s)}) + \Delta H_f\ (H_2O_{(g)} - \Delta H_f\ (H_{2(g)}) \qquad \text{(Equation 2)}$$

Now, you can compare equation 2 to equation 1 and see that they are exactly the same. Therefore, ΔH_1 is equal to the sum of ΔH_2 and ΔH_3.

Lesson Summary

- All elements in their natural state have a $\Delta H_f = 0$ kJ/mol.
- Hess's Law states that if multiple reactions are combined, the enthalpy (ΔH) of the combined reaction is equal to the sum of all the individual enthalpies.
- If we were to reverse a reaction the sign of the ΔH is also reversed.
- If you multiply an equation by a factor the ΔH is also multiplied by that same factor.

Review Questions

1. Define the Hess's Law and the need for using this method. **(Beginning)**

2. Draw a potential energy diagram to represent the reaction below. **(Beginning)**

$S_8(s) + 8Cl_2(g) \longrightarrow 8SCl_2(s)\ \Delta H = -376$ kJ

3. Which of the following does not have a $\Delta H_f = 0$? **(Beginning)**

(a) $H_2O_{(l)}$

(b) $O_{2(g)}$

(c) $H_{2(g)}$

(d) $Fe_{(s)}$

4. Which statement would describe an endothermic reaction? **(Intermediate)**

(a) The potential energy of the reactants is greater than the potential energy of the products.

(b) The potential energy of the reactants is less than the potential energy of the products.

(c) Energy is released in the chemical reaction.

(d) The energy required to break bonds is more than the energy produced when bonds are formed.

5. Given the reaction: $2HCl(g) \rightarrow H_2(g) + Cl_2(g)$, ΔH = 185 kJ, what would be the ΔH for the following reaction: $\frac{1}{2} H_2(g) + \frac{1}{2} Cl_2(g) \rightarrow HCl(g)$? **(Intermediate)**

(a) 185

(b) -185

(c) 92.5

(d) -92.5

6. Which of the following reactions represents that for a ΔH_f? **(Intermediate)**

(a) $4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$

(b) $SO_2(g) + \frac{1}{2} O_2(g) \rightarrow SO_3(g)$

(c) $2Al(s) + \frac{3}{2} O_2(g) \rightarrow Al_2O_3(s)$

(d) $\frac{1}{2} C_4H_{10}(g) + \frac{1}{2} H_2(g) \rightarrow C_2H_6(g)$

7. Hydrogen sulfide can mix with carbon dioxide to make a very smelly liquid, carbon disulfide. Given that the enthalpies of formation for $CO_2(g)$, $H_2S(g)$, $CS_2(l)$, and $H_2O(l)$ are -393.5 kJ/mol, -20.6 kJ/mol, 116.7 kJ/mol, and -285.8 kJ/mol, respectively, calculate ΔH_{rxn}. **(Intermediate)**

8. Ethene is a common compound used in the production of plastics for plastic bottles. Using the following data, calculate the ΔH_{rxn} for ethene. $2C(g) + 2H_2(g) \rightarrow C_2H_4(g)$ **(Intermediate)**

Further Reading / Supplemental Links

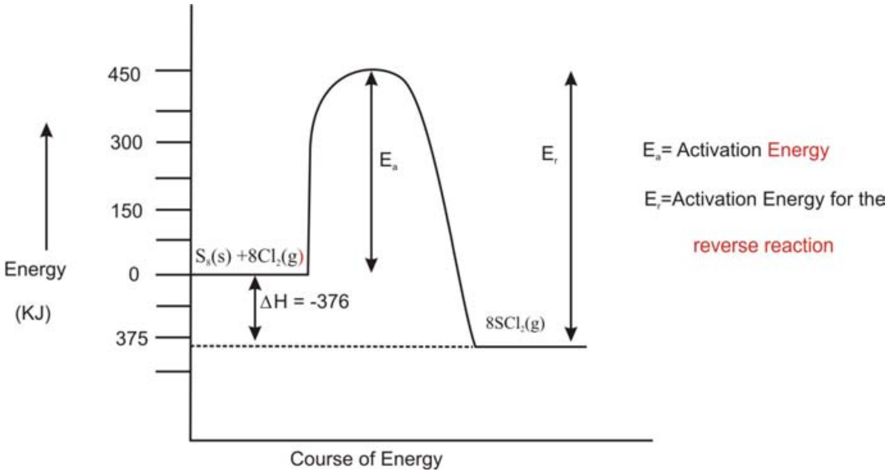
http://schools.matter.org.uk

Vocabulary

activation energy	The minimum amount of energy necessary for a reaction to take place.
potential energy diagrams	Show endothermic chemical reaction; the activation of energy and the potential energy of the reactants.
enthalpy of formation	The heat required to form one mole of a substance from its elements at standard temperature and pressure.
Hess's Law	If multiple reactions are combined, the enthalpy (ΔH) of the combined reaction is equal to the sum of all the individual enthalpies.

Review Answers

1. Hess's Law states that if multiple reactions are combined, the enthalpy (ΔH) of the combined reaction is equal to the sum of all the individual enthalpies. This law is essential in that if there are reactions where the compounds may not be able to be produced from their elements and therefore there is not value for the ΔH_f. Other times, there may be side reactions happening and therefore there is a need for a more indirect method for calculating the value of the ΔH_{rxn}.



2.

3. (a) $H_2O_{(l)}$

4. (b) The potential energy of the reactants is less than the potential energy of the products.

5. (d) -92.5 kJ

6. (c) $2Al(s) + \frac{3}{2} O_2(g) \longrightarrow Al_2O_3(s)$

7. $CO_2(g) + 2H_2S(g) \longrightarrow CS_2(l) + 2H_2O(l)$

$\Delta H_{rxn} = [\Delta H_f(CS_2(l)) + 2 \times \Delta H_f(H_2O(l))] - [\Delta H_f(CO_2(g)) + 2 \times \Delta H_f(H_2S(g))]$

ΔH_{rxn} = [116.7 kJ/mol + 2 (-285.8 kJ/mol)] - [-393.5 kJ/mol + 2 (-20.6 kJ/mol)]

ΔH_{rxn} = [-454.9 kJ/mol] - [-434.7 kJ/mol]

ΔH_{rxn} = -20.2 kJ/mol

8.

$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l)$	ΔH = -285.8 kJ/mol
$C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l)$	ΔH = -1411.2 kJ/mol
$C(g) + O_2(g) \longrightarrow CO_2(g)$	ΔH = -393.5 kJ/mol
$2(H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l))$	2(ΔH = -285.8 kJ/mol)
$2(C(g) + O_2(g) \longrightarrow CO_2(g))$	2(ΔH = -393.5 kJ/mol)
$2CO2_{(g)} + 2H_2O(l) \longrightarrow C_2H_4(g) + 3O_2(g)$	(ΔH = -1411.2 kJ/mol) × -1

$$\begin{array}{ll}
2H_2(g) + \cancel{O_2(g)} \rightarrow \cancel{2H_2O}(l) & \Delta H = -571.6\ \text{KJ/mol} \\
2C(g) + \cancel{2O_2(g)} \rightarrow \cancel{2CO_2(g)} & \Delta H = -787\ \text{KJ/mol} \\
\cancel{2CO_2(g)} + \cancel{2H_2O(l)} \rightarrow C_2H_4(g) + \cancel{3O_2(g)} & \Delta H = 1411.2\ \text{KJ/mol} \\
\hline
2C(g) + 2H_2(g) \rightarrow C_2H_4(g) & \Delta H = 52.6\ \text{kJ/mol}
\end{array}$$

Spontaneous Processes

Lesson Objectives

- Define a spontaneous and non-spontaneous reaction.
- Identify processes as either spontaneous or non-spontaneous.
- Describe how endothermic and exothermic reactions can be spontaneous or non-spontaneous.
- Explain the lack of correlation between spontaneity and speed of reaction.

Introduction

Some events or reactions occur without any outside forces. For example, if you drop a spoonful of sugar into a cup of water, it automatically dissolves. The sugar is said to spontaneously dissolve in water. The word spontaneous is defined as happening without external cause. It comes from the Latin term *sponte* meaning voluntary. In science, however, a spontaneous reaction is considered to be one that has more to do with the starting and ending conditions of the system and if the change from the start to the finish will occur without any outside influences. Rusting of iron is spontaneous under the right conditions but to undo this process would not be spontaneous! In other words, if you wanted to remove rust from a piece of iron, this is not a spontaneous reaction. In this lesson we will consider spontaneous and non-spontaneous reactions in light of what we just learned with respect to enthalpy.

Change That Occurs Without Outside Assistance

Some events in life happen under a specific set of conditions. For example, if you are standing at the top of a ski hill on a pair of downhill skis and you give a little push with your poles, the likelihood of the event that you will start moving down the hill is quite probable. The event of downhill skiing is a spontaneous. ***A spontaneous event (or reaction)*** is a change that occurs under a specific set of conditions. A ball rolling down a hill, the water falling down in a waterfall, and the dispersion of the smell of a perfume when sprayed in a room (expansion of a gas), are all spontaneous events. A ***non-spontaneous event (or reaction)*** would be a change that will not occur under a specific set of conditions. Can you picture a cold cup of hot chocolate becoming warmer on your desk as you sit and listen to your chemistry teacher? Probably not, because something else will happen to the hot chocolate in order to heat it up. For non-spontaneous events, something else, outside of the reaction, must be done in order to get the event (or reaction) to occur. This might be to apply a force to make a ball roll up a hill or to ski up the mountain. Other factors that could drive the reaction could be to add heat, a catalyst, or to increase the pressure.

Sample question: Which of the following would be considered spontaneous? Which would be considered non-spontaneous? Explain.

(a) cooling a cup of hot coffee at room temperature

(b) ice melting at room temperature

(c) compression of gas to fill a tire

(d) water flowing downhill

Solution:

(a) Cooling a cup of hot coffee is spontaneous because heat flows spontaneously from a hotter substance to a cooler one.

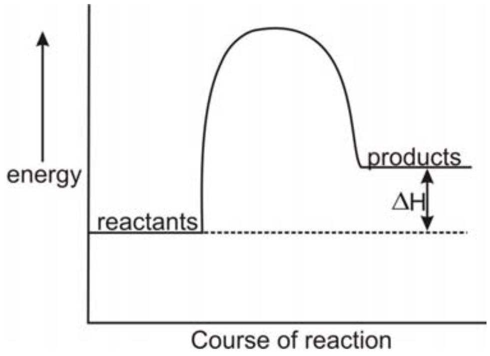
(b) Ice melting is spontaneous above 0°C because above this temperature water is normally at the liquid state.

(c) Compression of gas to fill a tire is non-spontaneous because a pressure has to be applied to a gas in order to compress it.

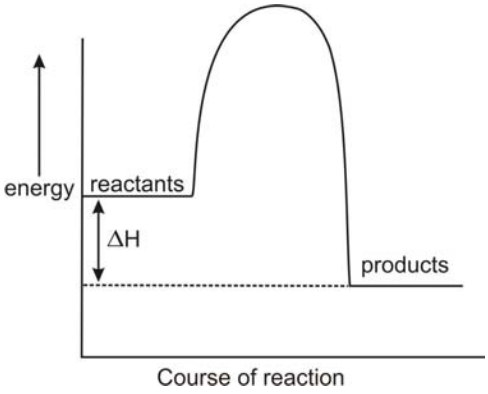
(d) Water flowing downhill is spontaneous because water will always flow down.

Exothermic or Endothermic Can Be Spontaneous

A spontaneous reaction can be either endothermic or exothermic just as a non-spontaneous reaction can. Consider the potential energy diagrams from the previous section. Both the endothermic and the exothermic potential energy diagrams are shown below.



Endothermic Reaction (*Created by:* Therese Forsythe, *License:* CC-BY-SA)



Exothermic Reaction (*Created by:* Therese Forsythe, *License:* CC-BY-SA)

Often but not always, a spontaneous process will be one that will result in a decrease in energy in the system. Therefore, water will spontaneously flow down a waterfall, a ball will roll down a hill, and gas will expand to fill a container. All of these changes will occur spontaneously leaving the products (or product state) with less energy than the reactants (or reactant state).Added to this, if a reaction is spontaneous in one direction, it is non-spontaneous in the opposite direction. For example a ball rolling down a hill would be spontaneous but rolling up a hill would be non-spontaneous.

Being spontaneous doesn't necessarily mean, however, that the reaction is exothermic. Highly exothermic reactions tend to be spontaneous but weakly exothermic or endothermic reactions can be spontaneous under the right conditions. In other words, spontaneous reactions can be endothermic the same as non-spontaneous reactions can be exothermic. Look at Equation 1 below. This equation represents the phase change of solid water (ice) to liquid water at 25°C.

$H_2O(s) \rightarrow H_2O(l)$ $\Delta H = 6.01$ kJ/mol (Equation 1)

We have already said that ice will spontaneously melt above 0°C and Equation 1 indicates the phase change is spontaneous. Combustion, however, is spontaneous and it is exothermic (Equation 2).

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l) \quad \Delta H = -2219.9 \text{ kJ/mol} \quad \text{(Equation 2)}$$

Therefore, spontaneity does not dictate whether a reaction is endothermic or exothermic. A spontaneous reaction is more likely to be exothermic but can be endothermic. Non-spontaneous reactions are more likely to be endothermic but can be exothermic. The deciding factor for these systems is the temperature.

Thermodynamics and Kinetics

A spontaneous process is all about the initial and final states. Reactions are considered spontaneous if, given the necessary activation energy, reactants form the products without any external forces. Therefore, for example, an ice cube will melt (Equation 2), an iron nail will rust in the present of oxygen dissolved water (Equation 3), and a sparker will burn (Equation 4). Some of these reactions are fast and some are slow. The oxidation of iron (Equation 3) is slow. After the sparkler is lit (Equation 4), the reaction from start to finish is quite fast. They are still, indeed, spontaneous.

$$H_2O(s) \rightarrow H_2O(l) \quad \text{(Equation 2)}$$

$$2\ Fe(s) + \frac{3}{2}\ O_2(g) + 3\ H_2O(l) \rightarrow 2\ Fe(OH)_3(s) \quad \text{(Equation 3)}$$

$$2\ KClO_3(s) \rightarrow 2\ KCl(s) + 3\ O_2(g) \quad \text{(Equation 4)}$$

Figure 1: Sparklers (*Source:* http://commons.wikimedia.org/wiki/File:Sparkler.jpg, *Author:* Gabriel Pollard, *License:* Creative Commons Attribution ShareAlike 2.5)

The rate of these reactions is the study of chemical kinetics; whether or not a reaction is spontaneous is the study of thermodynamics. If the reaction occurs quickly or slowly has little to do with the reaction being spontaneous. A spontaneous reaction means only that it occurs without any continuous outside support.

Lesson Summary

- A ***spontaneous event (or reaction)*** is a change that occurs under a specific set of conditions and without any continuous external support. A ***non-spontaneous event (or reaction)*** would then be a change that will not occur under a specific set of conditions.
- Spontaneous reactions are usually exothermic but can be endothermic as well. Non-spontaneous reactions are usually endothermic but can be exothermic as well. Being spontaneous does not indicate how fast, just that it occurs without external assistance. Speed of a reaction deals with kinetics.

Review Questions

1.Distinguish between spontaneous and non-spontaneous reactions. **(Intermediate)**

2. Why are spontaneous reactions usually exothermic (but still can be endothermic)? **(Intermediate)**

3. Which of the following processes would be spontaneous? **(Intermediate)**

(a) dissolving table salt

(b) climbing Mt. Everest

(c) separating helium from nitrogen in a mixture of gases

(d) none of these are spontaneous

4. Which of the following processes would be non-spontaneous? **(Intermediate)**

(a) iron rusting in air

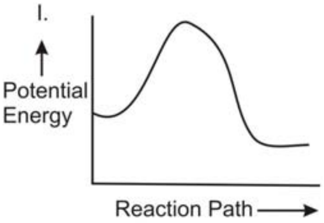
(b) ice melting at 10°C

(c) a wild fire

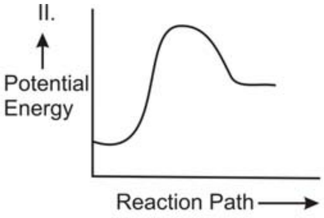
(d) the reaction of CO_2 and H_2O

5. Which of the following reactions are spontaneous? **(Intermediate)**

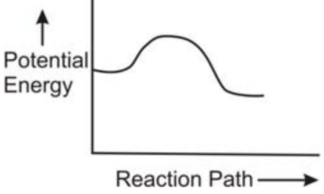
I.



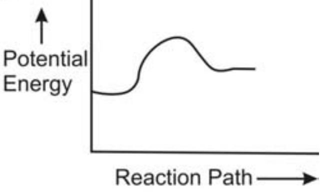
II.



III.



IV.



(a) I and II

(b) I and III

(c) II and IV

(d) Not enough information is given

6. If a reaction is spontaneous and fast, draw a likely potential energy diagram. **(Intermediate)**

Further Reading / Supplemental Links

http://learner.org/resources/series61.html'"

The ***learner.org*** website allows users to view streaming videos of the Annenberg series of chemistry videos. You are required to register before you can watch the videos but there is no charge. The website

has one video that relates to this lesson called ***The Driving Forces*** .

Vocabulary

spontaneous event (or reaction)	A change that occurs without outside inference; does not relate to rate of a reaction.
non-spontaneous event (or reaction)	A change that will only occur with outside inference.
ionization	A special type of dissociation reaction where a molecule ionizes in water to produce H^+ cations and the anion. Ionization reactions are specific to acids.

Review Answers

1. A spontaneous event (or reaction) is a change that occurs under a specific set of conditions and without any continuous external support. A non-spontaneous event (or reaction) would then be a change that will not occur under a specific set of conditions.

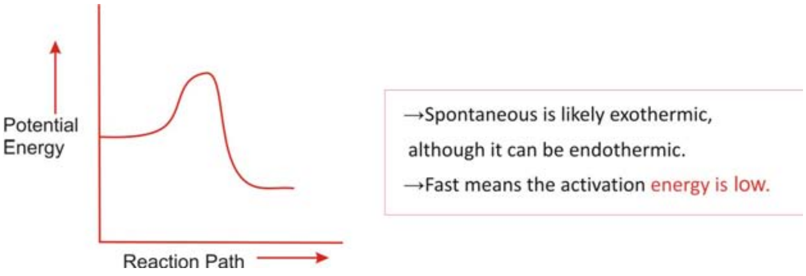
2. If we use the examples of spontaneous processes such as a ball rolling down a hill or water running down a waterfall, we make the assumption that spontaneous processes occur to decrease energy in a system and are therefore exothermic. A large number of them are. But not all of them like the melting of ice, which is endothermic (ΔH = 6.01 kJ/mol) but is still spontaneous.

3. (a) dissolving table salt

4. (d) the reaction of CO_2 and H_2O

5. (d) not enough information is given

6.



→Spontaneous is likely exothermic, although it can be endothermic.
→Fast means the activation energy is low.

Entropy

Lesson Objectives

- Define entropy.
- Calculate entropy.
- Relate entropy to the tendency toward spontaneity.
- Describe the factors that affect the increase or decrease in disorder.

Introduction

In this section of the chapter we explore the disorder of a system. Look at the diagrams of the two chessboards below.

At the start of a chess game, the chess pieces are all in place, there is order to the set-up of the board. After the game begins, and you and your opponent have been playing for a while, there is more disorder to the design of the pieces on the board.

The same is true for reactions. Some reactions start out with more order than they end up with on the product side. Other reactions begin with a higher amount of disorder and when the products form, the products have a high amount of order. The study of the disorder of reactions is known as entropy. The second law of thermodynamics states that the total entropy of the universe is continually increasing. This is the focus of this lesson.

The Measure of the Disorder of a System

In the previous section we considered the fact that whether or not a reaction was spontaneous could not be determined based on the fact that it was exothermic or endothermic. We considered the melting of an ice cube, spontaneous above 0°C, but endothermic as seen in Equation 1.

$$H_2O_{(s)} \rightarrow H_2O_{(L)} \quad \Delta H = 6.01 \text{ kJ/mol} \quad \text{(Equation 1)}$$

We also can consider the combustion of methane gas, spontaneous again but this time exothermic as seen in Equation 2.

$$CH_{4(g)} + 2\,O_{2(g)} \rightarrow CO_{2(g)} + 2\,H_2O_{(L)} \quad \Delta H = -890 \text{ kJ/mol} \quad \text{(Equation 2)}$$

Entropy (S) is a measure of the disorder or randomness of a system. If there is more disorder in the system, there is more entropy. What does it mean to increase disorder? Go back to the structures of the solids, liquids, and gases. Look at Figure 1.

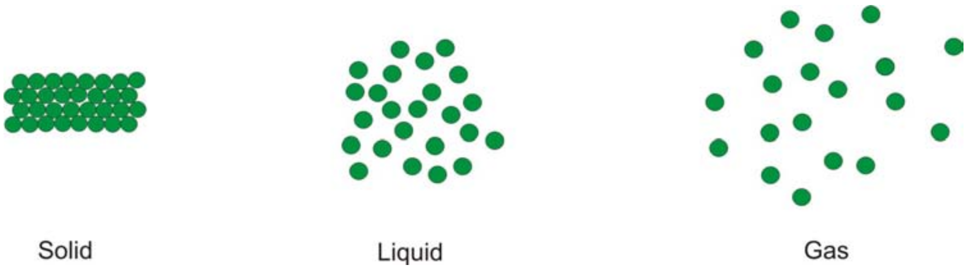


Figure 1: States of Matter.

(*Created by:* Therese Forsythe, *License:* CC-BY-SA)

The molecules in the gas have little or no attraction between the molecules which means that there are many more possibilities of where each molecule can be found in the space and therefore have greater disorganization. Liquids have some disorganization since there is some attraction between the molecules but that they can move somewhat more freely and have greater disorganization than the same molecules in the solid phase. In solids where there is great attraction between the molecules, there is much less possibility for the molecules to be unorganized. Therefore: $S_{gas} > S_{liquid} > S_{solid}$ because there is more disorder or randomness in a gas than there is in a liquid than in a solid.

The most commonly used example to illustrate disorder is to use a deck of playing cards. If you buy a brand new deck of playing cards, all of the cards are in four suits lined up from Ace through to King. This means the deck of cards has order. If, however, you were to take your new deck of cards and toss them up into the air, you now have disorder. You can, next be asked by the nearest adult in your life to pick up the mess and put the deck of cards back into order. This means you will once again put the cards into four suits lined up from Ace through to King.

For a system, the change in entropy, ΔS, is measured be finding the difference between the entropy of the products and the reactants the same as found for the change in enthalpy. Standard entropies are determined in the lab and published in standard entropy tables in the same manner as standard enthalpies. In fact, most times, both standard enthalpy and standard entropy are listed in the same table.

Table 1: Standard Enthalpy of Formation and Standard Entropies for some Selected Compounds

Name of Compound	Formation Reaction	Standard Enthalpy of Formation, ΔH_f° (kJ/mol of product)	Standard Entropy, S°, (J/mol·°C)
aluminum oxide	$2\ Al_{(s)} + \frac{3}{2}\ O_{2(g)} \rightarrow Al_2O_{3(s)}$	-1669.8	+51
ammonia	$\frac{1}{2}\ N_{2(g)} + \frac{3}{2}\ H_{2(g)} \rightarrow NH_{3(g)}$	-46.1	+193
carbon dioxide	$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$	-393.5	+214
carbon monoxide	$C_{(s)} + \frac{1}{2}\ O_{2(g)} \rightarrow CO_{(g)}$	-110.5	+198
copper (I) oxide	$Cu_{(s)} + \frac{1}{2}\ O_{2(g)} \rightarrow CuO_{(s)}$	-156	+43
iron (III) oxide	$Fe_{(s)} + \frac{3}{2}\ O_{2(g)} \rightarrow Fe_2O_{3(s)}$	-822.2	+90.
magnesium oxide	$Mg_{(s)} + \frac{1}{2}\ O_{2(g)} \rightarrow MgO_{(s)}$	-602	+27
methane	$C_{(s)} + 2\ H_{2(g)} \rightarrow CH_{4(g)}$	-74.8	+188
nitrogen monoxoide	$\frac{1}{2}\ N_{2(g)} + \frac{1}{2}\ O_{2(g)} \rightarrow NO_{(g)}$	+90.	+211
nitrogen dioxide	$\frac{1}{2}\ N_{2(s)} + O_{2(g)} \rightarrow NO_{2(g)}$	+34	+240
sodium chloride	$Na_{(s)} + \frac{1}{2}\ Cl_{2(g)} \rightarrow NaCl_{(s)}$	-411	+72
sulfur dioxide	$S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)}$	-297	+248
sulfur trioxide	$S_{(s)} + \frac{3}{2}\ O_{2(g)} \rightarrow SO_{3(g)}$	-393.2	+257
water (gaseous)	$H_{2(g)} + \frac{1}{2}\ O_{2(g)} \rightarrow H_2O_{(g)}$	-241.8	+189
water (liquid)	$H_{2(g)} + \frac{1}{2}\ O_{2(g)} \rightarrow H_2O_{(L)}$	-285.8	+70.

[It is important to note in the above table that the units for enthalpy of formation and entropy are **not** the same. Enthalpies of formation in the table have energy units in kilojoules while entropy has energy units in joules. If these values are entered into a formula together, one of them must be converted so that all energy units are the same.]

Therefore the change in entropy for a reaction (ΔS_{rxn}) can be found using the following equation.

$\Delta S_{rxn} = S_{products} - S_{reactants}$

Sample Question 1: Given the following data, calculate the ΔS_{rxn} for the following reaction.

$NH_{3(g)} + HCl_{(g)} \longrightarrow NH_4Cl_{(s)}$ $\Delta S_{rxn} = ?$

Given that $S(NH_{3(g)})$ = 111.3 J/K·mol, $S(HCl_{(g)})$ = 267.3 J/K·mol, $S(NH_4Cl_{(s)})$ = 94.56 J/K·mol .

Solution:

$\Delta S_{rxn} = S_{products} - S_{reactants}$

$\Delta S_{rxn} = S(NH_4Cl_{(s)}) - [S(NH_{3(g)}) + S(HCl_{(g)})]$

ΔS_{rxn} = (94.56 J/K·mol) - (193 J/K·mol + 187 J/K·mol)

ΔS_{rxn} = (94.56 J/K·mol) - (380 J/K·mol)

ΔS_{rxn} = -285 J/K·mol

Therefore $NH_{3(g)} + HCl_{(g)} \longrightarrow NH_4Cl_{(s)}$ ΔS_{rxn} = -285 J/K·mol.

What does it means when ΔS_{rxn} is negative? In this system, two gases are coming together to form a solid and the value of ΔS_{rxn} is negative. We can make a conclusion that if the order of the system increases, then the change in entropy value (ΔS) will be negative. In other words, if a system goes from a state of high disorder (two moles of gas) to a state of low disorder (one mole of solid), the entropy change is negative. Let's try another example.

Sample question 2: For the reaction $CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2(g)}$ at 25°C, calculate the value of ΔS_{rxn}.

Given $S(CaCO_{3(s)})$ = 92.9 J/K·mol; $S(CaO_{(s)})$ = 39.8 J/K·mol; and $S(CO_{2(g)})$ = 213.6 J/K·mol.

Solution:

$\Delta S_{rxn} = S_{products} - S_{reactants}$

$\Delta S_{rxn} = [S(CaO_{(s)}) + S(CO_{2(g)})] - S(CaCO_{3(s)})$

ΔS_{rxn} = [39.8 J/K·mol + 213.6 J/K·mol] - (92.9 J/K·mol)

ΔS_{rxn} = (253.4 J/K·mol) - (92.9 J/K·mol)

ΔS_{rxn} = 160.5 J/K·mol

Therefore: $CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$ $\Delta S_{rxn} = 160.5$ J/K·mol.

In this problem, the system becomes more disordered since a solid and a gas are the produced. The value of the entropy change for the reaction is positive. We make a conclusion that if the disorder of the reaction increases, then the change in entropy value (ΔS) will be positive. In other words, if a system goes from a state of low disorder to a state of high disorder, the entropy change is positive.

Entropy and Spontaneous Reactions

A reaction will tend to be spontaneous if the reaction moves from a state of low disorder to a state of high disorder. Look at the example below.

$C_{(s)} + H_2O_{(g)} + \text{energy} \rightarrow H_{2(g)} + CO_{(g)}$. (Equation 3)

In Equation 3, the enthalpy is positive ($\Delta H > 0$). We also know that in the reaction there are two moles of reactants (one of which is a solid) and two moles of products (both of which are gases). Gases have the highest entropies because they have higher disorder than solids or liquids. Therefore this system is one in which moves from a state of low disorder to a state of high disorder. It will tend to be spontaneous. Chemical reactions are driven by the combination of a tendency toward minimum enthalpy (lowest potential energy) and a tendency toward maximum entropy (greatest disorder).

Generalizations for Determining Entropy

Less Organized Phases Contain More Entropy

There are a number of factors that affect the disorder of a system. For instance, when a liquid is formed from a solid, the disorder increases (Equation 4) or a gas is formed from a liquid (Equation 5). As described earlier, the solid molecules are in a fixed position whereas the liquid molecules are free to move around (increasing the disorder) and the gas molecules have even more freedom to move around (increasing disorder again).

$Na_{(s)} \rightarrow Na_{(L)}$ $\Delta S = 51.4$ J/K × mol (Equation 4)

$C_2H_5OH_{(L)} \rightarrow C_2H_5OH_{(g)}$ $\Delta S = 122.0$ J/K·mol (Equation 5)

We can also predict that disorder increases when a solid or liquid dissolves in water. Equation 6 shows solid ammonium chloride dissolving in water. Notice the value of ΔS is positive indicating the increase in disorder. Entropy increases in this system since the particles are no longer held in place due to their electrostatic attractions in the crystal while in solution there are many more possibilities for the particles to occupy.

$NH_4Cl_{(s)} \rightarrow NH_4{}^{+}{}_{(aq)} + Cl^{-}{}_{(aq)}$ $\Delta S = 74.7$ J/K·mol (Equation 6)

The system therefore increases in disorder and the entropy is positive. A gas, however, decreases in disorder when it dissolved in water. The gas molecules have less possible positions and thus the disorder decreases; the sign of ΔS would be negative.

Generally, large molecules have a larger entropy than smaller molecules of simpler structures. For example, when we consider methane, CH_4, ethane, C_2H_6, and propane, C_3H_8, we can see that the relationships between their entropies will be that $S_{propane} > S_{ethane} > S_{methane}$. Propane, with more atoms, has more possibilities of rotating and twisting around than ethane and therefore greater entropy.

Increase in Number of Particles Increases Entropy

Equation 8 represents water being produced from its elements.

$2\ H_{2(g)} + O_{2(g)} \longrightarrow 2\ H_2O_{(L)}$ $\Delta S = -326.0$ J/K × mol (Equation 8)

Notice that there are three moles of reactants combining to produce two moles of products. Remember that gas particles have the highest entropy and with three moles of gas reactants, the higher entropy is on the reactant side of the chemical equation. The negative value of entropy means the disorder for the system is decreasing. Since the number of particles is decreasing, the particles are going from a gas state to a liquid state, and the disorder is decreasing, $\Delta S < 0$.

For the reaction in Equation 9, the reverse is happening.

$2\ H_2O_{2(L)} \longrightarrow 2\ H_2O_{2(L)} + O_{2(g)}$ $\Delta S = 125.6$ J/K × mol (Equation 9)

In Equation 9 there are two moles of reactant forming three moles of products. Looking at this equation, we see that these two moles of the reactant are in the liquid state and they form products in both the liquid and gas state. The gas particles will have higher entropies than the liquids. An increase in the number of particles, and the formation of the gas product, means an increase in disorder and therefore $\Delta S > 0$. The driving force for this reaction is the oxygen gas being produced.

Sample question: Predict whether the entropy will be positive or negative for each of the following:

(a)$Br_{2(g)} \longrightarrow Br_{2(L)}$

(b)$Ca(OH)_{2(s)} \longrightarrow Ca^{2+}{}_{(aq)} + 2\ OH^{-}{}_{(aq)}$

(c)$CO_{(g)} + 3\ H_{2(g)} \longrightarrow CH_{4(g)} + H_2O_{(g)}$

Solution:

(a)$Br_{2(g)} \longrightarrow Br_{2(L)}$; going from a gas to a liquid decreases the disorder of the system, therefore $\Delta S < 0$.

(b) $Ca(OH)_{2(s)} \longrightarrow Ca^{2+}{}_{(aq)} + 2\ OH^{-}{}_{(aq)}$; disorder increases when a solid or liquid dissolves in water, therefore $\Delta S > 0$.

(c) $CO_{(g)} + 3\ H_{2\ (g)} \longrightarrow CH_{4(g)} + H_2O_{(g)}$; there are four moles of reactants forming two moles of products. A decrease in the number of particles means a decrease in disorder and therefore $\Delta S < 0$.

Higher Temperature Favors More Entropy

When the temperature of a substance is increases, the molecules have greater average kinetic energy and therefore move around with greater velocity. The greater velocity of the particles means they collide more often and with greater force. The greater force of the collisions cause the molecules to spread further apart and therefore, they will have greater entropy. Increasing the temperature of a system favors the tendency toward greater randomness or maximum entropy.

Lesson Summary

- Entropy (S) is a measure of the disorder of a system. If the order of the reaction increases, then the change in entropy value (ΔS) will be negative. If the order of the reaction decreases, then the change in entropy value (ΔS) will be positive.
- A system that goes from a state of low disorder to a state of high disorder will tend to be spontaneous. The disorder of a system increases if a liquid is formed from a solid, a gas is formed from a liquid and

when a solid or liquid dissolves in water.

- A gas decreases in disorder when it dissolved in water. Entropy increases with greater molecules with more atoms Increasing disorder when reactions increase in # of particles.

Review Questions

1. Define Entropy. **(Beginning)**

2. Give an everyday example of entropy. **(Beginning)**

3. Which of the following examples will result in an increase in entropy? **(Intermediate)**

(a) $H_2O_{(L)} \rightarrow H_2O_{(s)}$

(b) $(NH_4)_2SO_{4(s)} \rightarrow 2\ NH_4{}^+{}_{(aq)} + SO_4{}^{2-}{}_{(aq)}$

(c) $H_2O_{(g)} \rightarrow H_2O_{(L)}$

(d) $Ag^{1+}{}_{(aq)} + Cl^-{}_{(aq)} \rightarrow AgCl_{(s)}$

4. Which of the following would have the greatest entropy? **(Intermediate)**

(a) $CO_{2(s)}$

(b) $H_2O_{(g)}$

(c) $CCl_{4(L)}$

(d) $CHCl_{3(L)}$

5. From the following equations, select those that tend to be spontaneous. **(Intermediate)**

(I) $N_{2(g)} + O_{2(g)} \rightarrow N_2O_{5(g)}$ + heat

(II) $H_2O_{(s)}$ + heat $\rightarrow H_2O_{(L)}$

(III) $N_{2(g)} + O_{2(g)} \rightarrow 2\ NO_{(g)}$ $\Delta H = 180.6$ kJ/mol

(IV) $C_6H_{12}O_{6(s)} + 6\ O_{2(g)} \rightarrow 6\ CO_{2(g)} + 6\ H_2O_{(L)}$ $\Delta H = -2802$ kJ/mol

(V) $CaCl_{2(s)} \rightarrow Ca^{2+}{}_{(aq)} + 2Cl^-{}_{(aq)}$ + heat

(a) I, II, and V

(b) I and III

(c) III and IV

(d) I, IV, and V

6. Calculate the entropy of the following reactions. **(Intermediate)**

(a) $CH_3CH_2OH_{(L)} + 3\ O_{2(g)} \rightarrow 2\ CO_{2(g)} + 3H_2O_{(L)}$

(b) $2\ AsF_{3(L)} \longrightarrow 2\ As_{(s)} + 3\ F_{2(g)}$

Compound	ΔS	Compound	ΔS
$CH_3CH_2OH(l)$	213. J/K × mol	As(s)	35.1 J/K × mol
$O_2(g)$	69.9 J/K × mol	$F_2(g)$	202.7 J/K × mol
$CO_2(g)$	160.7 J/K × mol	$AsF_3(l)$	181.2 J/K × mol
$H_2O(l)$	205.0 J/K × mol		

7. (3) Predict whether the entropy will be positive or negative for each of the following: **(Intermediate)**

(a) $CO_2(s) \longrightarrow CO_2(g)$

(b) $C_{12}H_{22}O_{11}(s) \longrightarrow C_{12}H_{22}O_{11}(aq)$

(c)$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$

Further Reading / Supplemental Links

http://en.wikipedia.org

Vocabulary

entropy A measure of the disorder of a system.

Review Answers

1. Entropy (S) is a measure of the disorder or randomness of a system.

2. Answers may vary. The chessboard is used in the introduction. Another example could be folded socks vs. unfolded, a deck of cards organized vs. thrown in a pile.

3. (b) $(NH_4)_2SO_4(s) \longrightarrow 2NH_4^+(aq) + SO_4^{2-}(aq)$

4. (a) $CO_2(s)$

5. (d) I, IV, and V

6. (a) $\Delta S_{rxn} = \Delta S_{products} - \Delta S_{reactants}$

$\Delta S_{rxn} = [2\Delta S(CO_2(g)) + 3\Delta S(H_2O(l))] - [\Delta S(CH_3CH_2OH(l)) + 3\ \Delta S(O_2(g))]$

$\Delta S_{rxn} = [2(160.7)\ J/K\cdot mol) + 3(205.0\ J/K\cdot mol)] - [(213\ J/K\cdot mol) + 3(69.9\ J/K\cdot mol)]$

$\Delta S_{rxn} = [936.4\ J/K\cdot mol] - [422.7\ J/K\cdot mol]$

$\Delta S_{rxn} = 513.7\ J/K \times mol$

(b)$\Delta S_{rxn} = \Delta S_{products} - \Delta S_{reactants}$

$\Delta S_{rxn} = [2\Delta S(As) + 3\Delta S(F_2)] - 2\Delta S(AsF_3)$

$\Delta S_{rxn} = 2(35.1\ J/K\cdot mol) + 3(202.7\ J/K\cdot mol) - 2(181.2\ J/K\cdot mol)]$

$\Delta S_{rxn} = 70.2\ J/K\cdot mol + 608.1\ J/K\cdot mol - 362.4\ J/K\cdot mol$

$\Delta S_{rxn} = -115.9\ J/K\cdot mol$

7. (a) $CO_2(s) \longrightarrow CO_2(g)$; $S_{solid} < S_{gas}$, therefore disorder increases and entropy increases, thus the $S > 0$.

(b) Sugar, as a solid, has lower entropy than sugar dissolved in a liquid. $S_{solid} < S_{liquid}$, therefore entropy increases and $S > 0$.

$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$; there are three moles of reactants forming two moles of products. A decrease in the number of particles means a decrease in disorder and therefore $\Delta S < 0$.

Gibbs Free Energy

Lesson Objectives

- Define Gibbs Free Energy.
- Calculate Gibbs Free Energy given the enthalpy and entropy.
- Use Gibbs Free Energy to predict spontaneity.

Introduction

Until this part in the chapter, we have been learning how to predict spontaneity of systems. Systems are considered to be spontaneous if the disorder increases from reactants to products. However, the spontaneity of the system is also dependent on the other thermodynamic factor, which is enthalpy.

In the latter part of the 1800s, a Yale physics professor named J. Willard Gibbs published a paper that related the enthalpy of a system to its entropy. It is this relationship, according to Gibbs, that would allow chemists to determine the spontaneity of the system at a specific temperature. The relationship is known as free energy. In this final lesson of the chapter, we will explore Gibbs free energy.

Gibbs Free Energy

Previously we have said that a system tended to be spontaneous if the enthalpy decreased or the entropy increased. However there are systems that are spontaneous that do not follow that pattern. For instance, ice melts at room temperature. True, entropy increases but enthalpy also increases. How do we know which will dominate a change? ***Gibbs free energy*** is defined as the maximum energy available to do useful work and can be determined by the combined effect of the change in the enthalpy of the system and change in the entropy of the reaction measured at a specific temperature.

Gibbs Free Energy Equation

The definition of free energy is shown in Equation 1.

$G = H - TS$ (Equation 1)

Where H is the heat content (enthalpy) of a substance; S is its entropy and T is the Kelvin temperature. However, since the only way we can know these values is to determine the change that takes place, Equation 2 is more useful, assuming that the temperature does not change.

$\Delta G = \Delta H - T\Delta S$ (Equation 2)

This equation tells us that the change in free energy for an equation is equal to the change in enthalpy minus the change in entropy times the Kelvin temperature. The free energy available is the energy from the change in enthalpy of the bonds less the amount TΔS. Or to look at it another way, the higher the temperature the more the disorder and the less available the energy becomes.

For Gibbs free energy, a spontaneous change is one where ΔG is negative. If a change takes place at low temperature and involves little change in entropy, TΔS will be negligible and ΔG will be spontaneous for an exothermic change (-ΔH). Combustion is a good example and is shown in Equation 3.

$2\ C_4H_{10(g)} + 13\ O_{2(g)} \rightarrow 8\ CO_{2(g)} + 10\ H_2O_{(g)} + \text{energy}$ (Equation 3)

For this reaction ΔH = -5315 kJ while ΔS = 312 J/K so ΔG will definitely be negative. All combustion reactions are spontaneous at room temperature.

For highly endothermic changes (high positive ΔH), ΔG can only be negative (that is spontaneous) if TΔS is large. This means that either the temperature is high or there is a large increase in entropy. An example of this is when solid carbon reacts with water in Equation 4.

$C_{(s)} + H_2O_{(L)} + \text{energy} \rightarrow H_{2(g)} + CO_{(g)}$ (Equation 4)

ΔS is positive because there is greater order in the solid carbon, which is being converted to the disorder of a gas. The temperature must be high for this reaction to occur (1170 K or higher) and in fact the reaction will stop or even reverse if the temperature decreases. Both conditions are met for ΔG to be negative for this endothermic reaction due to the increase in entropy and the high temperature.

In order to calculate Gibbs free energy, we will use the formula that shows the dependence on both the system's enthalpy change and entropy change at a specific temperature: $\Delta G = \Delta H - T\Delta S$.

Sample question: In the production of ammonia at 25°C, the entropy was found to be -198.0 J/K·mol. Calculate the Gibbs free energy for the production of ammonia.

$N_{2(g)} + 3\ H_{2(g)} \rightarrow 2\ NH_{3(g)}$ $\Delta H = -93.0$ kJ/mol

Solution:

$\Delta H = -93.0$ kJ/mol

$T = 25°C + 273.15$

$= 298.15$ K

$\Delta H = -198.0$ J/K·mol

= -0.198 J/K·mol

$\Delta G = \Delta H - T\Delta S$

ΔG = (-93.0 kJ/mol) - (298.15 K)(-0.198 kJ/K·mol)

ΔG = (-93.0 kJ/mol) - (-59.0 kJ/mol)

ΔG = -34.0 kJ/mol

The Sign of ΔG and Spontaneity

The sign of ΔG indicates spontaneity. If the sign of ΔG is positive, the reaction is non-spontaneous; if ΔG is negative the reaction is spontaneous. If ΔG is zero, the reaction is at equilibrium. In the production of ammonia, ΔG was found to be -34.0 kJ/mol at 25°C or 298.15 K. Therefore at this temperature the production of ammonia is a spontaneous process. What would happen if the temperature were increased?

Sample question: Calculate the Gibbs free energy for the production of ammonia at 200°C, the entropy was found to be -198.0 J/K·mol.

$N_{2(g)} + 3\ H_{2(g)} \longrightarrow 2\ NH_{3(g)}\ \Delta H = -93.0$ kJ/mol

Solution:

ΔH = -93.0 kJ/mol

T = 200°C + 273.15

= 473.15 K

ΔS = -198.0 J/K·mol

= -0.198 J/K·mol

$\Delta G = \Delta H - T\Delta S$

ΔG = (-93.0 kJ/mol) - (473.15 K) (-0.198 kJ/K·mol)

ΔG = (-93.0 kJ/mol) - (-93.7 kJ/mol)

ΔG = 0.7 kJ/mol)

At 200°C, ΔG is positive so the reaction is now non-spontaneous. Gibbs free energy is temperature dependent. At high temperatures, some systems that are spontaneous will become non-spontaneous (as is the case with $NH_{3(g)}$ formation) and some systems that are non-spontaneous will become spontaneous. Table 1 summarizes the conditions that relate ΔH, ΔS, ΔG, and temperature in order to determine spontaneity.

Table 1: Summary for Gibbs Free Energy

ΔH	ΔS	ΔG	**Spontaneity**	**Example**
Positive	Positive	Positive at low temperatures Negative at high temperatures	Spontaneous at high temperatures	$CoCl_{2(g)} \longrightarrow CO_{(g)} + Cl_{2(g)}$ at 535°C
Negative	Positive	Negative	Spontaneous at all temperatures	$CH_{4(g)} + 2\ O_{2(g)} \longrightarrow CO_{2(g)} + 2\ H_2O_{(g)}$

Negative	Negative	Negative at low temperatures Positive at high temperatures	Spontaneous at low temperatures	$N_{2(g)} + 3\ H_{2(g)} \longrightarrow 2\ NH_{3(g)}$ at 150°C
Positive	Negative	Positive	Non-spontaneous at all temps	$O_{2(g)} \longrightarrow 2\ O_{(g)}$

Sample question: Calculate ΔG for the reaction $Cu_{(s)} + H_2O_{(g)} \longrightarrow CuO_{(s)} + H_{2(g)}$ when $\Delta H = 84.5$ kJ/mol, $\Delta S = -48.7$ J/K·mol , and T = 150°C.

Is the reaction spontaneous or non-spontaneous at 150°C.

Solution:

$\Delta H = 84.5$ kJ/mol

T = 150°C + 273.15

= 423.15 K

$\Delta S = -48.7$ J/K·mol

= -0.0487 kJ/K·mol

$\Delta G = \Delta H - T\Delta S$

G = (84.5 kJ/mol) - (423.15 K)(-0.0487 kJ/K·mol)

ΔG = (84.5 kJ/mol) - (-20.6 kJ/mol)

ΔG = 105 kJ/mol

ΔG is positive so the reaction is non-spontaneous. Also looking at Table 1, ΔH is positive and ΔS is negative, ΔG will always be positive and therefore will always be non-spontaneous.

Lesson Summary

- Gibbs Free Energy equation: $\Delta G = \Delta H - T\Delta S$. The sign of ΔG indicates spontaneity or non-spontaneity. If the sign of ΔG is positive, the reaction is non-spontaneous; if ΔG is negative, the reaction is spontaneous. If ΔG is zero, the reaction is at equilibrium.

Summary of Gibbs Free Energy

ΔH	ΔS	ΔG	**Spontaneity**
+	+	+ at low T - at high T	Spontaneous at high T
-	+	-	Spontaneous
-	-	- at low T + at high T	Spontaneous at low T

+	-	+	Non-spontaneous

Review Questions

1. Define Gibbs free energy. **(Beginning)**

2. Summarize the conditions of spontaneity according to Gibbs free energy equation. **(Intermediate)**

3. For the reaction $C_2H_5OH(L) \longrightarrow C_2H_5OH(g)$, $\Delta S = 122.0$ J/K × mol , and $\Delta H = 42.59$ kJ/mol at 25°C. Which of the following statements is true? **(Intermediate)**

(a) the reaction will always be spontaneous

(b) the reaction will always be non-spontaneous

(c) the reaction will be spontaneous only at high temperatures

(d) the reaction will be spontaneous only at high temperatures

4. For the reaction $C_6H_6(l) + 3H_2(g) \longrightarrow C_6H_{12}(l)$, $\Delta S = -101.6$ J/K × mol , and $\Delta H = -205.4$ kJ/mol at 25°C. Which of the following statements is true? **(Intermediate)**

(a) the reaction will always be spontaneous

(b) the reaction will always be non-spontaneous

(c) the reaction will be spontaneous only at high temperatures

(d) the reaction will be spontaneous only at low temperatures

5. For the reaction $COCl_2(g) \longrightarrow CO(g) + Cl_2(g)$, $\Delta H = 109.6$ kJ/mol and $\Delta S = 137.1$ J/K × mol. What is the value of ΔG at 25.0°C? **(Intermediate)**

(a) 68.7 kJ/mol

(b) 106 kJ/mol

(c) -3.32×10^3 kJ/mol

(d) -4.08×10^4 kJ/mol

6. Hydrazine, $N_2H_{4(L)}$, has an important use in the space industry as rocket fuel. The preparation of hydrazine is shown in the equation below. If the value of ΔS is -393.8 J/K·mol at 15°C, what is the value of ΔG? **(Intermediate)**

$N_2O(g) + 3H_2(g) \longrightarrow N_2H_4(l) + H_2O(l)$ $\Delta H = -317.0$ kJ

(a) 1.132×10^5 kJ/mol

(b) 5.590×10^3 kJ/mol

(c) -311.1 kJ/mol

(d) -203.5 kJ/mol

7. Which of the following regarding reaction spontaneity is true? **(Intermediate)**

A. A reaction with a positive ΔS° will always be spontaneous.

B. A reaction with a negative ΔH° will always be spontaneous.

C. A reaction with a positive ΔS° and a negative ΔH° will always be spontaneous.

D. A reaction with a negative ΔS° and a negative ΔH° will always be spontaneous.

E. A reaction with a positive ΔS° and a positive ΔH° will always be spontaneous.

8. Using the data provided in the table, find the values of (a) ΔH, (b) ΔS, and finally (c) ΔG at 100°C. Is the system spontaneous or non-spontaneous? **(Intermediate)**

$CuO(s) + H_2(g) \longrightarrow Cu(s) + H_2O(g)$

	ΔH	ΔS
CuO(s)	-155.2 kJ/mol	43.5 J/K × mol
$H_2(g)$	0 kJ/mol	131.0 J/K × mol
Cu(s)	0 kJ/mol	33.3 J/K × mol
$H_2O(g)$	-241.8 kJ/mol	188.7 J/K × mol

Further Reading / Supplemental Links

http://en.wikipedia.org/wiki/Gibbs_free_energy

Vocabulary

Gibbs free energy The maximum energy available to do useful work.

Review Answers

1. Gibbs free energy is the maximum energy available to do useful work.

2. According to the table below that summarizes the conditions of enthalpy (ΔH) and entropy (ΔS) that produce the negative ΔG, row 2 conditions always produce spontaneous reactions, row 1 only at high temperatures, and row 3 only at low temperatures. (Using the equation $\Delta G = \Delta H - T\Delta S$)

Row	ΔH	ΔS	ΔG	**Spontaneity**
1	Positive	Positive	Positive at low temperatures Negative at high temperatures	Spontaneous at high temperatures
2	Negative	Positive	Negative	Spontaneous

3	Negative	Negative	Negative at low temperatures Positive at high temperatures	Spontaneous at low temperatures
4	Positive	Negative	Positive	Non-spontaneous

3. (c) the reaction will be spontaneous only at high temperatures

4. (d) the reaction will be spontaneous only at high temperatures

5. (a) 68.7 kJ/mol

6. (d) -203.5 kJ/mol

7. C

8.

(a) $\Delta H_{rxn} = \Delta H_{products} - \Delta H_{reactants}$

$\Delta H_{rxn} = [\Delta H(Cu_{(s)}) + \Delta H(H_2O_{(g)})] - [\Delta H(CuO_{(s)}) + \Delta H(H_{2\ (g)})]$

$\Delta H_{rxn} = [0\ \text{kJ/mol} + -241.8\ \text{kJ/mol}] - [-155.2\ \text{kJ/mol} + 0\ \text{kJ/mol}]$

$\Delta H_{rxn} = [-241.8\ \text{kJ/mol}] - [-155.2\ \text{kJ/mol}]$

$\Delta H_{rxn} = -86.60\ \text{kJ/mol}$

(b) $\Delta S_{rxn} = \Delta S_{products} - \Delta S_{reactants}$

$\Delta S_{Hrxn} = [\Delta S(Cu_{(s)}) + \Delta S(H_2O_{(g)})] - [\Delta S(CuO_{(s)}) + \Delta S(H_{2\ (g)})]$

$\Delta S_{rxn} = [33.3\ \text{J/K} \times \text{mol} + 188.7\ \text{J/K} \times \text{mol}] - [43.5\ \text{J/K} \times \text{mol} + 131.0\ \text{J/K} \times \text{mol}]$

$\Delta S_{rxn} = [222\ \text{J/K} \times \text{mol}] - [174.5\ \text{J/K} \times \text{mol}]$

$\Delta S_{rxn} = 47.5\ \text{J/K} \times \text{mol}$

(c) ΔH =-86.60 kJ/mol

$\Delta H = -86.60\ \text{kJ/mol}$

$T = 100°\text{C} + 273.15$

$= 373.15\ \text{K}$

$\Delta S = 47.5\ \text{J/K} \times \text{mol}$

$= 0.0475\ \text{kJ/K} \times \text{mol}$

$\Delta G = \Delta H - T\Delta S$

$\Delta G = (-86.60\ \text{kJ/mol}) - (373.15\ \text{K})(0.0475\ \text{kJ/K} \times \text{mol})$

$\Delta G = (-86.60\ \text{kJ/mol}) - (17.7\ \text{KJ/mol})$

$\Delta G = -104.3\ \text{kJ/mol}$

Since ΔG is negative, the reaction is spontaneous.

28. Electrochemistry

Origin of the Term Oxidation

Lesson Objectives

- The student will define the term "oxidation."

Introduction

Previously we have used the term “oxidation” in reference to oxidation state of atoms. For instance, we specified that the oxidation state of an atom in the alkali family is 1+. This occurs because these atoms always lose one electron to form their ions. Or, in contrast, the oxidation state of an atom in the halogen family is 1- . And again, this is because a halogen atom tends to gain an electron to form its ions.

Now, however, we are going to understand this term, that is, oxidation, was used at a much earlier time and then develop this concept later in the chapter.

Phlogiston

The term “phlogiston” was coined by Georg Stahl in a paper published in 1718. Stahl was expanding on a concept originated by his teacher, Joachim Becker. The phlogiston theory held that all flammable materials contain a substance named phlogiston in addition to the other components of the material. Phlogiston was described as being colorless, tasteless, and odorless. The only way to experience phlogiston was to observe it departing a burning material. The escaping phlogiston could be observed as orange and yellow light and smoke that accompanied combustion (Figure 1). When pieces of wood or paper or other flammable materials were burned, the phlogiston escaped into the air and the residue of the flammable material weighed less than the original material and this observation supported the concept that some substance was leaving the burning material. Other supporting observations were that once a substance was completely burned, the residue could not be burned further – because all its phlogiston was gone. The fact that when a material was burned in a closed container, it soon stopped burning – because the air had a maximum capacity for absorbing phlogiston and once the air had absorbed the maximum, it could no longer support combustion. For the same reason, the same air from the container would not support the combustion of another material nor would it support life. According to the theory, a dephlogisticated material would not burn and phlogisticated air (air that had its maximum fill of phlogiston) would not support combustion or life. The theory of phlogiston was quite widely accepted. When nitrogen was discovered in 1772, it was referred to as phlogisticated air because it would not support combustion nor life and when oxygen was discovered by Priestly in 1774, it was referred to as dephlogisticated air because it could accept more phlogiston, that is, support combustion and life.

Figure 1: Escaping phlogiston. (*Created by:* Richard Parsons, *License:* CC-BY-SA)

The first evidence of a problem with the theory (a contradictory observation) occurred with the combustion of certain metals such as magnesium. Experimenters determined that when magnesium burned, it gained mass even though it was supposed to be losing phlogiston. Some proponents of the phlogiston theory attempted to save the theory by explaining that metallic phlogiston had “negative mass” or that phlogiston was lighter than air and so had a buoyancy effect. These suggestions were not very convincing and in this case, as often is the case, the propping up of a theory with strange explanations, was an indication that the phlogiston theory was doomed.

Lavoisier and Combustion

The phlogiston theory remained the dominant theory of combustion until Antoine Lavoisier (1743-1794) demonstrated that combustion was actually a combination of the flammable material with some component of the air. Lavoisier used the work of Joseph Priestly (the discoverer of oxygen) to demonstrate that if *all* the products of combustion (smoke, ash, etc.) were retained by carrying out the combustion in a closed container, then all combustions, not just those of magnesium, actually gained mass rather than lost mass. Lavoisier also demonstrated that the increase in mass of the combustible material was exactly equal to the loss of mass of the air in the container.

Lavoisier suggested that combustion was the combination of the flammable material with some component of the air – namely oxygen. This theory of combustion was quickly accepted and the phlogiston theory was relegated to the scrap heap of theories. You should not think that the acceptance and later rejection of the phlogiston theory as some unfortunate flaw in the scientific method. It is, rather, an example of the normal functioning of the scientific method.

Lesson Summary

- The phlogiston theory of combustion suggested that "phlogiston" was escaping from the combustible material into the air.
- Lavoisier's theory of combustion was that the combustible material was combining with some component of the air.

Review Questions

1. What would be the experimental difference between phlogisticated air and de-phlogisticated air? **(Intermediate)**

Vocabulary

combustion	A group of chemical reactants in which the reactants are fuel and oxygen gas.
phlogiston	The “fire substance” from a former theory of combustion.

Review Answers

1. Phlogisticated air would not support combustion while de-phlogisticated air would support combustion.

Oxidation – Reduction

Lesson Objectives

- The student will assign the correct oxidation number to any element in a compound or ion.
- In an oxidation-reduction equation, the student will identify the substance being oxidized, the substance being reduced, the oxidizing agent, and the reducing agent

Introduction

Many important chemical reactions involve the exchange of one or more electrons. The stoichiometric calculations that chemists make on chemical reactions require a balanced equation. The “inspection” method for balancing equations works well and quickly for many reactions, but when a more complex electron exchange is involved, a new method for equation balancing is needed.

Definition of Oxidation and Reduction

After Lavoisier, a substance was said to be oxidized when it reacted with oxygen. A reaction with oxygen was called oxidation. Today, the words “oxidized” and “oxidation” are still used for those situations but now we have a much broader second meaning for these words. Today, the broader sense of the word “oxidation” is defined as losing electrons. When a substance reacts with oxygen, it almost always loses electrons to the oxygen so we are simply extending the term oxidation to mean losing electrons whether to oxygen or any other substance. A substance is oxidized when it donates one or more of its electrons to another substance.

The other half of this process, the gaining of electrons, also needs a name. When an atom or an ion gains electrons, the charge on the particle is decreased. For example, if a sulfur atom whose charge is zero (0) gains two electrons, its charge becomes 2- and if an Fe^{3+} ion gains an electron, its charge changes from 3+ to 2+. In both cases, 0 to 2- and 3+ to 2+, the charge on the particle is reduced by the gain of electrons. The word “reduction” is defined to mean “the gain of electrons.” In chemical systems, these two processes must occur simultaneously and the number of electrons lost in the oxidation must be the same as the number of electrons gained in the reduction. In oxidation-reduction reactions, electrons are transferred from one substance to another. Here’s an example of an oxidation – reduction reaction.

$$2\,Ag^{+}{}_{(aq)} + Cu_{(s)} \longrightarrow 2\,Ag_{(s)} + Cu^{2+}{}_{(aq)}$$

In this reaction, the silver ions are gaining electrons to become silver atoms. Therefore, the silver ions are being reduced. The copper atoms are losing electrons to become copper ions and are therefore, being oxidized. Whenever, a chemical reaction involves electrons being transferred from one substance to another, the reaction is an oxidation – reduction reaction.

Oxidizing and Reducing Agents

When a substance is oxidized, it loses electrons. In chemical reactions, that requires that another substance take on those electrons and be reduced. Therefore, when a substance undergoes oxidation, it causes another substance to be reduced. The substance that caused another substance to be reduced is called a **reducing agent.** As you can see, the substance undergoing oxidation and the reducing agent are the same substance.

Similarly, when a substance gains electrons, it is reduced. By gaining electrons, it is causing some other substance to give up those electrons. Therefore, by undergoing reduction, the substance is causing another substance to be oxidized and is called an **oxidizing agent**. Again, the substance undergoing reduction and the oxidizing agent are the same substance.

$$2\,Ag^{+}{}_{(aq)} + Cu_{(s)} \longrightarrow 2\,Ag_{(s)} + Cu^{2+}{}_{(aq)}$$

In the oxidation-reduction reaction above, silver ions are being **reduced** and are the **oxidizing agent.** Similarly, copper atoms are being **oxidized** and are the **reducing agent.** These substances are always on the reactant side of the equation. Another point of terminology is that chemists, like you, tired of saying or writing the term oxidation-reduction so they shortened the term to **redox.** An oxidation-reduction reaction can be referred to as a redox reaction.

Oxidation Numbers

In order to balance equations for reactions involving oxidation and reduction, it is necessary to have a bookkeeping system to keep track of the transferred electrons. The bookkeeping system chemists use to keep track of electrons in oxidation-reduction reactions is called **oxidation numbers.** The assignment of oxidation numbers to all the atoms or ions in a reaction follows a set of rules. For the most part, these rules will have the oxidation number of a particle be “the number of electrons the atom has gained or lost from its elemental state.” For example, for a Ca^{2+} ion, the calcium ion has clearly lost two electrons from its elemental form and therefore, its oxidation number is 2+. Similarly, it is clear that a fluoride ion, F^-, has gained one electron from its elemental state and therefore its oxidation number is 1-. As you learn how to assign oxidation numbers, it will become obvious that there are cases where the oxidation number of an atom does NOT represent the actual number of electrons gained or lost, but we will assign oxidation numbers according to the rules and the system works even if some atom is assigned a fractional oxidation number.

The *Rule #1* for assigning oxidation numbers is for the oxidation numbers of substances in their elemental form. ***Substances in elemental form have oxidation numbers of zero (0)*** . It is clear that substances in elemental form have neither gained nor lost any electrons from their elemental state.

Examples of Oxidation Numbers for Substances in Elemental Form

Substance	Oxidation Number
Fe	0
Ag	0
H_2	0
O_2	0
Cl_2	0
S_8	0

Rule #2 for assigning oxidation numbers relates to monatomic ions. ***For monatomic ions, the oxidation number is the same as the charge on the ion.*** Again, it should be apparent that the charge on the ion is an indication of how many electrons have been gained or lost.

Examples of Oxidation Numbers for Monatomic Ions

Substance	Oxidation Number
Ca^{2+}	2+
Ag^+	1+
Fe^{3+}	3+
S^{2-}	2-
F^-	1-
Na^+	1+

Rule #3 is for the atoms of family IA, the alkali metals, in compounds. Alkali metals always lose their single valence electron when they combine. Therefore, ***for IA metals, the oxidation number in compounds is 1+*** .

Examples of Oxidation Numbers for Alkali Metals in Compounds

Substance	Oxidation Number for the Metal
NaCl	1+
Na_2S	1+
Na_2SO_4	1+
$NaC_2H_3O_2$	1+
$KClO_4$	1+

Rule #4 is for the atoms of family IIA, the alkali earth metals, in compounds. Alkali earth metals always lose both of their valence electrons when they combine chemically, so ***for IIA metals, the oxidation number in compounds is 2+*** .

Examples of Oxidation Numbers for Alkali Earth Metals in Compounds

Substance	**Oxidation Number for the Metal**
MgF_2	2+
$Ca(NO_3)_2$	2+
$BaCrO_4$	2+
$Mg(OH)_2$	2+
CaO	2+

Rule #5 concerns hydrogen atoms when they are in compounds. A hydrogen atom has only one electron and in the great majority of compounds that hydrogen forms, it either completely or at least partially loses that electron. ***For hydrogen, in compounds where hydrogen is the more electropositive atom, the oxidation number is 1+.***

Examples of Oxidation Numbers for Hydrogen in Compounds

Substance	**Oxidation Number for Hydrogen**
HF	1+
H_2O	1+
$HC_2H_3O_2$	1+
$Mg(OH)_2$	1+
CH_4	1+

But, there is an exception to this rule for hydrogen. It is possible for hydrogen to form compounds with some metals that are even more electropositive than hydrogen. In these cases, hydrogen becomes an electron acceptor instead of an electron donor. Active metals lose or partially lose their valence electrons to hydrogen. Since hydrogen is acting as the more electronegative element in these compounds, the compounds are named hydrides. ***In hydrides, the oxidation number of hydrogen is 1-.***

Examples of Oxidation Numbers for Hydrogen in Hydride Compounds

Substance	**Oxidation Number for Hydrogen**
LiH (lithium hydride)	1-
NaH (sodium hydride)	1-
MgH_2 (magnesium hydride)	1-

Rule #6 is about the oxidation number of oxygen in compounds. Oxygen is a very electronegative element and in almost all its compounds, it draws two electrons completely or partially from a bonding element. Therefore, ***the oxidation number for oxygen in compounds is almost always 2-.***

Examples of Oxidation Numbers for Oxygen in Compounds

Substance	**Oxidation Number for Oxygen**
H_2O	2-

MgO	2-
H_2SO_4	2-
$Na_2Cr_2O_7$	2-
$C_6H_{12}O_6$	2-

Like hydrogen, there is an exception to the rule for oxygen. In a group of compounds named "peroxides" (H_2O_2, hydrogen peroxide, Na_2O_2, sodium peroxide, etc.), each of the oxygen atoms shares a bond with the other oxygen atom and therefore, the oxygen atoms only accept one electron from the other element. Therefore, ***in peroxides, oxygen has an oxidation number of 1-.***

Examples of Oxidation Numbers for Oxygen in Peroxides

Substance	**Oxidation Number for Oxygen**
H_2O_2	1-
Na_2O_2	1-

Some other elements exhibit only one possible gain, loss, or sharing of electrons when they form compounds. Aluminum, for example, always loses or partially loses three electrons when it forms compounds and so its oxidation number in compounds is 3+. Zinc always loses or partially loses two electrons when it combines, so its oxidation number in compounds is 2+. The halogens (family VIIA) always gain one electron in binary compounds and would have an oxidation number of 1- in these compounds. Some of the halogen atoms form compounds where there are three elements and one of them is oxygen ($HClO_3$, for example). In these compounds, the halogen atom is almost never 1-.

There will be quite a few atoms whose oxidation number may be different in different compounds and for these; you will have to calculate their oxidation numbers. To allow you make such calculations, there is a general rule that ***the sum of the oxidation numbers of all the atoms in a compound must be zero and the sum of all the oxidation numbers of the atoms in a polyatomic ion must equal the charge on the ion.***

Example 1:

What is the oxidation number of sulfur in Na_2SO_4?

Solution:

We have three pieces of information that will allow us to calculate the oxidation number of sulfur. We know that the sum of the oxidation numbers of all the atoms will equal zero.

$2(\text{Na}) + 1(\text{S}) + 4(\text{O}) = 0$

We also know the oxidation number of sodium from rule 3 is 1+ and the oxidation number of oxygen from rule 6 is 2-. We simply plug these values into the equation and solve for the oxidation number of sulfur.

$2(1+) + 1(x) + 4(2-) = 0$ and $x = 6+$

Example 2:

What is the oxidation number of chromium in $K_2Cr_2O_7$?

Solution:

2(K) + 2(Cr) + 7(O) = 0

2(1+) + 2(x) + 7(2-) = 0

and

x = 6+

Example 3:

What is the oxidation number of nitrogen in the nitrate ion, NO_3^-?

Solution:

1(N) + 3(O) = -1

1(x) + 3(2-) = -1

and

x = 5+

Example 4:

What is the oxidation number of phosphorus in the phosphate ion, PO_4^{3-}?

Solution:

1(P) + 4(O) = 3-

1(x) + 4(2-) = 3-

and

x = 5+

Example 5:

What is the oxidation number of iron in Fe_2O_3?

Solution:

2(Fe) + 3(O) = 0

2(x) + 3(2-) = 0

and

x = 3+

Example 6:

What is the oxidation number of iron in Fe_3O_4?

Solution:

This example was chosen specifically to make a point.

3(Fe) + 4(O) = 0

3(x) + 4(2-) = 0

and

x = 8/3

In this case, we get an oxidation number that is not a whole number. Since this number supposedly represents the number of electrons gained or lost from the elemental state, we should feel uncomfortable about an oxidation number of 8/3. We know that an atom did not lose a fraction of an electron. The reason that this oxidation number is a fraction is because some of the iron atoms in Fe_3O_4 lost 3 electrons and some lost 2 electrons. The 8/3 oxidation number is the average oxidation number for the iron atoms. However, this situation does not cause a problem. You can use the 8/3 oxidation number in the oxidation number bookkeeping system and it gives correct results.

Lesson Summary

- Oxidation is the loss of electrons or a gain in oxidation number.
- Reduction is the gain of electrons or a decrease in oxidation number.
- The oxidizing agent is the substance causing oxidation and therefore, the oxidizing agent itself is reduced.
- The reducing agent is the substance causing reduction and therefore, the reducing agent itself is oxidized.
- Oxidation and reduction always occur simultaneously.
- A reaction involving the gain and loss of electrons is called an oxidation-reduction or redox reaction.
- We use a bookkeeping system called **oxidation numbers** to keep track of the electrons gained and lost during a redox reaction.
- The oxidation number of an uncombined element is zero.
- The oxidation number of a monatomic ion is the same as the charge on the ion.
- The oxidation number of hydrogen in most of its compounds is 1+ but in hydrides, it is 1-.
- The oxidation number of oxygen in most of its compounds is 2+ but in peroxides, it is 1+.
- In neutral compounds, the sum of the oxidation numbers of all the atoms in the compound must equal zero.
- In polyatomic ions, the sum of the oxidation numbers of all the atoms in the ion must be equal to the charge on the ion.

Review Questions

1. Indicate the oxidation numbers for each of the following atoms. **(Beginning)**

A. Mn^{2+}

B. Al

C. Al in Al_2O_3

D. Br in NaBr

E. Fe in Fe_2O_3

F. arsenic in AsO_4^{3-}

G. chlorine in ClO_4^{-}

H. sulfur in H_2SO_3

2. In the following reaction, identify the element that is being oxidized and the element that is being reduced. **(Intermediate)**

$MnO_2 + 4\ HCl \rightarrow MnCl_2 + Cl_2 + 2\ H_2O$

Vocabulary

oxidation	(1) A chemical combination with oxygen (old definition). (2) A loss of electrons in an atom or an increase in the oxidation state of an atom (modern definition).
oxidation numbers	In ionic compounds, it is equal to the ionic charge. In covalent compounds, it is the charge assigned to the atom in accordance with a set of rules.
oxidation state	In ionic compounds, it is equal to the ionic charge. In covalent compounds, it is the charge assigned to the atom in accordance with a set of rules.
oxidizing agent	A substance that gains electrons in a chemical reaction or undergoes an increase in its oxidation state.
reducing agent	The substance in a redox reaction that loses electrons or increases its oxidation state.
reduction	The gain of electrons or decrease in oxidation state in a chemical reaction.

Review Answers

1.

A. 2+

B. 0

C. 3+

D. 1-

E. 3+

F. 5+

G. 7+

H. 4+

2. Some of the chlorine atoms in 4 HCl are changing their oxidation state from 1- to 0 and are therefore being oxidized. The manganese is changing its oxidation state from 4+ to 2+ and is therefore being reduced.

Balancing Redox Equations Using the Oxidation Number Method

Lesson Objectives

- Given a redox reaction, the student will determine which substances are changing their oxidation state.
- Given a redox reaction, the student will balance the equation using the oxidation number method.

Introduction

The method you have used previously to balance equations was by inspection, that is, it was a trial and error method. You would keep trying numbers, using intelligent guessing, until you get the simplest whole number ratio that balances. That method works very well and very quickly for simpler reactions – but with the more complex redox reactions, that method will not work. As an example, here is the net ionic (not balanced) equation for the reaction of silver ions with copper atoms.

$$Ag^{+}_{(aq)} + Cu_{(s)} \longrightarrow Ag_{(s)} + Cu^{2+}_{(aq)}$$

By the inspection method, this equation would be balanced with all ones. But that is not correct for this reaction. The properly balanced equation for this reaction is:

$$2\ Ag^{+}_{(aq)} + Cu_{(s)} \longrightarrow 2\ Ag_{(s)} + Cu^{2+}_{(aq)}$$

In non-redox reactions, all you are required to balance is the number of atoms or molecules of each species. In redox reactions, you must balance not only the number of atoms, ions or molecules of each species but you must also balance the gain and loss of electrons. Balancing redox reactions requires process that may have up to five steps.

Change of Oxidation State

A redox reaction occurs when an atom in the products has a different oxidation number than it had in the reactants. Since oxidation is always accompanied by reduction, there will usually be two species that change their oxidation state between the reactant and product side of the equation. In the following equation, oxidation numbers have been assigned to each atom in the equation.

$$\overset{1+}{H}\overset{5+}{N}\overset{2-}{O}_3 + \overset{1+}{H}_2\overset{2-}{S} \rightarrow \overset{2+}{N}\overset{2-}{O} + \overset{0}{S} + \overset{1+}{H}_2\overset{2-}{O}$$

When we check the oxidation numbers of each atom on the two sides of the equation, we discover that nitrogen has changed its oxidation state from 5+ to 2+. We may note that nitrogen has been reduced by gaining three electrons. Sulfur has also changed its oxidation state, going from 2- to 0. Sulfur, therefore, has been oxidized by losing two electrons. This is a redox reaction. You may have learned the names of the four types of chemical reactions in an earlier chapter; synthesis, decomposition, single replacement, and double replacement. In the four types of chemical reactions, only double replacement is NOT a redox reaction.

Balancing Redox Equations

The steps involved in balancing redox reactions by the oxidation number method will be pointed out in the following example.

Example 7:

Balance the following redox equation.

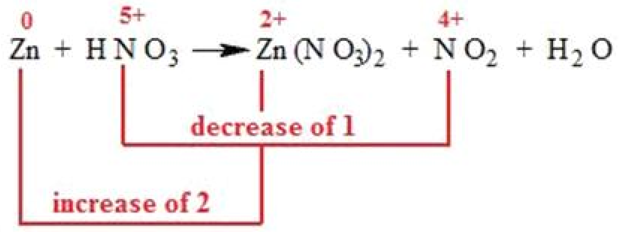
$Zn + HNO_3 \rightarrow Zn(NO_3)_2 + NO_2 + H_2O$

Solution

Step 1. Determine the oxidation numbers of all atoms in the equation.

$$\overset{0}{Zn} + \overset{1+}{H}\overset{5+}{N}\overset{2-}{O_3} \rightarrow \overset{2+}{Zn}(\overset{5+}{N}\overset{2-}{O_3})_2 + \overset{4+}{N}\overset{2-}{O_2} + \overset{1+}{H_2}\overset{2-}{O}$$

Step 2. Select the substances that are changing their oxidation number (there will usually be exactly two but not always).



Step 3. Pick coefficients for the species that are changing their oxidation numbers so that the increase and decrease of oxidation numbers are equal.

$$1\ Zn + 2\ HNO_3 \rightarrow 1\ Zn(NO_3)_2 + 2\ NO_2 + H_2O$$

One atom of zinc is taking on two electrons and that requires two atoms of nitrogen to give up one electron each . . . the other two atoms of nitrogen are keeping the same oxidation number.

Step 4. Nitrogen appears in two places in the products – in NO_2 and in $Zn(NO_3)_2$. The coefficient for nitrogen in the reactants must account for all the nitrogen in the products. Therefore, the coefficients of $Zn(NO_3)_2$ and NO_2 remain 1 and 2 respectively, but the coefficient for HNO_3 must become 4.

$$1\ Zn + 4\ HNO_3 \rightarrow 1\ Zn(NO_3)_2 + 2\ NO_2 + H_2O$$

This is NOT changing the balance of the gain and loss of electrons because only two of the nitrogen atoms from HNO_3 are undergoing reduction. The other two atoms of nitrogen are keeping the same oxidation number and going into the $Zn(NO_3)_2$.

Step 5. The final step is to balance (by inspection) all the remaining substances that are not involved in oxidation or reduction. In this case, the only substance remaining to be balanced is H_2O. The coefficient of water must be a 2 to account for the four hydrogen atoms in HNO_3.

$$1\ Zn + 4\ HNO_3 \rightarrow 1\ Zn(NO_3)_2 + 2\ NO_2 + 2\ H_2O$$

Of course, the coefficients of one would not be written as they are here. Coefficients of one are understood and not written. They were only included here for instruction.

Example 8:

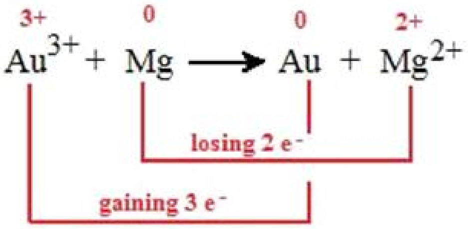
Balance the following redox reaction.

$Au^{3+} + Mg \rightarrow Au + Mg^{2+}$

Solution

Assign oxidation numbers.

$$\overset{3+}{Au^{3+}} + \overset{0}{Mg} \rightarrow \overset{0}{Au} + \overset{2+}{Mg^{2+}}$$



Determine the atoms whose oxidation state is changing.

Assign coefficients to balance the gain and loss of electrons.

$2\,Au^{3+} + 3\,Mg \rightarrow 2\,Au + 3Mg^{2+}$

With these coefficients, the total gain of electrons is 6 and the total loss of electrons is 6. The number of atoms of each type is also equal and the total charge on each side of the equation is equal. No further steps are necessary to balance this equation.

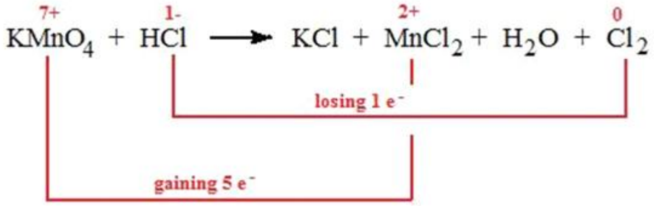
Example 9:

Balance the following redox equation $KMnO_4 + HCl \rightarrow KCl + MnCl_2 + H_2O + Cl_2$

Assign oxidation numbers.

$$\overset{1+}{K}\,\overset{7+}{Mn}\,\overset{2-}{O_4} + \overset{1+}{H}\,\overset{1-}{Cl} \rightarrow \overset{1+}{K}\,\overset{1-}{Cl} + \overset{2+}{Mn}\,\overset{1-}{Cl_2} + \overset{1+}{H_2}\overset{2-}{O} + \overset{0}{Cl_2}$$

Determine the atoms whose oxidation state are changing.



We should note that chlorine appears three times in the products but in only one of those forms is it changing its oxidation state. We will take care of the one that changes first and the take care of the other two later.

In order to balance the gain and loss of electrons, we need five manganese atoms reacting for each chlorine that ends up in Cl_2. We could use a coefficient of 1 for the manganese and a coefficient of 5 for the HCl but you notice that would require a coefficient of 2½ for the Cl_2. It's OK to do that, we can fix it later, but it's easier to fix it now. We can use a coefficient of 5 for the Cl_2, a coefficient of 10 for the HCl, and a coefficient of 2 for the manganese compounds. Those coefficients will produce a gain of 10 electrons and a loss of 10 electrons and the four substances involved in the oxidation and reduction will be balanced.

$2\ KMnO_4 + 10\ HCl \rightarrow KCl + 2\ MnCl_2 + H_2O + 5\ Cl_2$

We still need to balance the KCl and the water and we do that by inspection. All of the oxygen atoms in $KMnO_4$ must go to the water since that is the only oxygen in the products. Since there are 8 oxygen atoms represented in the reactants, the coefficient for water must be 8. The two potassium atoms in $KMnO_4$ must go to the KCl since that is the only potassium in the products. Therefore, the coefficient for KCl must be 2.

$2\ KMnO_4 + 10\ HCl \rightarrow 2\ KCl + 2\ MnCl_2 + 8\ H_2O + 5\ Cl_2$

Finally, we must adjust the coefficient of HCl to account for the chloride atoms in KCl and $MnCl_2$ and we must make sure the hydrogen atoms in water are balanced by the hydrogen atoms in HCl. The HCl must provide the 10 chloride atoms in Cl_2 plus the 2 chloride atoms in KCl and the 4 chloride atoms in $MnCl_2$. As a result, we must adjust the coefficient of HCl to 16. That coefficient for HCl will also account for the 16 hydrogen atoms in water.

$2\ KMnO_4 + 16\ HCl \rightarrow 2\ KCl + 2\ MnCl_2 + 8\ H_2O + 5\ Cl_2$

You must realize that changing the coefficient for HCl does not unbalance the gain and loss of electrons because only 10 of those chlorine ions are undergoing oxidation to Cl_2.

Lesson Summary

- The steps to balance a redox reaction include:

1) Assign oxidations numbers to all the atoms in the skeleton equation.

2) Identify the atoms that are changing their oxidation state from reactants to products.

3) Choose coefficients for the atoms that are changing their oxidation state such that the number of electrons being gained is exactly equal to the number of electrons being lost.

4) Balance the non-redox components of the equation by inspection.

5) Check that atoms are balanced, electron gain and loss is balance, and that charge is balanced.

Review Questions

1. Balance the following equation using the oxidation number method. **(Challenging)**

$HNO_3 + Br_2 \rightarrow HBrO_3 + NO_2 + H_2O$

2. Balance the following equation using the oxidation number method. **(Challenging)**

$Zn + HNO_3 \rightarrow Zn(NO_3)_2 + NO_2 + H_2O$

3. In terms of electron gain and loss, explain why chlorine undergoes both oxidation and reduction in the following unbalanced reaction. **(Challenging)**

$Cl_2 + KOH \rightarrow KCl + KClO_3 + H_2O$

4. Balance the equation in the previous problem. **(Challenging)**

Further Reading / Supplemental Links

http://www.wfu.edu/~ylwong/redox/

Review Answers

1. $10\ HNO_3 + Br_2 \rightarrow 2\ HBrO_3 + 10\ NO_2 + 4\ H_2O$

2. $Zn + 4\ HNO_3 \rightarrow Zn(NO_3)_2 + 2\ NO_2 + 2\ H_2O$

3. Some of the chlorine in Cl_2 changes it oxidation state to 1- in the KCl and is therefore reduced. Some of the chlorine in Cl_2 changes its oxidation state to 5+ in $KClO_3$ and is therefore oxidized.

4. $3\ Cl_2 + 6\ KOH \rightarrow 5\ KCl + KClO_3 + 3\ H_2O$

Electrolysis

Lesson Objectives

- Given a diagram of an electrolysis apparatus including the compound being electrolyzed, the student will identify the anode and the cathode.

- Given a diagram of an electrolysis apparatus including the compound being electrolyzed, the student will write the oxidation and reduction half-reactions.

Introduction

Electrolysis involves using an electric current to force an otherwise nonspontaneous chemical reaction to occur.

Electric Current

Any flow of electric charge is an **electric current.** Electrons are far easier to remove from atoms than protons and so most of the electric current you experience in daily life is electron flow. Electrons move easily through a piece of metal because of the freedom of movement of valence electrons in the metallic bond. The movement of electrons through a piece of metal is called **metallic conduction.** *A battery is a two terminal device which causes the electrons at one terminal to have a higher electric potential energy than the electrons at the other terminal. If these high potential energy electrons are provided with a low-resistance path to follow, they will flow along the path from the high potential energy terminal (the negative terminal) to the low potential energy terminal (the positive terminal). A metal wire provides such a low resistance path for electrons. The potential energy lost by the electrons as they move from high electric potential energy to low electric potential energy is converted into heat and light by the light bulb filament.* An electric current also exists when positive or negative ions move along a path. The movement of ions through a solution is called **ionic conduction**. Electric current of all types flow because there is a difference in electric potential energy at two positions. A common device for providing this difference in electric potential energy is a battery. A battery has two terminals and chemical reactions inside the battery cause one terminal to have higher electric potential energy than the other terminal. The higher potential energy terminal is called the negative terminal and the other terminal is called the positive terminal. If a low resistance path is provided, electrons will flow along the path from high to low potential energy.

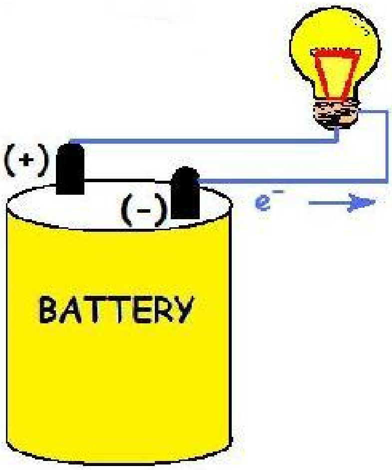


Figure 2: A battery connected to a light bulb is a complete circuit. (*Created by:* Richard Parsons, *License:* CC-BY-SA)

Current Through an Electrolyte

If we attach pieces of metal by wires to the terminals of a battery and suspend the pieces of metal (called electrodes) in an ionic solution as shown below, the high potential energy electrons will flow onto the negative electrode. Simultaneously, some electrons will flow off the other electrode leaving it positive.

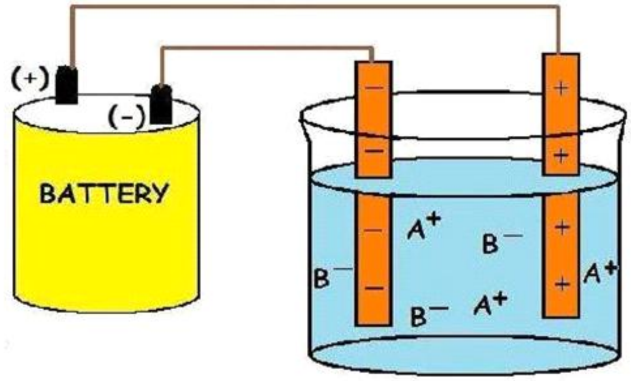


Figure 3: Electrolysis.

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The cations (A^+) in the solution are attracted to the negative electrode and will migrate through the solution to contact the negative electrode. When a 1+ cation contacts the negative electrode, it will pick up an electron from the electrode and become a neutral atom. In this way, electrons leave the negative electrode. You should recognize that those cations that pick up an electron and become atoms have been reduced.

At the same time the positive ions are migrating toward the negative electrode, anions (B^-) are migrating toward the positive electrode. When a negative ion touches the positive electrode, it gives up its extra electron to the electrode and becomes a neutral atom. In this way, electrons are added to the positive electrode. Even though the electrons that leave the negative terminal of the battery and the ones that arrive at the positive terminal are not the same electrons, the circuit is nevertheless complete and current flows through the circuit just as if a wire had been placed between the two electrodes. The anions that donate electrons to the positive electrode are oxidized. The processes that occur at the two electrodes are simultaneous. You should also realize that the ions in the solution are being consumed by this process and current will only flow as long as there are ions to accept and donate electrons. When the solution runs out of ions, current flow stops. When a current flows through an electrolyte in this manner, the electrolytic solution is called the internal part of the circuit and the wires and battery are called the external part of the circuit.

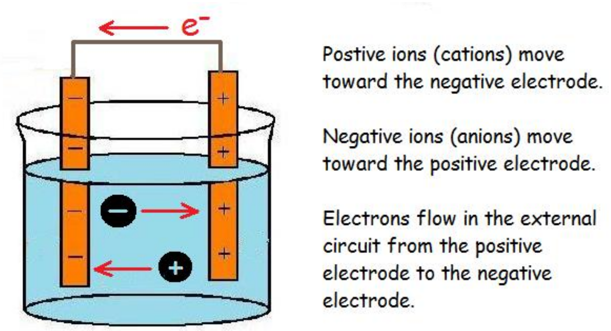

Figure 4: Ion flow allows electrical conductivity. (*Created by:* Richard Parsons, *License:* CC-BY-SA)

Electrolysis of Liquid NaCl

Solid sodium chloride consists of alternating sodium ions and chloride ions in a tightly packed, three-dimensional, pattern called a crystal lattice. Ionic solids do not conduct electric current because the ions cannot migrate through the solid material. If sodium chloride is heated to a high enough temperature, however, it melts to a liquid and in liquid structures, ions can migrate. Therefore, ionic substances in liquid form will conduct electricity in approximately the same way as ions in solution.

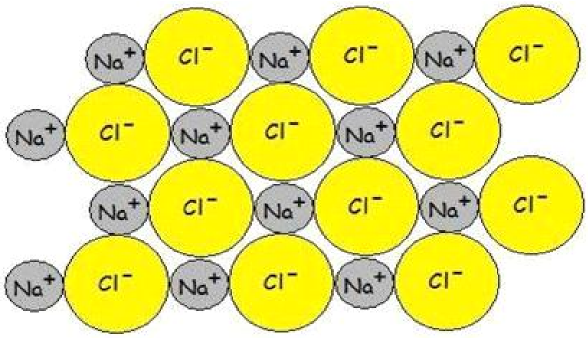

Figure 5: Sodium chloride crystal, NaCl.

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If electrodes connected to battery terminals are placed in liquid sodium chloride, the sodium ions will migrate toward the negative electrode and be reduced while the chloride ions migrate toward the positive electrode and are oxidized. The processes that occur at the electrodes can be represented by what are called half-equations.

At the positive electrode: $Na^+ + e^- \rightarrow Na$ (reduction)

At the negative electrode: $2\ Cl^- \rightarrow Cl_2 + 2\ e^-$ (oxidation)

Half-equations are very helpful in discussing and analyzing processes but half-reactions cannot occur as they appear. Both oxidation and reduction must occur at the same time so the electrons are donated and absorbed nearly simultaneously.

The two half-reactions may be added together to represent a complete reaction. In order to add the half-reactions, the number of electrons donated and the number of electrons accepted must be equal. In the case of the oxidation of chloride ion and the reduction of sodium ion, the sodium half-reaction must be doubled so that each half-reaction involves two electrons.

$2(Na^+ + e^- \rightarrow Na) = 2\ Na^+ + 2\ e^- \rightarrow 2\ Na$

$2\ Cl^- \rightarrow Cl_2 + 2e^-$

$2\ Na^+ + 2e^- + 2\ Cl^- \rightarrow 2\ Na + Cl_2 + 2e^-$

The two electrons on each side of the equation can be cancelled and we are left with the net reaction for the **electrolysis** of sodium chloride.

$2\ Na^+ + 2Cl^- \rightarrow 2\ Na + Cl_2$

Electrolysis is a process that involves forcing a current through a liquid or solution to cause a non-spontaneous chemical reaction to occur. Many chemical reactions occur spontaneously because the products have less potential energy that the reactants and processes occur spontaneously many times if they are moving toward lower potential energy. In electrolysis reactions, the products have more potential energy than the reactants. Electrolysis reactions will not run unless energy is put into the system from outside. In the case of electrolysis reactions, the energy is provided by the battery.

Electrolysis of Water

If we place electrodes connected to the terminals of a battery into pure water, no current is conducted and no electrolysis occurs. This is because ions must be present in order for a current to be conducted. Even though water is very slightly ionized to H^+ and OH^- ions, the concentrations of these ions is too small to produce electrolysis. When a small amount of a substance that supplies ions in solution, such as H_2SO_4 or Na_2SO_4, is added to the water in the electrolysis set up, hydrogen gas is rapidly produced at the negative electrode and oxygen gas is produced at the positive electrode. We will now call the negative electrode the **cathode** and the positive terminal the **anode.** The cathode is the electrode where **reduction** occurs and the anode is the electrode where **oxidation** occurs. **Cations** (positive ions) were so named because they are attracted to the **cathode** and **anions** (negative ions) were so named because they are attracted to the **anode.**

In the electrolysis of water, oxidation and reduction half-reactions are:

half-reaction at the cathode: $4\ H_2O + 4\ e^- \longrightarrow 2H_{2(g)} + 4\ OH^-$

half reaction at the anode: $2\ H_2O \longrightarrow O_{2(g)} + 4\ H^+ + 4\ e^-$

and the net reaction is: $6\ H_2O \longrightarrow 2\ H_{2(g)} + O_{2(g)} + 4\ H^+ + 4\ OH^-$

(This is the net reaction if the two half-reactions occur in separate chambers. If the two half-reactions occur in the same chamber, the hydrogen and hydrogen ions react to form water.)

Electroplating

With appropriate treatment of the electrode material and appropriate adjustment of the level of current from the battery, it is possible to get the metal being reduced in an electrolysis process to adhere strongly to the electrode. The use of electrolysis to coat one material with a layer of metal is called **electroplating.** Usually, electroplating is used to cover a cheap metal with a layer of more expensive and more attractive metal. Sometimes, electroplating is used to get a surface metal that is a better conductor of electricity. When you wish to have the surface properties of gold (attractive, corrosion resistant, or good conductor) but you don't want to have the great cost of making the entire object out of solid gold, the answer may be to use cheap metal to make the object and then electroplate a thin layer of gold on the surface.

To silver plate an object like a spoon (silverware that's plated is less expensive than pure silver), the spoon is placed in the position of the cathode in an electrolysis set up with a solution of silver nitrate. When the current is turned on, the silver ions will migrate through the solution, touch the cathode (spoon) and adhere to it. With enough time and care, a layer of silver can be plated over the entire spoon. The anode for this operation would often be a large piece of silver from which silver ions would be oxidized and these ions would enter the solution. This is a way of ensuring a steady supply of silver ions for the plating process.

Half-reaction at the cathode: $Ag^+ + e^- \longrightarrow Ag$

Half-reaction at the anode: $Ag \longrightarrow Ag^+ + e^-$

Some percentage of the gold and silver jewelry sold is electroplated. The connection points in electric switches are often gold plated to improve electrical conductivity and most of the chromium pieces on automobiles are chromium plated.

Lesson Summary

- An electric current consists of a flow of charged particles.
- When direct current is passed through a solution of an electrolyte, cations are attracted to the negative electrode where they gain electrons and anions are attracted to the positive electrode where they lose electrons.
- The electrode where oxidation occurs is called the anode and the electrode where reduction occurs is called the cathode.
- In electroplating, the object to be plated is made the cathode in an electrolysis.

Review Questions

1. Write the equations for the reactions that occur at the anode and at the cathode in the electrolysis of molten KBr. **(Intermediate)**

Vocabulary

anode	The electrode at which oxidation occurs.
battery	A group of two or more cells that produces an electric current.
cathode	The electrode at which reduction occurs.
electrolysis	A chemical reaction brought about by an electric current.
electroplating	A process in which electrolysis is used as a means of coating an object with a layer of metal.

Review Answers

1.

Cathode: $K^+ + e^- \longrightarrow K$

Anode: $2\ Br^- \longrightarrow Br_2 + 2\ e^-$

Galvanic Cells

Lesson Objectives

- The student will describe the conditions necessary for a cell to be standard cell.
- Given a table of standard reduction potentials and a diagram or description of a Galvanic cell, the student will balance the redox equation, calculate the standard cell potential, and determine the direction of

electron flow in the external circuit.

Introduction

Electrochemistry can be defined as the study of the interchange of electrical and chemical energy. Electrochemical reactions generate an electric current from a spontaneous chemical reaction.

Spontaneous Redox Reactions

The last section dealt with electrolysis, which are redox reactions that are NOT spontaneous. Such reactions require an external source of energy in order to occur. In this section, we will deal with redox reactions that ARE spontaneous. These reactions occur because the products contain less potential energy in their bonds than the reactants. The energy produced from excess potential energy not only allows the reaction to occur but also often gives off energy to the surroundings. Some of these reactions can be physically arranged so the energy given off is given off in the form of an electric current. These are the type of reactions that occur inside batteries. When a reaction is arranged to produce an electric current as it runs, the arrangement is called an **electrochemical cell** or a **Galvanic Cell.**

If a strip of copper is placed in a solution of silver nitrate, a reaction takes place.

$2\ Ag^+ + Cu \rightarrow 2\ Ag + Cu^{2+}$

In this reaction, copper atoms are donating electrons to silver ions so the silver ions are reduced to silver atoms and copper atoms are oxidized to copper(II) ions.

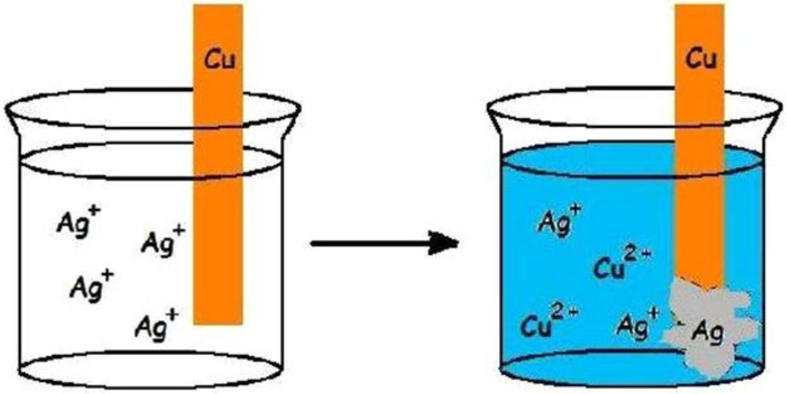

Figure 6: Redox reaction in one beaker.

(*Created by:* Richard Parsons, *License:* CC-BY-SA)

As the reaction occurs, an observer would see the solution slowly turn blue (Cu^{2+} ions are blue in solution) and a mass of solid silver atoms would build up on the copper strip.

Electrochemical Cells

This reaction, $2\ Ag^+ + Cu \rightarrow 2\ Ag + Cu^{2+}$, is one that could be physically arranged to produce an external electric current. To do this, the two half-reactions must occur in separate compartments and the separate compartments must remain in contact through an ionic solution and an external wire.

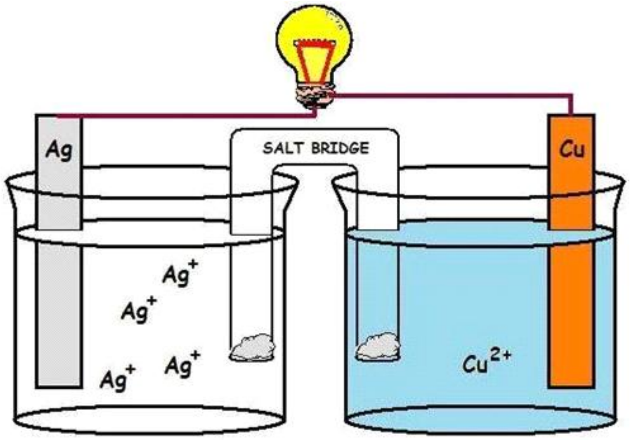

Figure 7: Electrochemical Cell.

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In this electrochemical cell, the copper metal must be separated from the silver ions to avoid a direct reaction. Each electrode in its solution could be represented by a half-reaction.

$$Cu \rightarrow Cu^{2+} + 2\ e^-$$

$$Ag \rightarrow Ag^+ + e^-$$

The external wire will allow electrons to flow between the metal strips. In each half-cell, atoms may be oxidized to ions and leave excess electrons on the electrode. It can be determined experimentally that electrons will flow in the wire from the copper electrode to the silver electrode. We may look at the causes of the direction of electron flow in various ways. We could say that silver ions have a greater electron affinity than copper ions and so the silver atoms pull the electrons through the wire from copper. On the other hand, we could say that copper atoms have a greater tendency to give up electrons than silver so the copper electrode becomes more negative and pushes the electrons through the wire toward the silver electrode. Whichever way we look at it, the electrons flow from copper to silver in the external wire. The silver electrode, therefore, will acquire an excess of electrons which causes the silver half-reaction to run in the reverse direction.

$$Ag^+ + e^- \rightarrow Ag$$

As the electrons on the silver electrode are used up in the reduction of silver ions, more copper atoms are oxidized and more electrons sent through the wire. The net reaction for the entire cell is

$$2\ Ag^+_{\ (aq)} + Cu_{(s)} \rightarrow 2\ Ag_{(aq)} + Cu^{2+}_{\ (aq)}$$

The cell produces an electric current in the external wire and will continue to do so as long as there are sufficient reactants (Ag^+ and Cu) to continue the reaction.

You probably noticed there is another piece of apparatus in the cell that we haven't mentioned yet. There is an upside-down U-tube connecting the two beakers and labeled SALT BRIDGE. This U-tube is filled with an ionic solution and the ends are fitted with porous plugs. An ionic solution is chosen such that neither of its ions will react chemically with any of the other ions in the system. The porous plugs are there to avoid general mixing but to allow ion migration. As the cell runs, electrons are transferred from the copper half-cell to the silver half-cell. Unchecked, this would result in the silver half-cell becoming negatively charged and the copper half-cell becoming positively charged. Once the half-cells became charged in that manner, the reaction could only continue to run if it produced sufficient energy to take electrons away from a positive charge and push them onto an already negatively charged half-cell. Chemical reactions do not produce enough energy to push electrons against a charge gradient. The salt bridge is present to allow negative ions to flow from the silver half-cell to the copper half-cell and positive ions to flow from the copper half-cell to the silver half-cell. This migration of ions balances the charge movement of the electrons. Ions migrate to exactly counter balance the electron flow so that neither half-cell becomes charged. As long as the two beakers remain neutral, the reaction will continue to run. If the salt bridge were not present or were removed, the reaction would immediately stop.

We can now see that the silver electrode is a cathode because reduction occurs there and cations migrate toward the cathode. The copper electrode is an anode because oxidation occurs there and anions migrate toward the anode. As the cell runs and produces electric current, the mass of the silver electrode increases because when a silver ion is reduced to a silver atom, it attaches to the silver electrode. The copper electrode will lose mass because as the copper atoms are oxidized to copper ions, they dissolve in the solution. Eventually, the silver electrode will show a mass of attached solid silver and the copper electrode will develop holes and edges which show evidence of the reaction wearing away the strip. The electrons that pass through the external circuit can do useful work such as lighting lights, running cell phones, and so forth. When you take physics, you will learn how to calculate the amount of work that can be done by an electric current. Several cells can be operated together to produce greater current. When we have a series of cells operating together as one, we call the arrangement a battery.

If the light bulb is removed from the circuit with the electrochemical cell and replaced with a voltmeter, the voltmeter will measure the voltage (electrical potential energy per unit charge) of the combination of half-cells.

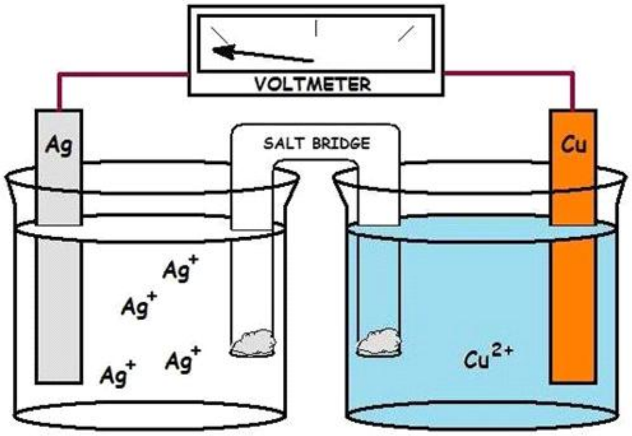

Figure 8: Electrochemical cell with voltmeter.

(*Created by:* Richard Parsons, *License:* CC-BY-SA)

The size of the voltage produced by a cell depends on the temperature, the metals used for electrodes, and the concentrations of the ions in the solutions. If you increase the concentration of the reactant ion (not the product ion), the reaction rate will increase and so will the voltage.

It may seem complicated to construct an electrochemical cell because of all their complexities. Electrochemical cells are actually easy to make and sometimes even occur accidentally. If you take two coins of different denomination and push them part way through the peel of a whole lemon and then connect the two coins with a wire, a small electric current will flow. Electrochemical cells occasionally occur accidentally when two water pipes of different material are connected. The reactions at the joint cause a great deal of corrosion. Plumbing professionals take great care to make sure such reactions do not occur at pipe joints.

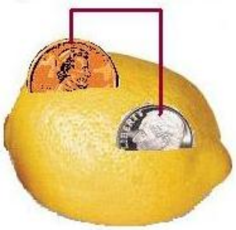

Figure 9: An electrochemical cell made with a lemon and a couple of coins. (*Created by:* Richard Parsons, *License:* CC-BY-SA)

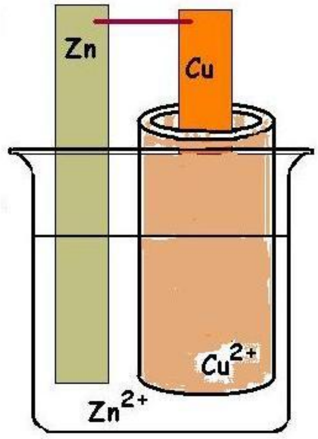

Figure 10: A porous cup cell.

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Another common way to construct an electrochemical cell is with the use of a porous cup (see Figure 10). A porous cup is made of some material that is permeable to ions and allows the ions to migrate through the walls. The cup is not, however, porous enough to allow liquid to flow through. Unfinished clay is one such substance. The porous cup is soaked in ionic solution to make sure the pores are filled with ionic solution and the one electrode and its solution are placed in the porous cup and the other electrode and its corresponding ionic solution is placed in a beaker. The porous cup with its contents is then set inside the beaker and a wire is connected between the electrodes. The walls of the porous cup act as the salt bridge in this cell.

The Standard Hydrogen Half-Cell

In the design of cells for specific purposes, it would be very convenient if chemists were able to predict which half-reaction would take electrons and which would lose and also predict the voltages that will be produced by various combinations of half-cells. It was mentioned earlier that both temperature and the concentrations of the ion solutions can change the reaction rate and the voltage of a cell. Therefore, the conditions for the comparison half-reactions must be standardized. The conditions chosen to be standard for half-cells are 25°C, 1.0 M for all solutions, and 1.0 atmosphere pressure. It would be convenient if a chemist could make up 100 standard half-cells and attach them to a voltmeter and measure the voltage of each standard half-cell. Unfortunately, as you know, half-cells will not run alone. There must be two half-cells connected together; one where oxidation occurs and one where reduction occurs. When you connect two half-cells together, you can indeed measure the voltage produced but you do not know how much of the voltage is due to each of the two standard half-cells.

Chemists solved the problem by assigning the standard hydrogen half-cell a potential of zero. When another standard half-cell was combined with the hydrogen half-cell, the cell voltage could be measured and the potential of the cell assigned to the other half-cell. For example, the standard silver half-cell, $Ag^+ + e^- \rightarrow Ag$, could be combined with the standard hydrogen half-cell, $2H^+ + 2e^- \rightarrow H_2$, and the resultant voltage of the cell measured. In this cell, the silver ions take electrons and hydrogen gives them up, that is, silver ions are reduced and hydrogen atoms are oxidized. Since both half cells were written in terms of reduction, in order to write the equation for the cell, the hydrogen half-reaction must be reversed.

$2\ Ag^+ + 2\ e^- \rightarrow 2\ Ag$ (reduction)

$H_2 \rightarrow 2\ H^+ + 2\ e^-$ (oxidation)

$2\ Ag^+ + H_2 \longrightarrow 2\ H^+ + 2\ Ag$ (net reaction)

When this cell runs, it produces a voltage of 0.80 volts. This voltage is assigned to the silver half-cell as its voltage when the silver ions are reduced. The assigned voltages of 0.80 V for the silver half-cell and 0.00 V for the hydrogen half-cell do not have any meaning in terms of voltages on an absolute scale, but they are perfectly accurate as an indication of the difference in the abilities of the two half-cells to take electrons. The silver half-cell has a greater pull on electrons than the hydrogen half-cell and it is stronger by 0.80 volts. When many half-cells have been combined with the hydrogen half-cell and the voltages measured, we have a list of half-cells in order of their strength at taking electrons and we have a numerical value for the difference in their strength compared to the hydrogen half-cell.

It was found that some of the standard half-cells are not strong enough to take electrons from the hydrogen half-cell. In fact, the hydrogen half-cell is the one that takes the electrons and forces the other half-reaction to be oxidized. Since the hydrogen half-cell was assigned a strength of zero and these half-cells are weaker than hydrogen, their assigned voltages are negative numbers. Here is an expanded list of half-reactions and their assigned voltages based on comparison to the hydrogen half-cell.

Standard Reduction Potentials

(All ion concentrations are 1.00 M, the temperature is 298 K, and gas pressure is 1.00 atm.)

Half-Reactions	**E° (volts)**
$F_{2(g)} + 2\ e^- \longrightarrow 2\ F^-$	+ 2.87
$MnO_4^{\ -} + 8\ H^+ + 5\ e^- \longrightarrow Mn^{2+} + 4\ H_2O$	+ 1.52
$Au^{3+} + 3\ e^- \longrightarrow Au_{(s)}$	+ 1.50
$Cl_{2(g)} + 2\ e^- \longrightarrow 2\ Cl^-$	+ 1.36
$Cr_2O_7^{\ 2-} + 14\ H^+ + 6\ e^- \longrightarrow 2\ Cr^{3+} + 7\ H_2O$	+ 1.33
$MnO_{2(s)} + 4\ H^+ + 2\ e^- \longrightarrow Mn^{2+} + 2\ H_2O$	+ 1.28
$1/2\ O_{2(g)} + 2\ H^+ + 2\ e^- \longrightarrow H_2O$	+ 1.23
$Br_{2(L)} + 2\ e^- \longrightarrow 2\ Br^-$	+ 1.06
$NO_3^{\ -} + 4\ H^+ + 3\ e^- \longrightarrow NO_{(g)} + 2\ H_2O$	+ 0.96
$Ag^+ + e^- \longrightarrow Ag$	+ 0.80
$Hg^{2+} + 2\ e^- \longrightarrow Hg_{(L)}$	+ 0.78
$NO_3^{\ -} + 2\ H^+ + e^- \longrightarrow NO_{2(g)} + H_2O$	+ 0.78
$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	+ 0.77
$I_{2(s)} + 2\ e^- \longrightarrow 2\ I^-$	+ 0.53
$Cu^{2+} + 2\ e^- \longrightarrow Cu_{(s)}$	+ 0.34
$SO_4^{\ 2-} + 4\ H^+ + 2\ e^- \longrightarrow SO_{2(g)} + 2\ H_2O$	+ 0.17
$Sn^{4+} + 2\ e^- \longrightarrow Sn^{2+}$	+ 0.15
$2\ H^+ + 2\ e^- \longrightarrow H_{2(g)}$	0.00

$Pb^{2+} + 2\ e^- \rightarrow Pb_{(s)}$	- 0.13
$Sn^{2+} + 2\ e^- \rightarrow Sn_{(s)}$	- 0.14
$Ni^{2+} + 2\ e^- \rightarrow Ni_{(s)}$	- 0.25
$Co^{2+} + 2\ e^- \rightarrow Co_{(s)}$	- 0.28
$Fe^{2+} + 2\ e^- \rightarrow Fe_{(s)}$	- 0.44
$Cr^{3+} + 3\ e^- \rightarrow Cr_{(s)}$	- 0.74
$Zn^{2+} + 2\ e^- \rightarrow Zn_{(s)}$	- 0.76
$2\ H_2O + 2\ e^- \rightarrow 2\ OH^- + H_{2(g)}$	- 0.83
$Mn^{2+} + 2\ e^- \rightarrow Mn_{(s)}$	- 1.18
$Al^{3+} + 3\ e^- \rightarrow Al_{(s)}$	- 1.66
$Mg^{2+} + 2\ e^- \rightarrow Mg_{(s)}$	- 2.37
$Na^+ + e^- \rightarrow Na_{(s)}$	- 2.71
$Ca^{2+} + 2\ e^- \rightarrow Ca_{(s)}$	- 2.87
$Sr^{2+} + 2\ e^- \rightarrow Sr_{(s)}$	- 2.89
$Ba^{2+} + 2\ e^- \rightarrow Ba_{(s)}$	- 2.90
$K^+ + e^- \rightarrow K_{(s)}$	- 2.92
$Li^+ + e^- \rightarrow Li_{(s)}$	- 3.00

Suppose we had five cities (A, B, C, D, E) located in the mountains and we could not measure the altitude of the cities from sea level but we could measure the difference in the altitude between city C and each of the other cities. We could assign city C to have an altitude of zero and then list the altitude of the other cities by their comparison to city C.

City A . . 5000 ft.
. .
City B . . 3000 ft.
. .
City C . . 0 ft.
. .
City D . . -1000 ft.
. .
City E . . -3000 ft.
. .

We could now find the difference between the altitudes of any two cities. City A is 2000 ft. higher than city B. City A is 6000 ft. higher than city D. City B is 6000 ft. higher than city E. The standard cell voltages work in the same way. We can now find the actual voltage for a cell composed of any two of the standard half-cells listed by finding the difference in their relative standard half-cell voltages.

Example 10:

In a cell formed by the $Cu^{2+} + 2\ e^- \rightarrow Cu$ and the $Zn^{2+} + 2\ e^- \rightarrow Zn$ standard half-cells, determine which half-cell will undergo oxidation, which will undergo reduction, find the voltage for the cell, and write the balanced equation for the cell.

Solution:

Simply by looking at the placement of the half-reactions in the standard reduction potential chart, we can determine that the copper half-cell is closer to the top of the chart than the zinc half-cell so we know that copper is better at attracting electrons and that half-reaction will run in the reduction direction. The zinc half-cell will be forced to give up electrons and be oxidized so that half-reaction will need to be reversed.

$Cu^{2+} + 2\ e^- \rightarrow Cu_{(s)}$ (reduction)

$Zn_{(s)} \rightarrow Zn^{2+} + 2\ e^-$ (oxidation)

In the cell, the zinc electrode will be the anode and zinc metal will be oxidized. The copper electrode will be the cathode and copper ions will be reduced. **When a half-reaction is reversed in direction, the sign of the E^o value must be changed.** Therefore, the two half-reactions with E^o values become

$Cu^{2+} + 2\ e^- \rightarrow Cu_{(s)}\ E^o = +\ 0.34$ volts

$Zn_{(s)} \rightarrow Zn^{2+} + 2\ e^-\ E^o = +\ 0.76$ volts

When the two half-reactions are added, we get both the balanced equation and the standard cell voltage.

$Cu^{2+} + 2\ e^- \rightarrow Cu_{(s)}\ E^o = +\ 0.34$ volts

$Zn_{(s)} \rightarrow Zn^{2+} + 2\ e^-\ E^o = +\ 0.76$ volts

$Zn_{(s)} + Cu^{2+} \rightarrow Zn^{2+} + Cu_{(s)}\ E^o_{\ NET} = +\ 1.10$ volts

You should note that reversing the sign of the half-reaction that reverses its direction and then adding the E^o's produces the difference between the original two values in the chart. (The difference between + 0.34 volts and – 0.76 volts is + 1.10 volts.)

Example 11:

For the standard cell involving the dichromate half cell, $Cr_2O_7^{\ 2-} + 14\ H^+ + 6\ e^- \rightarrow 2\ Cr^{3+} + 7\ H_2O$ whose E^o is + 1.33volts, and the silver half-cell, $Ag^+ + e^- \rightarrow Ag_{(s)}$, whose E^o is + 0.80 volts, determine what will be oxidized and reduced, name the oxidizing and reducing agents, find the $E^o_{\ NET}$ for the cell, and balance the net equation.

Solution:

When we find the two half-reactions in the standard potential chart, the dichromate half-reaction is closer to the top of the chart which means that it will run forward (reduction) and the silver half-reaction will be forced to reverse its direction (oxidation). We can write the two half-reactions in the direction they will run with the adjusted E^o sign for the silver half-cell.

(reduction) $Cr_2O_7{}^{2-} + 14\ H^+ + 6\ e^- \rightarrow 2\ Cr^{3+} + 7\ H_2O$ $E^o = +\ 1.33$volts

(oxidation) $Ag_{(s)} \rightarrow Ag^+ + e^-$ $E^o = -\ 0.80$ volts

When we check the number of electrons on the two sides of the equation, we recognize that we must multiply the silver half-reaction by 6 in order for the electrons to cancel out. This brings up a question – when we multiply the half-reaction by 6, do we multiply the E^o by 6? In the case of standard half-cells, in order for the half-cell to be standard, it MUST be at 25°C and the concentration of the ions MUST be 1.00 M. Hence, when you multiply a half-reaction in order to balance an equation, you may be doubling an amount of solution as in 250 mL becomes 500 mL but the molarity must remain exactly 1.00 M. Therefore, when you multiply a standard half-cell for balancing purposes, the E^o remains exactly the same. The only instance where the E^o of a standard half-cell changes is that the sign is changed if you reverse the direction of the reaction. The half-reactions and net reaction for this problem become:

$Cr_2O_7{}^{2-} + 14\ H^+ + 6\ e^- \rightarrow 2\ Cr^{3+} + 7\ H_2O$ $E^o = +\ 1.33$volts

$6\ Ag_{(s)} \rightarrow 6\ Ag^+ + 6e^-$ $E^o = -\ 0.80$ volts

---

$6\ Ag_{(s)} + Cr_2O_7{}^{2-} + 14\ H^+ \rightarrow 6\ Ag^+ + 2\ Cr^{3+} + 7\ H_2O$ $E^o = +\ 0.53$ volts

The chromium in $Cr_2O_7{}^{2-}$ is being reduced and is therefore, the oxidizing agent. It is acceptable to just say the dichromate ion is the oxidizing agent rather than specifying the chromium in the dichromate ion.

The silver metal is being oxidized and is as a result the reducing agent.

This may be a convenient place to mention that standard cells are only for some small fraction of second when you turn them on. When cells begin to run, the ions on the reactant side of the equation are being used up and the ions on the product side of the equation are being produced, thus, when a standard cell begins to run the molarities of the ions immediately change and are no longer exactly 1.00 M and consequently, the cell is no longer a standard cell.

Electrochemical Reactions and Metallic Corrosion

The corrosion of metals is usually an electrochemical reaction. The reaction is usually between a metal and oxygen and water in the surroundings. Since iron is an extremely common metal used for many purposes such as building construction, doors, fencing materials, ships hulls, bolts, screws, and nails, and iron is also readily rusted (corroded) in contact with oxygen and moisture, considerable effort is spent trying to keep iron from rusting. There are several common ways of protecting iron from corrosion.

The most common way of protecting iron objects from corrosion is to paint them so that the oxygen and moisture cannot touch the metal. This system would include storing the iron objects in thick grease to keep possible reactants away.

Metallic iron may also be coated with a protective layer of a more reactive metal. Iron objects are often electroplated with chromium or zinc to provide the protective layer. Sometimes iron objects are dipped in molten zinc to produce a layer of more reactive metal. Covering a metal with a layer of zinc is called galvanizing and is a fairly common practice with fence wire, nails, buckets and tubs.

In certain cases, iron can be alloyed with other metals to make the product more resistant to corrosion. Stainless steel is an alloy of iron and small amounts of chromium. The addition of the small amount of chromium makes the steel less susceptible to corrosion. The addition of small amounts of other substances in alloying with iron also yield other positive properties.

To protect ship hulls from corrosion, it is common to place a large mass of magnesium in electrical contact with the iron hull. The magnesium is more easily corroded than iron so that the reactants that contact the hull and would carry on electrochemical reactions with the hull will react with the magnesium first and the hull will remain intact. This system is called cathodic protection.

Lesson Summary

- The redox reaction in a Galvanic cell is a spontaneous reaction.
- Ion flow between the chambers of an electrochemical cell keeps the chambers neutral.
- Standard potentials for half-cells are determined by measuring the potential of an electrochemical cell in which the tested cell is paired with the standard hydrogen half-cell.
- All standard potentials are measured at standard cell conditions of 25°C and 1.00 M solutions of all ions.
- The voltage of a standard electrochemical cell is obtained by finding the difference between the reduction potentials of the two half-cells.
- Redox reactions can be balanced by combining the oxidation and reduction half-reactions found in the table of standard reduction potentials.

Review Questions

1. In a standard cell composed of the zinc and copper half-cells, will the current in the external circuit flow from Zn to Cu or from Cu to Zn? **(Intermediate)**

2. For a standard cell with the following balanced equation. **(Intermediate)**

$$Sn_{(s)} + 2\ Ag^+ \longrightarrow Sn^{2+} + 2\ Ag_{(s)}$$

A. what is being oxidized?

B. what is the reducing agent?

C. what is the $E^o{}_{NET}$?

D. after the reaction has reached equilibrium, what will be its voltage?

3. Balance the following equation using the half-reactions from the standard reduction potential chart. **(Challenging)**

$$Cr_2O_7{}^{2-} + Fe^{2+} + H^+ \longrightarrow Cr^{3+} + Fe^{3+} + H_2O$$

Further Reading / Supplemental Links

http://learner.org/resources/series61.html'"

The ***learner.org*** website allows users to view streaming videos of the Annenberg series of chemistry videos. You are required to register before you can watch the videos but there is no charge. The website has one video that relates to this lesson called ***The Busy Electron*** .

Dictionary of Scientific and Technical Terms, Sybil P. Parker, Editor in Chief, McGraw-Hill, 1994.

http://academic.pgcc.edu/~ssinex/E_cells.pdf

http://academic.pgcc.edu/~ssinex/E_cells.pdf http://en.wikipedia.org

Vocabulary

anode	The electrode at which oxidation occurs.
cathode	The electrode at which reduction occurs.
electrochemical cell	An arrangement of electrodes and ionic solutions in which a spontaneous redox reaction is used to produce a flow of electrons in an external circuit.
salt bridge	A U-shaped tube containing an electrolyte that connects two half-cells in an electrochemical cell.
voltage	The potential difference between two points in an electric circuit.

Review Answers

1. Since the copper half-cell is higher in the standard reduction potential chart, the copper will be reduced and the zinc will be oxidized. The electrons are produced at the electrode where oxidation occurs and are used at the electrode where reduction occurs. Therefore, in the external circuit, the electrons must flow from Zn to Cu.

2.

A. Sn

B. Sn

C. + 0.94 volts

D. At equilibrium, no net reaction occurs and therefore the E° would be zero.

3.

$$Cr_2O_7^{2-} + 14\ H^+ + 6\ e^- \rightarrow 2\ Cr^{3+} + 7\ H_2O$$

$$6(Fe^{2+} \rightarrow Fe^{3+} + e^-) = 6\ Fe^{2+} \rightarrow 6\ Fe^{3+} + 6\ e^-$$

$$Cr_2O_7^{2-} + 14\ H^+ + 6\ Fe^{2+} \rightarrow 2\ Cr^{3+} + 6\ Fe^{3+} + 7\ H_2O$$

29. Nuclear Chemistry

Discovery of Radioactivity

Lesson Objectives

- The student will describe the roles played by Henri Becquerel and Marie Curie played in the discovery of radioactivity.
- The student will list the most common emissions from naturally radioactive nuclei.

Introduction

No one could have known in the 1800s that the discovery of the fascinating science and art form of photography would eventually lead to the splitting of the atom. The basis of photography is the fact that visible light causes certain chemical reactions. If the chemicals are spread thinly on a surface but protected from light by a covering, no reaction occurs. When the covering is removed, however, light acting on the chemicals causes them to darken. With millions of cameras in use today we do not think of it as a strange phenomenon, but at the time of its discovery photography was a strange and wonderful thing. Even stranger was the discovery by Roentgen, that radiation other than visible light could expose photographic film. He found that film wrapped in dark paper would react when x-rays went through the paper and struck the film.

Becquerel and Radioactivity

When Becquerel heard about Roentgen's discovery, he wondered if his fluorescent minerals would give the same x-rays. Becquerel placed some of his rock crystals on top of a well-covered photographic plate and sat them in the sunlight. The sunlight made the crystals glow with a bright fluorescent light, but when Becquerel developed the film he was very disappointed. He found that only one of his minerals, a uranium salt, had fogged the photographic plate. He decided to try again, and this time, to leave them out in the sun for a longer period of time. Fortunately, the weather didn't cooperate and Becquerel had to leave the crystals and film stored in a drawer for several cloudy days. Before continuing his experiments, Becquerel decided to check one of the photographic plates to make sure the chemicals were still good. To his amazement, he found that the plate had been exposed in spots where it had been near the uranium containing rocks and some of these rocks had not been exposed to sunlight at all.

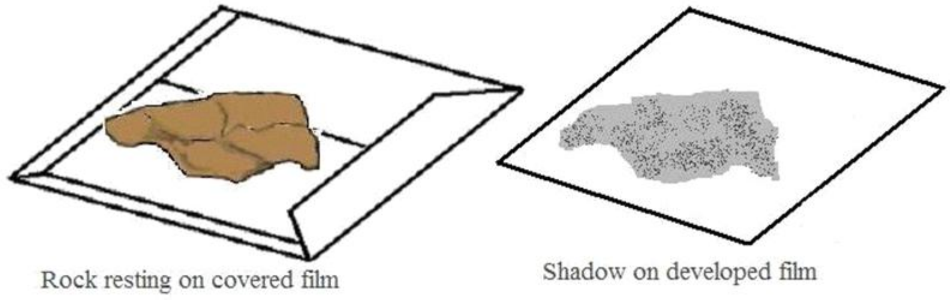

Figure 1: Bequerel’s radioactive rock sitting on an envelope containing photographic film.

(*Created by:* Richard Parsons, *License:* CC-BY-SA)

In later experiments, Becquerel confirmed that the radiation from the uranium had no connection with light or fluorescence, but the amount of radiation was directly proportional to the concentration of uranium in the rock. Becqueral had discovered **radioactivity**.

The Curies and Radium

One of Becquerel's assistants, a young Polish scientist named Maria Sklowdowska (to become Marie Curie after she married Pierre Curie), became interested in the phenomenon of radioactivity. With her husband, she decided to find out if chemicals other than uranium were radioactive. The Austrian government was happy to send the Curies a ton of pitchblende from the mining region of Joachimstahl because it was waste material that had to be disposed of anyway. The Curies wanted the pitchblend because it was the residue of uranium mining. From the ton of pitchblend, the Curies separated 0.10 g of a previously unknown element, radium, in the form of the compound, radium chloride. This radium was many times more radioactive than uranium.

By 1902, the world was aware of a new phenomenon called radioactivity and of new elements which exhibited natural radioactivity. For this work, Becquerel and the Curies shared the 1903 Nobel Prize and for subsequent work, Marie Curie received a second Nobel Prize. She is the only person ever to receive two Nobel Prizes in science.

Further experiments provided information about the characteristics of the penetrating emissions from radioactive substances. It was soon discovered that there were three common types of radioactive emissions. Some of the radiation could pass easily through aluminum foil while some of the radiation was stopped by the foil. Some of the radiation could even pass through foil up to a centimeter thick. The three basic types of radiation were named alpha, beta, and gamma radiation. The actual composition of the three types of radiation was still not known.

Eventually, scientists were able to demonstrate experimentally that the alpha particle, α , was a helium nucleus (a particle containing two protons and two neutrons), a beta particle, β , was a high speed electron, and gamma rays, γ , were a very high energy form of light (even higher energy than x-rays).

Lesson Summary

- Henri Becquerral, Marie Curie, and Pierre Curie shared the discovery of radioactivity.
- The most common emissions of radioactive elements were called alpha (α), beta (β), and gamma (γ) radiation.

Review Questions

Put the letter of the matching phrase on the line preceding the number. **(Beginning)**

___ 1. alpha particle a. high energy electromagnetic radiation
___ 2. beta particle b. a high speed electron
___ 3. gamma ray c. a helium nucleus

Vocabulary

alpha particle	An alpha particle is a helium-4 nucleus.
beta particle	A beta particle is a high speed electron, specifically an electron of nuclear origin.
gamma ray	Gamma radiation is the highest energy on the spectrum of electromagnetic radiation.
Marie Curie	Marie Curie was a physicist and chemist of Polish upbringing, and subsequently, French citizenship; a pioneer in the field of radioactivity and the only person to ever

win two Nobel prizes in science.

Review Answers

_c_ 1. alpha particle a. high energy electromagnetic radiation
_b_ 2. beta particle b. a high speed electron
_a_ 3. gamma ray c. a helium nucleus

Nuclear Notation

Lesson Objectives

- The student will state the information contained in the atomic number of a nucleus.
- The student will state the information contained in the mass number of a nucleus.
- The student will subtract the atomic number from the mass number to determine the number of neutrons in a nucleus.
- Students will read and write complete nuclear symbols (know the structure of the symbols and understand the information contained in them).

Introduction

Just as chemical formulas use symbols and chemical equations use symbols, nuclei are represented by symbols. The complete nuclear symbol contains the symbol for the element and numbers that relate to the number of protons and neutrons in that particular nucleus.

Atomic and Mass Numbers

The identity of an atom is determined by the number of protons in the nucleus of the atom. The number of protons in the nucleus of the atom is also known as the ATOMIC NUMBER. The atomic number is the smaller number appearing on the periodic table for each atom. The atomic number for hydrogen is 1. This means that if a nucleus has 1 proton in it, it is a hydrogen nucleus no matter how many neutrons it has. The mass number for a nucleus is the total number of protons and neutrons (nucleons) in the nucleus of an atom. Both the mass number and the atomic number for nuclei are always whole numbers because there are no fractions of nucleons. To find the number of neutrons in the nucleus, you would subtract the atomic number from the mass number. For example, if the atomic number for a nucleus was 8 and the mass number was 18, the nucleus would contain 8 protons (equal to the atomic number) and 10 neutrons (18 nucleons - 8 protons = 10 neutrons).

The Complete Nuclear Symbol

To write a complete nuclear symbol, the mass number is placed at the upper left (superscript) of the chemical symbol and the atomic number is placed at the lower left (subscript) of the symbol. The complete nuclear symbol for helium-4 is drawn below.

Figure 2: The complete nuclear symbol for helium-4.

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The following nuclear symbols are for a nickel nucleus with 31 neutrons and a uranium nucleus with 146 neutrons.

$${}^{59}_{28}\text{Ni} \qquad {}^{238}_{92}\text{U}$$

In the nickel nucleus represented above, the atomic number 28 indicates the nucleus contains 28 protons, and therefore, it must contain 31 neutrons in order to have a mass number of 59. The uranium nucleus has 92 protons as do all uranium nuclei and this particular uranium nucleus has 146 neutrons. Another way of representing these nuclei would be Ni-59 and U-238.

Dalton's original atomic theory stated that all atoms of an element were identical in every way, but it was later discovered by Thomson that atoms of an element were identical in every way except they could have different mass numbers. This mass difference results from nuclei of the same element having a different number of neutrons. In order to be the same element, nuclei must have the same number of protons, but they may have a different number of neutrons. Atoms with the same atomic number but a different mass number are called **isotopes**.

Hydrogen, for example, has three isotopes, shown in Figure 3. All three of hydrogen's isotopes must have one proton (to be hydrogen), but they have zero, one, or two neutrons in the nucleus. Originally, the names protium, deuterium, and tritium were suggested for the three isotopes of hydrogen, but about a year after the names were suggested it was felt that a new name indicated a new element, which these were not. Furthermore, naming compounds using these names would cause great difficulty. Nuclear scientists today use the names hydrogen-1, hydrogen-2, and hydrogen-3, but occasionally you will see or hear the other names.

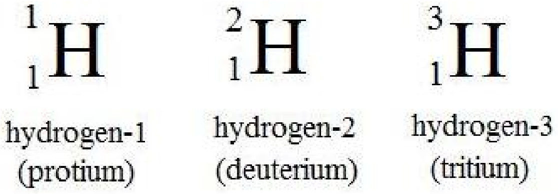

Figure 3: The three isotopes of hydrogen. (*Created by:* Richard Parsons, *License:* CC-BY-SA)

Lesson Summary

- The complete nuclear symbol has the atomic number (number of protons) of the nucleus as a subscript at the lower left of the chemical symbol and the mass number (number of protons + neutrons) as a superscript at the upper left of the chemical symbol.

Review Questions

1. Write the complete nuclear symbol for a nucleus of chlorine that contains 17 protons and 20 neutrons. **(Beginning)**

2. Write the complete nuclear symbol for a nucleus of oxygen that contains 8 protons and 10 neutrons. **(Beginning)**

3. If a nucleus of uranium has a mass number of 238, how many neutrons does it contain? **(Beginning)**

4. In the nuclear symbol for a beta particle, what is the atomic number? **(Beginning)**

5. Is it possible for isotopes to be atoms of different elements? Explain why or why not. **(Beginning)**

6. How many neutrons are present in a nucleus whose atomic number is one and whose mass number is one? **(Beginning)**

7. Name the element of an isotope whose mass number is 206 and whose atomic number is 82. **(Beginning)**

8. How many protons and how many neutrons are present in a nucleus of lithium-7? **(Beginning)**

9. What is the physical difference between a U-235 atom and a U-238 atom? **(Beginning)**

10. What is the difference in the chemistry of a U-235 atom and a U-238 atom? **(Challenging)**

Vocabulary

atomic number	The atomic number indicates the number of protons in the nucleus.
mass number	The mass number indicates the number of protons plus the number of neutrons in the nucleus.
electron	An electron is a fundamental sub-atomic particle that carries a negative charge.
neutron	A neutron is a sub-atomic particle with no electric charge and a mass slightly larger than a proton.
proton	A proton is a fundamental sub-atomic particle with a net positive charge.
nucleus	The nucleus of an atom if the very dense region, consisting of nucleons (proton and neutrons) at the center of an atom.
nuclei	Nuclei is the plural of *nucleus*.
nucleon	A nucleon is a constituent part (proton or neutron) of an atomic nucleus.
nuclide	A type of nucleus specified by its atomic number and mass number.

Review Answers

1. $^{37}_{17}\mathrm{Cl}$

2. $^{18}_{8}\mathrm{O}$

3. 146 neutrons

4. -1 (negative one)

5. No, isotopes cannot be of different elements. The definition of isotopes is that they have the SAME ATOMIC NUMBER and different mass numbers. If they have the same atomic number, they must be the same element.

6. Zero. The number of neutrons can be found by subtracting the atomic number from the mass number, in this case that would be 1 – 1 = 0.

7. 82 is the atomic number of lead, Pb.

8. 3 protons and 4 neutrons

9. The U-238 atom will be fractionally heavier due to the three extra neutrons in its nucleus.

10. The chemistry of the two atoms is exactly the same. The chemical behavior of atoms is determined by the nuclear charge and the number of valence electrons in the outermost energy level. These two characteristics for U-235 and U-238 are exactly the same. This is the reason that the isotopes cannot be separated chemically and must be separated by a physical means related to their difference in mass.

Nuclear Force

Lesson Objectives

- Students will compare the energy released per gram of matter in nuclear reactions to that in chemical reactions.
- Students will express the equation for calculating the change in mass during nuclear reactions that is converted into energy.
- Students will express the relationship between nuclear stability and the nuclei's binding energy per nucleon ratio.

Introduction

There are only four forces in nature that produce all interactions between objects. Gravity affects all particles and only attracts, never repels. It is the weakest of the four forces but acts over great distances. The electromagnetic force acts between electric charges and magnetic fields and causes all physical and chemical processes to occur. It can also act at large distances. The weak nuclear force is limited to the atomic nucleus and causes unstable particles and nuclei to decay. The strong nuclear force is also limited to the nucleus and binds quarks into nucleons and nucleons into nuclei.

Nuclear Force Overcomes Proton Repulsion

A nucleus (with one exception, hydrogen-1) consists of some number of protons and neutrons pulled together in an extremely tiny volume. Since protons are positively charged and like charges repel, it is clear that protons cannot remain together in the nucleus unless there is a powerful force holding them there. The force which holds the nucleus together is generated by nuclear binding energy. We are concerned not with just the total amount of binding energy a nucleus possesses, but also with how many nucleons (protons and neutrons) are present for the binding energy to hold together. It is more illuminating for us to consider the amount of **binding energy per nucleon** that a nucleus contains. A nucleus with a large amount of binding energy per nucleon will be held together tightly and is referred to as stable. When there is too little binding energy per nucleon, the nucleus will be less stable and may disintegrate (come apart). When nuclei come apart, they come apart violently accompanied by a tremendous release of energy in the form of heat, light, and radiation.

Mass Defect Becomes Binding Energy

We know that a proton has a mass of 1.00728 Daltons (also known as atomic mass units) and a neutron has a mass of 1.00867 Daltons. A helium-4 nucleus consists of two protons and two neutrons. The mass of these separate protons and neutrons would be:

$2 \times 1.00728 + 2 \times 1.00867 = 4.03190$ Daltons.

The actual mass of a helium-4 nucleus is known to be 4.00150 Daltons. It would appear that some mass has been lost when the particles formed a nucleus. This difference between the sum of the masses of the individual nucleons and the mass of the corresponding nucleus always occurs and has been called **mass defect**. The mass defect in this case is 0.03040 Daltons. This mass, of course, is not lost but is converted into energy – binding energy. Albert Einstein first theorized that mass and energy could be converted into one another and he produced the equation with which to calculate the conversion; $\mathbf{E = mc^2}$, where E is energy in Joules, m is the mass in kilograms, and c is the speed of light, 3×10^8 meters/second. If we think about the conservation of mass and energy, we can account for everything. Nothing is lost and nothing appears from nowhere. The conversion of a very small amount of mass into energy produces an immense amount of energy, as you might guess from the size of the number you get when you square the speed of light. If 1.00 gram of mass were converted to energy in this manner, it would produce 9.0×10^{13} Joules. This amount of energy would raise the temperature of 300 million liters of water from room temperature to boiling.

More Binding Energy per Nucleon Produces Stability

It is conventional to plot the binding energy per nucleon (total binding energy divided by the number of nucleons in the nucleus) versus the atomic mass of the nucleus. Such a graph is shown in Figure 4. The position of greatest binding energy per nucleon is held by iron-56. Nuclei both larger and smaller than iron-56 have less binding energy per nucleon and are therefore, less stable. In the graph below, binding energy is measured in Mev (million electron volts). One million electron volts is equal to 1.6 x 10^{-13} Joules. (This graph has been smoothed. The actual graph line zig zags up and down a little.)

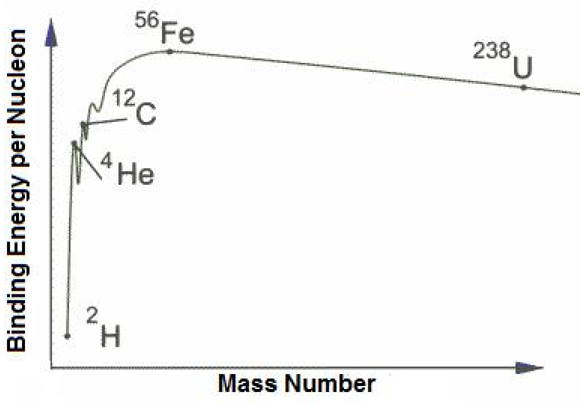

Figure 4: The graph of binding energy per nucleon for atoms between atomic number 1 and 92.

(*Created by:* Richard Parsons, *License:* CC-BY-SA)

Lesson Summary

- The proton-proton repulsion in a nucleus is overcome by binding energy to hold the nucleus together.
- The sum of the masses of the individual components of a nucleus is greater than the mass of the nucleus and the "lost" mass is called mass defect.
- Much of the mass defect is converted into binding energy according the Einstein equation, $E = mc^2$.
- The stability of a nucleus is determined by the amount of binding energy present for each nucleon.
- Nuclei with lower binding energy per nucleon may disintegrate.
- The nucleus with the greatest binding energy per nucleon is iron-56.

Review Questions

1. Iron-56 is a very stable nucleus while cobalt-60 is an unstable nucleus. Which nucleus would you expect to have more binding energy per nucleon? **(Beginning)**

2. Calculate the mass defect and binding energy for a mole of carbon-14 given the data below. **(Challenging)**

The molar mass of carbon-14 is 14.003241 g/mol.

The molar mass of a proton is 1.007825 g/mol.

The molar mass of a neutron is 1.008665 g/mol.

Mass in kilograms is converted into energy in Joules by multiplying the mass times the speed of light squared, $E = mc^2$.

The speed of light is 3.00×10^8 m/s.

$kg \cdot m^2/s^2$ = Joules

Vocabulary

binding energy	Binding energy is the amount of energy that holds a nucleus together, and therefore, also the amount of energy required to decompose a nucleus into its component nucleons.
mass defect	Mass defect is the difference between the sum of the masses of the nuclear components and the mass of the corresponding nucleus. Much of this lost mass is converted into binding energy.
nucleon	Nucleon is a collective name for neutrons and protons.

Review Answers

1. More binding energy per nucleon produces greater stability. Therefore, the iron-56 would have more binding energy per nucleon.

2. A carbon-14 nucleus contains 6 protons and 8 neutrons.

mass of 6 moles of protons = (6 moles)(1.007825 g/mole) = 6.04695 g

mass of 8 moles of neutrons = (8 moles)(1.008665 g/mole) = 8.06932 g

mass of 1.00 mole of carbon-14 nuclei should be = 14.11627 g

mass of 1.00 mole of carbon-14 nuclei actually is = 14.003241 g

mass defect = 14.11627 g - 14.003241 g = 0.113029 g = 1.13029×10^{-4} kg

$E = mc^2 = (1.13029 \times 10^{-4}\ kg)(3.00 \times 10^8\ m/s)^2 = 1.02 \times 10^{13}\ kg \cdot m^2/s^2 = 1.02 \times 10^{13}$ Joules

Nuclear Disintegration

Lesson Objectives

- Students will list some naturally occurring isotopes of elements that are radioactive.
- Students will describe the three most common emissions during natural nuclear decay.
- Students will express the changes in the atomic number and mass number of a radioactive nuclei when an alpha particle is emitted.
- Students will express the changes in the atomic number and mass number of a radioactive nuclei when a beta particle is emitted.
- Students will express the changes in the atomic number and mass number of a radioactive nuclei when a gamma ray is emitted.

- Students will express that protons and neutrons are not indivisible and are composed of particles called quarks.
- Students will express the number of quarks that make up a proton or neutron.

Introduction

Under certain conditions, less stable nuclei alter their structure to become more stable nuclei. Those unstable nuclei that are larger nuclei than iron-56 spontaneously disintegrate by ejecting particles. This process of decomposing to form a different nucleus is called radioactive decay. Many nuclei are radioactive; that is, they decompose by emitting particles and in doing so, become a different nucleus. All nuclei with 84 or more protons are radioactive and many elements with less than 84 protons have both stable and unstable isotopes.

Types of Radioactive Decay

In natural radioactive decay, three common emissions occur. When these emissions were originally observed, scientists were unable to identify them as some already known particle and so named them **alpha particles** (α), **beta particles** (β), and **gamma rays** (γ). At some later time, alpha particles were identified as helium-4 nuclei, beta particles were identified as electrons, and gamma rays as a form of electromagnetic radiation like x-rays except much higher in energy and even more dangerous to living systems.

Alpha Decay

The nuclear disintegration process that emits alpha particles is called alpha decay. An example of a nucleus that undergoes alpha decay is uranium-238. The alpha decay of U-238 is

$$^{238}_{92}\mathrm{U} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{234}_{90}\mathrm{Th}$$

In nuclear equations, it is required that the sum of the atomic numbers on the reactant side equal the sum of the atomic numbers on the product side and the same is true for the mass numbers on the two sides. In this equation,

atomic number : 92 = 2 + 90

mass number: 238 = 4 + 234.

Therefore, the equation is balanced.

Another alpha particle producer is thorium-230.

$$^{230}_{90}\mathrm{Th} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{226}_{88}\mathrm{Ra}$$

Confirm that this equation is correctly balanced.

Beta Decay

Another common decay process is beta particle production, or beta decay. It may occur to you that we have a logically difficult situation here. Nuclei do not contain electrons and yet during beta decay, an electron is emitted from a nucleus. At the same time that the electron is being ejected from the nucleus, a neutron is becoming a proton. It is tempting to picture this as a neutron breaking into two pieces with the pieces being a proton and an electron. That would be convenient for simplicity, but unfortunately that is not what happens; more about this at the end of this section.

In order to insert an electron into a nuclear equation and have the numbers add up properly, an atomic number and a mass number had to be assigned to an electron. The mass number assigned to an electron is zero (0) which is reasonable since the mass number is the number of protons plus neutrons and an electron contains no protons and no neutrons. The atomic number assigned to an electron is negative one (-1) because that allows a nuclear equation containing an electron to balance atomic numbers. Therefore, the nuclear symbol representing an electron (beta particle) is

$${}^{0}_{-1}\mathrm{e} \quad \text{or} \quad {}^{0}_{-1}\beta$$

Thorium-234 is a nucleus that undergoes beta decay. Here is the nuclear equation for this beta decay.

$${}^{234}_{90}\mathrm{Th} \rightarrow {}^{0}_{-1}\mathrm{e} + {}^{234}_{91}\mathrm{Pa}$$

Note that both the mass numbers and the atomic numbers add up properly:

atomic number: 90 = -1 + 91

mass number: 234 = 0 + 234

The mass numbers of the original nucleus and the new nucleus are the same because a neutron has been lost, but a proton has been gained and so the sum of protons plus neutrons remains the same. The atomic number in the process has been increased by one since the new nucleus has one more proton than the original nucleus. In this beta decay, a thorium-234 nucleus has become a protactinium-234 nucleus. Protactinium-234 is also a beta emitter and produces uranium-234.

$${}^{234}_{91}\mathrm{Pa} \rightarrow {}^{0}_{-1}\mathrm{e} + {}^{234}_{92}\mathrm{U}$$

Once again, the atomic number increases by one and the mass number remains the same; confirm that the equation is correctly balanced.

Protons and Neutrons are Made Up of Quarks

Protons and neutrons are not fundamental particles as electrons are. Protons and neutrons are composed of more fundamental particles called quarks. Quarks are fundamental particles not similar to electrons, but like electrons in that they have no smaller pieces. (If you think “quarks” is a somewhat fanciful name, the world of particle physics holds a lot of surprises for you.) Quarks come in six different types (particle physicists call them flavors). The six “flavors” of quarks are named *up, down, top, bottom, strange*, and *charmed*. Protons and neutrons are composed of a combination of *up* and *down* quarks. The *up* quark carries a charge of +2/3 and the *down* quark carries a charge of -1/3. A proton is composed of two *up* quarks and one *down* quark. Thus the charge on a proton is + 2/3 + 2/3 - 1/3 = 1. A neutron is composed of one up quark and two down quarks, hence its charge is + 2/3 – 1/3 – 1/3 = 0. With this information, you can see that a neutron is NOT composed of a proton and an electron. The beta particle produced during beta decay is created in the process of a neutron decaying to a proton. We will view the process in terms of the net effect which is changing a neutron into a proton and emitting an electron.

Gamma Radiation

Frequently, gamma ray production accompanies nuclear reactions of all types. In the alpha decay of U-238, two gamma rays of different energies are emitted in addition to the alpha particle.

$${}^{238}_{92}\mathrm{U} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{234}_{90}\mathrm{Th} + 2\,{}^{0}_{0}\gamma$$

Virtually all of the nuclear reactions in this chapter also emit gamma rays, but for simplicity the gamma rays are generally not shown. Nuclear reactions produce a great deal more energy than chemical reactions. Chemical reactions release the difference between the chemical bond energy of the reactants and products, and the energies released have an order of magnitude of 1 x 10^3 kJ/mol. Nuclear reactions release some of the binding energy and may convert tiny amounts of matter into energy. The energy released in a nuclear reaction has an order of magnitude of 1 x 10^8 kJ/mol.

Decay Series

The decay of a radioactive nucleus is a move toward becoming stable. Often, a radioactive nucleus cannot reach a stable state through a single decay. In such cases, a series of decays will occur until a stable nucleus is formed. The decay of U-238 is an example of this. The U-238 decay series starts with U-238 and goes through fourteen separate decays to finally reach a stable nucleus, Pb-206. There are similar decay series for U-235 and Th-232. The U-235 series ends with Pb-207 and the Th-232 series ends with Pb-208.

U-238 Decay Series

Nucleus	**Type of Decay**	**Product**
U-238	α	Th-234
Th-234	β	Pa-234
Pa-234	β	U-234
U-234	α	Th-230
Th-230	α	Ra-226
Ra-226	α	Rn-222
Rn-222	α	Po-218
Po-218	α	Pb-214
Pb-214	β	Bi-214
Bi-214	β	Po-214
Po-214	α	Pb-210
Pb-210	β	Bi-210
Bi-210	β	Po-210
Po-210	α	Pb-206

Several of the radioactive nuclei that are found in nature are present there because they are produced in one of the radioactive decay series. That is to say, there may have been radon on the earth at the time of its formation, but that original radon would have all decayed by this time. The radon that is present now is present because it was formed in a decay series.

Lesson Summary

- A nuclear reaction is one that changes the structure of the nucleus of an atom.
- The atomic numbers and mass numbers in a nuclear equation must be balanced.
- Protons and neutrons are made up of quarks.
- The two most common modes of natural radioactivity are alpha decay and beta decay.
- Most nuclear reactions emit energy in the form of gamma rays.

Review Questions

1. Write the nuclear equation for the alpha decay of radon-198. **(Intermediate)**

2. Write the nuclear equation for the beta decay of uranium-237. **(Intermediate)**

3. There are six known quarks. The experimenter who discovers particles in nuclear physics gets the right to name the new particle. This has resulted in some very fanciful names for quarks. The six quarks are named, **up** quarks, **down** quarks, **charmed** quarks, **strange** quarks, **top** quarks, and **bottom** quarks. (The top and bottom quarks were originally named *truth* and *beauty* quarks, but the names were changed for some reason.) Protons and neutrons are each made of only up and down quarks and they are made of three quarks each. The up quark carries a charge of + $\frac{2}{3}$ and the down quark carries a charge of - $\frac{1}{3}$. Determine by the final charge on the proton and neutron, what combination of three up and down quarks are required to make a proton and what combination will make a neutron? **(Intermediate)**

Vocabulary

alpha decay	Alpha decay is a common mode of radioactive decay in which a nucleus emits an alpha particle (a helium-4 nucleus).
beta decay	Beta decay is a common mode of radioactive decay in which a nucleus emits beta particles. The daughter nucleus will have a higher atomic number than the original nucleus.
quark	Quarks are physical particles that form one of the two basic constituents of matter. Various species of quarks combine in specific ways to form protons and neutrons, in each case taking exactly three quarks to make the composite particle.

Review Answers

1. $^{198}_{86}\text{Rn} \rightarrow {}^{4}_{2}\text{He} + {}^{194}_{84}\text{Po}$

2. $^{237}_{92}\text{U} \rightarrow {}^{0}_{-1}\text{e} + {}^{237}_{93}\text{Np}$

3. a proton = 2 up quarks and 1 down quark while a neutron = 2 down quarks and 1 up quark.

Nuclear Equations

Lesson Objectives

- The student will give definitions and examples of fission and fusion.
- The student will classify nuclear reactions as fission or fusion.
- Given a nuclear equation with one species missing, the student will be able to correctly fill in the missing particle.
- Students will write balanced equations for nuclear transmutations.

Introduction

Atomic nuclei with an inadequate amount of binding energy per particle are unstable and occasionally disintegrate in an organized fashion. Such disintegrations are referred to as *natural radioactivity*. It is also possible for scientists to smash nuclear particles together and cause nuclear reactions between normally stable nuclei. These disintegrations are referred to *artificial radioactivity*. None of the elements above #92 on the periodic table occur on earth naturally . . . they are all products of artificial radioactivity (man-made).

Fission and Chain Reactions

Nuclei that are larger than iron-56 become smaller and in the process become more stable. These large nuclei undergo nuclear reactions in which they break up into two or more smaller nuclei. These reactions are called **fission** reactions.

Conversely, nuclei that are smaller than iron-56 become larger nuclei in order to be more stable. These nuclei undergo a nuclear reaction in which smaller nuclei join together to form a larger nucleus. Such nuclear reactions are called **fusion** reactions. In both fission and fusion, large amounts of energy are given off in the form of heat, light, and gamma radiation. Nuclear fission was discovered in the late 1930s when U-235 nuclides were bombarded with neutrons and were observed to split into two smaller-mass nuclei.

$$^{1}_{0}\mathrm{n} + {}^{235}_{92}\mathrm{U} \rightarrow {}^{141}_{56}\mathrm{Ba} + {}^{92}_{36}\mathrm{Kr} + 3\ {}^{1}_{0}\mathrm{n}$$

The products shown are only one of many sets of products from the disintegration of a U-235 nucleus. Over 35 different elements have been observed in the fission products of U-235.

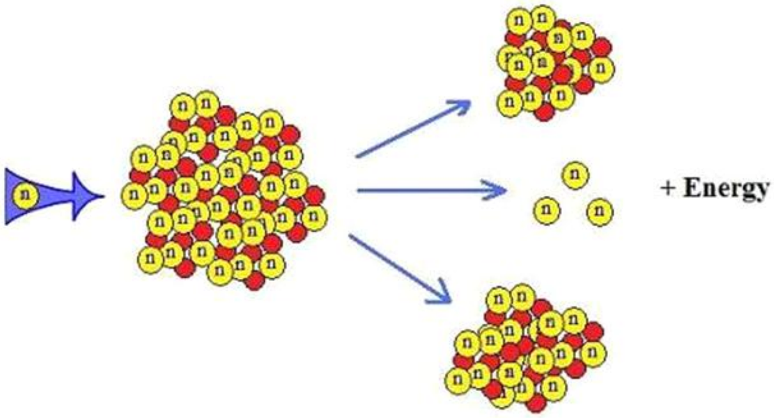

Figure 5: Fission

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When a U-235 nucleus captures a neutron, it undergoes fission producing two lighter nuclei and three free neutrons (Figure 5). The production of the free neutrons makes it possible to have a self-sustaining fission process – a nuclear **chain reaction.** If at least one of the neutrons goes on to cause another U-235 disintegration, the fission will be self-sustaining. If none of the neutrons goes on to cause another disintegration, the process dies out. If the mass of fissionable material is too small, the neutrons escape from the mass without causing another reaction and the reaction is said to be **subcritical.** When the mass of fissionable material is large enough, at least one of the neutrons will cause another reaction and the process will continue at a steady rate. This process is said to be **critical.**

When the mass is small enough, the neutron may escape without causing another reaction. When the mass is large, however, the neutron is very unlikely to escape.

Figure 6: When the critical mass is reached, the neutron will always cause another disintegration.

(*Created by:* Richard Parsons, *License:* CC-BY-SA)

If enough mass is present for the reaction to escalate rapidly, the heat buildup causes a violent explosion. This situation is called **supercritical.** The amount of mass necessary to maintain a chain reaction differs with each fissionable material and is called that material's **critical mass.**

Natural and Artificial Radioactivity

There are several ways in which nuclei can undergo reaction and change their identity. Some nuclei are unstable and spontaneously emit particles and electromagnetic radiation. Such spontaneous disintegration is known as **natural radioactivity.**

It is also possible to cause nuclear disintegration by striking a nucleus with another particle. This is called **artificial radioactivity.** Ernest Rutherford produced the first induced or artificial transmutation of elements by bombarding a sample of nitrogen gas with alpha particles.

$$^{14}_{7}\mathrm{N} + ^{4}_{2}\mathrm{He} \rightarrow ^{17}_{8}\mathrm{O} + ^{1}_{1}\mathrm{H}$$

Irene Joliet-Curie, the daughter of Pierre and Marie Curie, carried out a transmutation that produced an unstable (radioactive) nucleus from a stable nucleus. She bombarded aluminum with alpha particles, and after the bombardment was stopped the product continued to emit radiation. It was determined that the alpha particle bombardment transmuted aluminum-27 nuclei to phosphorus-30 nuclei. The phosphorus-30 is a positron emitter. Positrons are subatomic particles with the same mass as an electron, but carry a positive one (+1) charge instead of negative one (-1).

$$^{4}_{2}\mathrm{He} + ^{27}_{13}\mathrm{Al} \rightarrow ^{30}_{15}\mathrm{P} + ^{1}_{0}\mathrm{n}$$

$$^{30}_{15}\mathrm{P} \rightarrow ^{30}_{14}\mathrm{Si} + ^{0}_{1}\mathrm{P}$$

Fusion

The nuclear reaction shown below is a reaction in which a lithium-7 nucleus combines with a hydrogen-1 nucleus and produces two helium-4 nuclei and a considerable amount of energy.

$$^{1}_{1}\mathrm{H} + ^{7}_{3}\mathrm{Li} \rightarrow 2\ ^{4}_{2}\mathrm{He} + \mathrm{energy}$$

The combined mass of the lithium and hydrogen nuclei is 8.02329 Daltons and the combined mass of the two helium nuclei is 8.00520 Daltons. The mass lost is 0.01809 Daltons and is accounted for in the energy that is released. Nuclear reactions, in which two or more lighter-mass nuclei join together to form a single nucleus, are called **fusion** reactions or nuclear fusions. Of particular interest are fusion reactions in which hydrogen nuclei combine to form helium. Hydrogen nuclei are positively charged and repel each other. The closer the particles come, the greater is the force of repulsion. In order for fusion reactions to occur, the hydrogen nuclei must have extremely high kinetic energies so the velocities can overcome the forces of repulsion. These kinetic energies only occur at extreme temperatures such as those that occur in the cores of the sun and other stars. Nuclear fusion is the power source for the stars where the necessary temperature to ignite the fusion reaction is provided by massive gravitational pressure.

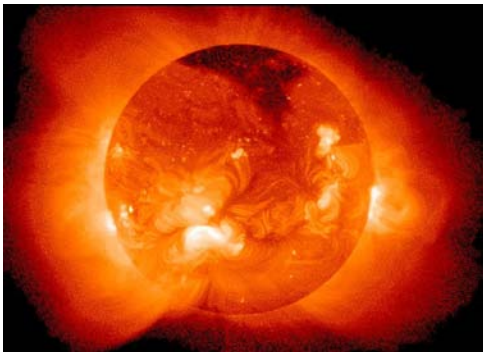


Figure 7: The energy that comes from the sun and other stars is produced by fusion.

(*Source:* http://commons.wikimedia.org/wiki/File:Sun-in-X-ray, *Author:* NASA Goddard Laboratory for Atmospheres, *License:* Public Domain)

The heat to ignite the fusion reaction in thermonuclear weapons (hydrogen bombs) is provided by a small fission reaction that is set off inside the mass of hydrogen. It is hoped that the fusion reactions that will someday occur in fusion reactors will be ignited by multiple lasers.

The conversion of hydrogen to helium in the sun requires several steps, but the net result is the fusion of four hydrogen-1 nuclei into one helium-4 nucleus.

$$4\ {}^{1}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He} + 2\ {}^{0}_{1}\mathrm{p} + \text{energy}$$

In stars more massive than our sun, fusion reactions involving carbon and nitrogen are possible. These reactions produce more energy than hydrogen fusion reactions.

The exact reactions involved in thermonuclear weapons are secret, but they most likely involve either a reaction between two hydrogen-2 nuclei or a reaction between a hydrogen-2 nucleus and a hydrogen-3 nucleus.

$${}^{2}_{1}\mathrm{H} + {}^{2}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He} + \text{energy}$$

$${}^{2}_{1}\mathrm{H} + {}^{3}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{1}_{0}\mathrm{n} + \text{energy}$$

Intensive research is now being conducted to develop fusion reactors for electricity generation. The two major problems slowing up the development is finding a practical means for generating the intense temperature needed and developing a container than won't melt under the conditions of a fusion reaction. Electricity-producing fusion reactors are still a distant dream.

Lesson Summary

- In nuclear reactions, the sum of the atomic numbers and the sum of the mass numbers on the two sides of the equation must be equal.
- Naturally radioactive elements exist in the earth and are either alpha or beta emitters.
- Artificial transmutation of elements can be accomplished by bombarding the nuclei of some elements with alpha or subatomic particles.
- Nuclear fission refers to the splitting of atomic nuclei.

- Nuclear fusion refers to the joining together to two or more smaller nuclei to form a single nucleus.

Review Questions

1. Only one particle is missing from this equation. What are its atomic and mass numbers? **(Intermediate)**

$$^{14}_{7}\mathrm{N} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{1}_{1}\mathrm{H} + ?$$

2. To what element does the missing particle in question #1 belong? **(Intermediate)**

3. When a U-235 nucleus is struck by a neutron, the nucleus may be split into Ce-144 and Sr-90 nuclei, also emitting four electrons and two neutrons. Write the equation for this nuclear reaction. **(Intermediate)**

4. Complete the following nuclear equation by supplying the missing particle. **(Intermediate)**

$$^{196}_{85}\mathrm{At} \rightarrow {}^{4}_{2}\mathrm{He} + ?$$

5. Complete the following nuclear equation by supplying the missing particle. **(Intermediate)**

$$^{208}_{84}\mathrm{Po} \rightarrow {}^{4}_{2}\mathrm{He} + ?$$

6. Complete the following nuclear equation by supplying the missing particle. **(Intermediate)**

$$^{210}_{86}\mathrm{Rn} \rightarrow {}^{4}_{2}\mathrm{He} + ?$$

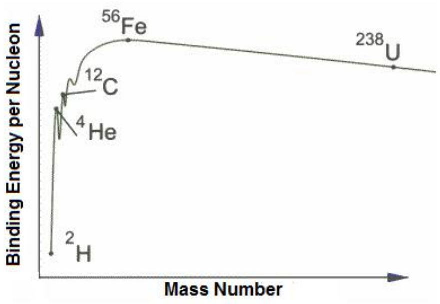
7. Complete the following nuclear equation by supplying the missing particle. **(Intermediate)**

$$^{201}_{80}\mathrm{Hg} + ? \rightarrow {}^{201}_{79}\mathrm{Au}$$

8. Complete the following nuclear equation by supplying the missing particle. **(Intermediate)**

$$? + \rightarrow {}^{210}_{84}\mathrm{Po} + {}^{0}_{-1}\mathrm{e}$$

9.



Use information in the chart above to decide if carbon-12 nuclei were to be transmuted into other nuclei that were more stable, would this more likely be accomplished by fission or by fusion? **(Intermediate)**

Vocabulary

artificial radioactivity	Induced radioactivity that is produced by bombarding an element with high-velocity particles.
chain reaction	A multi-stage nuclear reaction that sustains itself in a series of fissions in which the release of neutrons from the splitting of one atom leads to the splitting of others.
critical mass	The smallest mass of a fissionable material that will sustain a nuclear chain reaction at a constant level.
fission	A nuclear reaction in which a heavy nucleus splits into two or more smaller fragments, releasing large amounts of energy.
fusion	A nuclear reaction in which nuclei combine to form more massive nuclei with the simultaneous release of energy.
natural radioactivity	The radioactivity that occurs naturally, as opposed to induced radioactivity. Also known as spontaneous fission.

Review Answers

1. atomic number = 8 and mass number = 17

2. all atoms with atomic number 8 are oxygen

3. $^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{144}_{58}\mathrm{Ce} + {}^{90}_{38}\mathrm{Sr} + 4\,{}^{0}_{-1}\mathrm{e} + 2\,{}^{1}_{0}\mathrm{n}$

4. $^{192}_{83}\mathrm{Bi}$

5. $^{204}_{82}\mathrm{Pb}$

6. $^{206}_{84}\mathrm{Po}$

7. $^{0}_{-1}\mathrm{e}$

8. $^{210}_{83}\mathrm{Bi}$

9. The nuclei with larger mass numbers than C-12 are more stable (have more binding energy per nucleon) whereas the nuclei with smaller mass numbers than C-12 are generally less stable. Therefore, we should expect C-12 to under fusion to increase nuclear stability.

Radiation Around Us

Lesson Objectives

- The student will compare qualitatively the ionizing and penetration power of α , β , and γ particles.

- Students will calculate the amount of radioactive material that will remain after an integral number of half-lives.
- Students will describe how carbon-14 is used to determine the age of carbon containing objects.

Introduction

All of us are subjected to a certain amount of ionizing radiation every day. This radiation is called background radiation and comes from a variety of natural and artificial radiation sources. Approximately 82% of background radiation comes from natural sources. These include 1) sources in the earth; naturally occurring radioactive elements which are incorporated in building materials and also in the human body, 2) sources from space in the form of cosmic rays, and 3) sources in the atmosphere such as radioactive radon gas released from the earth and radioactive atoms like carbon-14 produced in the atmosphere by bombardment from high-energy cosmic rays.

Background Radiation

Approximately 15% of background radiation comes from medical x-rays and nuclear medicine. The remaining 3% of background radiation comes from man-made sources such as: smoke detectors, luminous dials and signs, radioactive contamination due to historical nuclear weapons testing, normal operation of facilities used for nuclear power and scientific research, emissions from burning fossil fuels (primarily coal-burning power plants without ash-capture facilities), emissions from the improper disposal of radioactive materials used in nuclear medicine[1].

Public health agencies do not feel that the level of background radiation is a serious threat to public health, but they recommend that individuals limit their exposure to ionizing radiation as much as possible[2]. To this goal, the medical profession has significantly reduced the number of x-rays recommended: skin tests for tuberculosis are recommended over x-rays and most dentists recommend dental x-rays every other check-up instead of every check-up.

The Ionizing and Penetration Power of Radiation

With all the radiation from natural and man-made sources, we should quite reasonably be concerned about how all the radiation might affect our health. The damage to living systems is done by radioactive emissions when the particles or rays strike tissue, cells, or molecules and alter them. These interactions can alter molecular structure and function; cells no longer carry out their proper function and molecules, such as DNA, no longer carry the appropriate information. Large amounts of radiation are very dangerous, even deadly. The ability of radiation to damage molecules is analyzed in terms of what is called **ionizing power.** When a radiation particle interacts with atoms, the interaction can cause the atom to lose electrons and thus become ionized. The greater the likelihood that damage will occur by an interaction is the ionizing power of the radiation. Much of the threat from radiation is involved with the ease or difficulty of protecting oneself from the particles. How thick of a wall do you need to hide behind to be safe? The ability of each type of radiation to pass through matter is expressed in terms of **penetration power.** The more material the radiation can pass through, the greater the penetration power and the more dangerous they are.

Comparing only the three common types of ionizing radiation, alpha particles have the greatest mass. Alpha particles have approximately four times the mass of a proton or neutron and approximately 8,000 times the mass of a beta particle. Because of the large mass of the alpha particle, it has the highest ionizing power and the greatest ability to damage tissue. That same large size of alpha particles, however, makes them less able to penetrate matter. They collide with molecules very quickly when striking matter, add two electrons and become a harmless helium atom. Alpha particles have the least penetration power and can be stopped by a thick sheet of paper. They are also stopped by the outer layer of dead skin on people. This may seem to remove the threat from alpha particles but only from external sources. In a situation like a nuclear explosion or some sort of nuclear accident where radioactive emitters are spread around in the environment, the emitters can be inhaled or taken in with food or water and once the alpha emitter is inside you, you have no protection at all.

Beta particles are much smaller than alpha particles and therefore, have much less ionizing power (less ability to damage tissue), but their small size gives them much greater penetration power. Most resources say that beta particles can be stopped by a one-quarter inch thick sheet of aluminum. Once again, however, the greatest danger occurs when the beta emitting source gets inside of you.

Gamma rays are not particles but a high energy form of electromagnetic radiation (like x-rays except more powerful). Gamma rays are energy that has no mass or charge. Gamma rays have tremendous penetration power and require several inches of dense material (like lead) to shield them. Gamma rays may pass all the way through a human body without striking anything. They are considered to have the least ionizing power and the greatest penetration power.

When researching thicknesses and materials required to stop various types of radiation, different estimates are encountered. There are apparently two reasons for this: 1) some estimates are based on stopping 95% of beta particles while other estimates are based on stopping 99% of beta particles, and 2) different beta particles emitted during nuclear reactions may have very different energies – some very high energy beta particles may not be stopped by the normal barrier. The safest amount of radiation to avoid damage to the human body is zero. It isn't possible to be exposed to zero ionizing radiation so the next best goal is to be exposed to as little as possible.

Definition of Half-Life

During natural radioactive decay, not all atoms of an element are instantaneously changed to atoms of another element. The decay process takes time and there is value in being able to express the rate at which a process occurs. In chemical reactions as well as radioactive decay, a useful concept is **half-life,** which is the time required for half of the starting material to be consumed. Half-lives can be calculated from measurements on the change in mass of a nuclide and the time it takes to occur. For a particular group of radioactive nuclei, it is not possible to know which nuclei will disintegrate or when they will disintegrate. The only thing we know is that in the time of that substance's half-life, half of the original nuclei will disintegrate.

Selected Half-Lives

The half-lives of many radioactive isotopes have been determined and they have been found to range from extremely long half-lives of 10 billion years to extremely short half-lives of fractions of a second.

TABLE OF SELECTED HALF-LIVES

ELEMENT	**MASS NUMBER**	**HALF-LIFE**	**ELEMENT**	**MASS NUMBER**	**HALF-LIFE**
Uranium	238	4.5 billion years	Californium	251	800 years
Neptunium	240	1 hour	Nobelium	254	3 seconds
Plutonium	243	5 hours	Carbon	14	5,770 years
Americium	246	25 minutes	Carbon	16	0.74 seconds

The quantity of radioactive nuclei at any given time will decrease to half as much in one half-life. For example, if there were 100 g of Cf-251 in a sample at some time, after 800 years, there would be 50 g of Cf-251 remaining and after another 800 years, there would only be 25 g remaining.

Radioactive Dating

An ingenious application of half-life studies established a new science of determining ages of materials by half-life calculations. For geological dating, the decay of U-238 can be used. The half-life of U-238 is 4.5 x 10^9 years. The end product of the decay of U-238 is Pb-206. After one half-life, a 1.00 gram sample of uranium will have decayed to 0.50 grams of U-238 and 0.43 grams of Pb-206. By comparing the amount of U-238 to the amount of Pb-206 in a sample of uranium mineral, the age of the mineral can be estimated. Present day estimates for the age of the Earth's crust from this method is at least 4 billion years.

Organic material is radioactively dated using the long-lived nuclide of carbon, carbon-14. This method of determining the age of organic material was given the name radiocarbon dating. The carbon dioxide consumed by living systems contains a certain concentration of $^{14}CO_2$. When the organism dies, the acquisition of carbon-14 stops but the decay of the C-14 in the body continues. As time goes by, the ratio of C-14 to C-12 decreases at a rate determined by the half-life of C-14. Using half-life equations, the time since the organism died can be calculated. These procedures have been used to determine the age of organic artifacts and determine, for instance, whether art works are real or fake.

Lesson Summary

- 82% of background radiation comes from natural sources. These include 1) sources in the earth; naturally occurring radioactive elements which are incorporated in building materials and also in the human body, 2) sources from space in the form of cosmic rays, and 3) sources in the atmosphere such as radioactive radon gas released from the earth and radioactive atoms like carbon-14 produced in the atmosphere by bombardment from high-energy cosmic rays.
- Approximately 15% of background radiation comes from medical x-rays and nuclear medicine. The remaining 3% of background radiation comes from man-made sources such as: smoke detectors, luminous dials and signs, radioactive contamination due to historical nuclear weapons testing, normal operation of facilities used for nuclear power and scientific research, emissions from burning fossil fuels (primarily coal-burning power plants without ash-capture facilities), emissions from the improper disposal of radioactive materials used in nuclear medicine.
- Of the three common nuclear emissions, alpha particles produce the greatest damage to cells and molecules but are the least penetrating. Gamma rays are the most penetrating but generated the least damage.
- C-14 dating procedures have been used to determine the age of organic artifacts.

Review Questions

1. Which of the three common emissions from radioactive sources requires the heaviest shielding? **(Beginning)**

2. The half-life of radium-226 is about 1600 years. How many grams of a 2.00 gram sample will remain after 4800 years? **(Intermediate)**

3. Sodium-24 has a half-life of about 15 hours. How much of an 16.0 grams sample of sodium-24 will remain after 60.0 hours? **(Intermediate)**

4. A radioactive isotope decayed from 24.0 grams to 0.75 grams in 40.0 years. What is the half-life of the isotope? **(Intermediate)**

5. What nuclide is commonly used in the dating of organic artifacts? **(Beginning)**

6. Why does an ancient wood artifact contain less carbon-14 than a piece of lumber sold today? **(Intermediate)**

7. The half-life of C-14 is about 5,700 years. An organic relic is found to contain C-14 and C-12 in a ratio that is about one-eighth as great as the ratio in the atmosphere. What is the approximate age of the relic? **(Intermediate)**

8. Even though gamma rays are much more penetrating than alpha particles, it is the alpha particles that are more likely to cause damage to an organism. Explain why this is true. **(Intermediate)**

9. The radioactive isotope calcium-47 has been used in the study of bone metabolism; radioactive iron-59 has been used in the study of red blood cell function; iodine-131 has been used in both diagnosis and

treatment of thyroid problems. Suggest a reason why these particular elements were chosen for use with the particular body function. **(Challenging)**

Vocabulary

background radiation	Radiation that comes from environment sources including the earth's crust, the atmosphere, cosmic rays, and radioisotopes. These natural sources of radiation account for the largest amount of radiation received by most people.
half-life	The half-life of a radioactive substance is the time interval required for a quantity of material to decay to half its original value.

Review Answers

1. gamma rays

2. 0.25 gram

3. 1.00 gram

4. 8.0 years

5. carbon-14

6. The wooden artifact ceased to interact with the atmosphere when the tree was cut down. Lumber being sold today was cut down recently. The ratio of carbon-14 to carbon-12 decreases over time because the carbon-14 decays to carbon-12. A tree cut down thousands of years ago would have a smaller ratio of C-14 to C-12 than a tree cut down in the last few years.

7. A drop in the ratio to one-eighth represents three half-lives (1/2, 1/4, 1/8).   3 x 5,700 = 17,100 years

8. Radiation is characterized by its penetration power and its ionizing power. Penetration power indicates how much material the radiation can pass through without being stopped and the ionizing power indicates how likely the radiation is to damage an organism that it strikes. Alpha particles, due to their mass, have very high ionizing power and are much more likely to damage an organism than the mass-less gamma ray.

9. Calcium is a component of bone structure so the radioactive calcium will be directed by the body to bone construction. Iron is a component of red blood cells so the body will direct much of the radioactive iron to red blood cells. The body collects iodine in the thyroid gland, so the radioactive iodine will be directed by the body to the thyroid.

Applications of Nuclear Energy

Lesson Objectives

- The student will trace the energy transfers that occur in a nuclear power reactor from the binding energy of the nuclei to the electricity that leaves the plant.
- The student will define the term "breeder reactor."
- The student will list some medical uses of nuclear energy.

Introduction

It is unfortunate that when the topics of radioactivity and nuclear energy come up, most thoughts probably go to weapons of war. The second thought might be about the possibility of nuclear energy contributing to the solution of the energy crisis. Nuclear energy, however, has many applications beyond bombs and the generation of electricity. Radioactivity has huge applications in scientific research, several fields of medicine both in terms of imaging and in terms of treatment, industrial processes, some very useful appliances, and even in agriculture.

Fission Reactors

A nuclear reactor is a device in which a nuclear chain reaction is carried out at a controlled rate. When the controlled chain reaction is a fission reaction, the reactor is called a fission reactor. Fission reactors are used primarily for the production of electricity although there are a few fission reactors used for military purposes and for research. The great majority of electrical generating systems all follow a reasonably simple design. The electricity is produced by spinning a coil of wire inside a magnetic field.

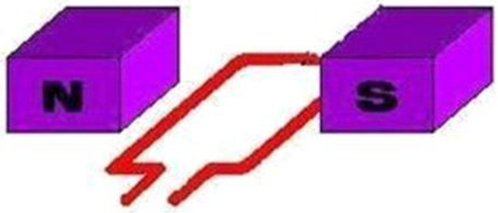


Figure 8: The basics of an electric generator.

(*Created by:* Richard Parsons, *License:* CC-BY-SA)

When the loop is spun, electric current is produced. The direction of the electric current is in one end of the loop and out the other end. The machine built to accomplish this task is called an **electric generator.** Another machine usually involved in the production of electric current is a **turbine.** Although actual turbines can get very complicated, the basic idea is simple. Most of you have seen a child's pinwheel toy. When you blow through the fan blades of the pin wheel, it spins. A turbine is a pipe with many fan blades attached to an axle that runs through the pipe.

When a fluid (air, steam, water) is forced through the pipe, it spins the fan blades which in turn spin the axle. To generate electricity, the axle of a turbine is attached to the loop of wire in a generator. When a fluid is forced through the turbine, the fan blades turn, the turbine axle turns, and the loop of wire inside the generator turns, thus generating electricity. The essential difference in various kinds of electrical generating systems is the method used to spin the turbine. For a wind generator, the turbine is a windmill. In a geothermal generator, steam from a geyser is forced through the turbine. In hydroelectric generating plants, water falling over a dam passes through the turbine and spins it. In fossil fuel (coal, oil, natural gas) generating plants, the fossil fuel is burned and the heat is used to boil water into steam and then the steam passes through the turbine and makes it spin. In a fission reactor generating plant, a fission reaction is used to boil the water into steam and the steam passes through the turbine to make it spin. Once the steam is generated by the fission reaction, a nuclear power plant is essentially the same as a fossil fuel plant.

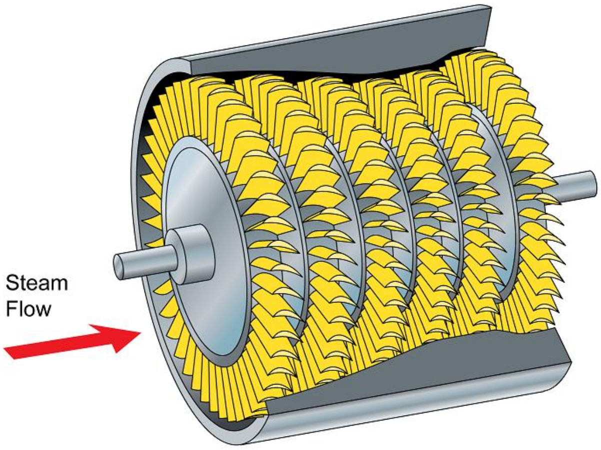


Figure 9: A steam turbine. (*Source:* CK-12 Foundation, *License:* CC-BY-SA)

Naturally occurring uranium is composed almost totally of two uranium isotopes. It contains more than 99% uranium-238 and less than 1% uranium-235. It is the uranium-235, however, that is **fissionable** (will undergo fission). In order for uranium to be used as fuel in a fission reactor, the percentage of uranium-235 must be increased, usually to about 3%. (Uranium in which the U-235 content is more than 1% is called **enriched uranium**.) Somehow, the two isotopes must be separated so that enriched uranium is available for use as fuel. Separating the isotope by chemical means (chemical reactions) is not successful because the isotopes have exactly the same chemistry. Remember that chemical reactions are controlled by the electron configuration of the atom and all the isotopes of an element have the same electron configuration and hence the same chemistry. The only essential difference between U-238 and U-235 are their atomic masses and as a result the separation of the two isotopes will require a physical means that takes advantage of their difference in mass. The modern physical means used to separate the isotopes of uranium involve a **gas centrifuge.** Research separation of isotopes can also be accomplished with a **mass spectrograph.** You may wish to research these techniques on your own.

Once the supply of U-235 is acquired, it is placed in a series of long cylindrical tubes called **fuel rods.** These fuel cylinders are bundled together with **control rods** (Figure 9) made of neutron-absorbing material. The amount of U-235 in all the fuel rods taken together is adequate to carry on a chain reaction but is less than the critical mass. (In the United States, all public nuclear power plants contain less than a critical mass of U-235 and therefore, could never produce a nuclear explosion. The amount of heat generated by the chain reaction is controlled by the rate at which the nuclear reaction occurs. The rate of the nuclear reaction is dependent on how many neutrons are emitted by one U-235 nuclear disintegration *and* strike a new U-235 nucleus to cause another disintegration. The purpose of the control rods is to absorb some of the neutrons and thus stop them from causing further disintegrations. The control rods can be raised or lowered into the fuel rod bundle. When the control rods are lowered all the way into the fuel rod bundle, they absorb so many neutrons that the chain reaction essentially stops. When more heat is desired, the control rods are raised so they catch fewer neutrons, the chain reaction speeds up and more heat is generated. The control rods are operated in a fail-safe system so that power is necessary to hold them up; and during a power failure, gravity will pull the control rods down into shut off position.

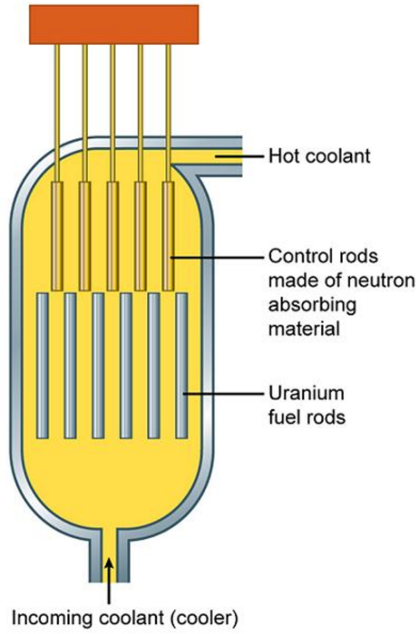


Figure 10: Reaction vessel showing control rods. (*Source:* CK-12 Foundation, *License:* CC-BY-SA)

U-235 nuclei can capture neutrons and disintegrate more efficiently if the neutrons are moving slower than the speed at which they are released. Fission reactors use a **moderator** surrounding the fuel rods to slow down the neutrons. Water is not only a good coolant but also a good moderator so a common type of fission reactor has the fuel core submerged in a huge pool of water. This type of reaction is called a Light Water Reactor or LWR. All public electricity generating fission reactors in the United States are LWRs.

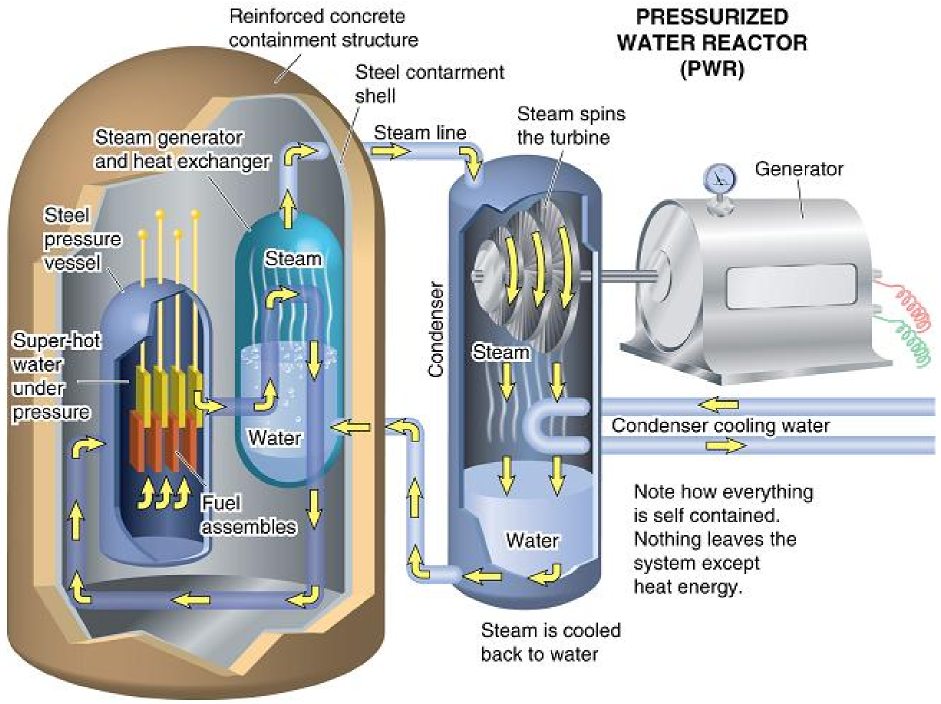


Figure 11: A fission reactor.

(*Source*: CK-12 Foundation, *License:* CC-BY-SA)

You can follow the operation of an electricity-generating fission reactor in Figure 10. The reactor core is submerged in a pool of water. The heat from the fission reaction heats the water and the water is pumped into a heat exchanger container where the heated water boils the water in the heat exchanger. The steam from there is forced through a turbine which spins a generator and produces electricity. After the water passes through the turbine, it is condensed back to liquid water and pumped back to the heat exchanger.

In the United States, heavy opposition to the use of nuclear energy was mounted in the late 1960s and early 1970s. Every environmentalist organization in the US opposed the use of nuclear energy and the constant pressure from environmentalist groups brought increased public fear and therefore, opposition. This is not true today; at least one environmental leader has published a paper in favor of nuclear powered electricity generation.

In 1979, a reactor core meltdown at Pennsylvania's Three Mile Island nuclear power plant reminded the entire country of the dangers of nuclear radiation. The concrete containment structure (six feet thick walls of reinforced concrete), however, did what it was designed to do – prevent radiation from escaping into the environment. Although the reactor was shut down for years, there were no injuries or deaths among nuclear workers or nearby residents[3]. Three Mile Island was the only serious accident in the entire history of civilian power plants (103 plants operating for 40 years) in the United States. There has never been a single injury or death due to radiation in any public nuclear power plant in the U.S. The accident at Three Mile Island did, however, frighten the public so that there has not been a nuclear plant built in the U.S. since the accident.

The 103 nuclear power plants operating in the U.S. deliver approximately 19.4% of American electricity with zero greenhouse gas emission. There are 600 coal-burning electric plants in the US delivering 48.5% of American electricity and producing 2 billion tons of CO_2 annually, accounting for 40% of U.S. CO_2 emissions and 10% of global emissions. These coal burning plants also produce 64% of the sulfur dioxide emissions, 26% of the nitrous oxide emissions, and 33% of mercury emissions.[4]

Breeder Reactors

U-235 is the only naturally occurring fissile isotope and it constitutes less than 1% of naturally occurring uranium. It has been projected that the world's supply of U-235 will be exhausted in less than 200 years. It is possible, however, to convert U-238 to a fissionable isotope which will function as a fuel for nuclear reactors. The fissionable isotope is plutonium-239 and is produced by the following series of reactions.

$$^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{239}_{92}\mathrm{U} \longrightarrow {}^{0}_{-1}\mathrm{e} + {}^{239}_{93}\mathrm{Np} \longrightarrow {}^{0}_{-1}\mathrm{e} + {}^{239}_{94}\mathrm{Pu}$$

The final product from this series of reactions is plutonium-239 which has a half-life of 24,000 years and is another nuclear reactor fuel. This series of reactions can be made to occur inside an operating nuclear reactor by replacing some of the control rods with rods of U-238. As the nuclear decay process proceeds inside the reactor, it produces more fuel than it uses. It would take about 20 such breeder reactors to produce enough fuel to operate one addition reactor. The use of breeder reactors would extend the fuel supply a hundred fold. The problem with breeder reactors, however, is that plutonium is an extremely deadly poison and unlike ordinary fission reactors, it is possible for out-of-control breeder reactors to explode. None of the civilian nuclear power plants in the U. S. are breeder reactors.

Radiation Detectors

A variety of methods have been developed to detect nuclear radiation. One of the most commonly used instruments for detecting radiation and measuring the rate is the **Geiger counter.**

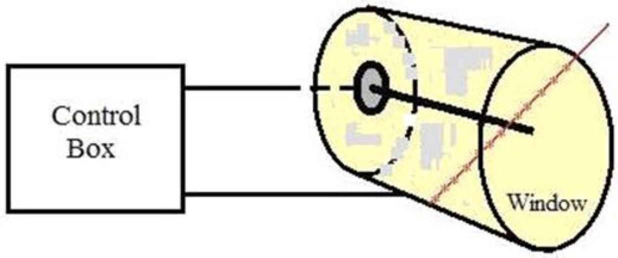


Figure 11: A Geiger Counter.

(*Created by:* Richard Parsons, *License:* CC-BY-SA)

The detecting component of the Geiger counter is the Geiger-Muller tube. This tube is a cylinder filled with an inert gas and it has a window in one end made of porous material that will not allow the inert gas to escape but will allow radiation particles to enter. A conducting wire extends into the center of the tube and is electrically insulated from the tube where it passes through the wall. The wire and walls are part of an electric circuit with a potential difference between the walls and the wire. Electric current does not flow because the circuit is not complete. The inert gas does not conduct electricity and therefore a gap exists in the circuit. When a radiation particle enters the tube through the window, the particle creates a line of ionized gas particles along its path through the tube. The line of ions does conduct electric current and an electric current will flow along the ionized path. The ions only exist for a very short period because the ions of inert gas will quickly regain the lost electrons and become atoms again – which do not conduct. The result is a very short burst of electric current whenever a radiation particle passes through the tube. The control box provides the electric potential for the tube and also provides some means for demonstrating the burst of current. Some machines simply make a clicking sound for each burst of current while others may provide a dial or a digital meter.

Other methods used for the detection of nuclear radiation include, 1) scintillation counters – a screen coated with a material that gives off a small flash of light when struck by a particle, 2) cloud chambers (Figure 12) – a chamber of supersaturated gas that produce a condensation trail along the path of a radiation particle, and 3) bubble chambers – a chamber of superheated liquid that produces a trail of bubbles along the path of a radiation particle.

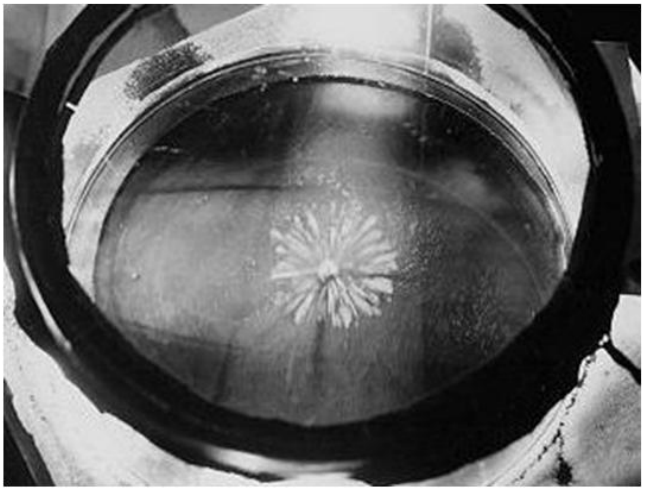


Figure 12: Cloud Chamber showing vapor trails produced by sub-atomic particles.

(*Source:* http://www.nasa.gov/multimedia/imagegallery/image_feature_928_prt.htm), *Created by:* NASA, *Modified by:* Richard Parsons, *License:* Public Domain)

Cloud chambers and bubble chambers have an additional value because the vapor trails or bubble trails left by the nuclear radiation particle are long-lasting enough to be photographed and therefore can be studied in great detail.

Particle Accelerators

In the early 1900's, the use of alpha particles for bombarding low atomic number elements became a common practice. Researchers found that the alpha particles were absorbed by the nuclei and a proton was ejected. This was the first artificially caused transmutation of one element into another. In order to continue these bombardments with alpha particles or protons, the speed of the bombarding particle had to be increased. Several machines were devised to accelerate the particles to the required speeds.

The cyclotron was developed by Ernest Lawrence in 1930 and used to accelerate charged particles so they would have sufficient energy to enter the nuclei of target atoms. A cyclotron consists of two hollow half cylinders called "dees" because of their D-shapes. (Like a huge birthday cake which has been cut in half and the two halves separated by a short distance.)

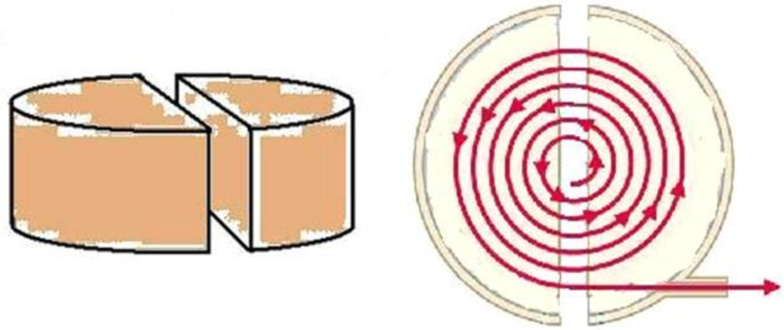


Figure 13: Cyclotron

(*Created by:* Richard Parsons, *License:* CC-BY-SA)

The two dees have opposite charges with a potential difference of at least 50,000 volts and the charges on the dees can be rapidly reversed so that each dee alternately becomes positive and then negative. The cyclotron also has a powerful magnetic field passing through it so that moving charged particles will be caused to travel in a curved path. Charged particles produced from a source in the center of the area between the dees are attracted first into one dee and then into the other as the charge on the dees alternate. As the particle moves back and forth in the dees, it is caused to follow a curved path due to the magnetic field. The motion of the particle is that of a spiral with ever increasing speed. As the circular path of the particle nears the outside edge of the cyclotron, it is allowed to exit through a window and strikes whatever target is placed outside the window.

A linear accelerator is a long series of tubes which are connected to a source of high frequency alternating voltage. As the charged particles leave each tube, the charge on the tubes are altered so the particle is repelled from the tube it is leaving and attracted to the tube it is approaching. In this way, the particle is accelerated between every pair of tubes. The largest linear accelerators are located at the Fermilab in Illinois and at Stanford University.

A number of the elements listed in the periodic table are not found in nature. These elements may never have been present on earth or since they have short half-lives, they may have originally been present but have completely decayed to more stable elements. These elements include all elements with atomic numbers greater than 92 plus technetium (#43) and promethium (#61). The transuranium elements (those with atomic numbers greater than 92) are all made man elements and many of them were produced in the cyclotron in the radiation laboratory at the University of California at Berkeley under the direction of Glenn Seaborg. Some very rare elements presence in the earth are assumed to be due not from the original material present in the earth but rather as daughter products of other disintegrating nuclei.

Nuclear Medicine

The field of nuclear medicine has expanded greatly in the last twenty years. A great deal of the expansion has come in the area of imaging. This section will focus on nuclear medicine involving the types of nuclear radiation introduced in this chapter. The x-ray imaging systems will not be covered.

Radioiodine (I-131) Therapy involves imaging and treatment of the thyroid gland. The thyroid gland is a gland in the neck that produces two hormones that regulate metabolism. In some individuals, this gland becomes overactive and produces too much of these hormones. The treatment for this problem uses radioactive iodine (I-131) which is produced for this purpose in research fission reactors or by neutron bombardment of other nuclei.

The thyroid gland uses iodine in the process of its normal function. Any iodine in food that enters the bloodstream is usually removed by, and concentrated in the thyroid gland. When a patient suffering from an overactive thyroid swallows a small pill containing radioactive iodine, the I-131 is absorbed into the bloodstream just like non-radioactive iodine and follows the same process to be concentrated in the thyroid. The concentrated emissions of nuclear radiation in the thyroid destroy some of the gland's cells and control the problem of the overactive thyroid.

Smaller doses of I-131 (too small to kill cells) are also used for purposes of imaging the thyroid. Once the iodine is concentrated in the thyroid, the patient lays down on a sheet of film and the radiation from the I-131 makes a picture of the thyroid on the film. The half-life of iodine-131 is approximately 8 days so after a few weeks, virtually all of the radioactive iodine is out of the patient's system. During that time, they are advised that they will set off radiation detectors in airports and will need to get special permission to fly on commercial flights.

Positron Emission tomography or PET scan is a type of nuclear medicine imaging. Depending on the area of the body being imaged, a radioactive isotope is either injected into a vein, swallowed by mouth, or inhaled as a gas. When the radioisotope is collected in the appropriate area of the body, the gamma ray emissions are detected by a PET scanner (often called a gamma camera) which works together with a computer to generate special pictures providing details on both the structure and function of various organs. PET scans are used to:

- detect cancer
- determine the amount of cancer spread
- assess the effectiveness of treatment plans
- determine blood flow to the heart muscle
- determine the effects of a heart attack
- evaluate brain abnormalities such as tumors and memory disorders
- map brain and heart function

External Beam Therapy (EBT) is a method of delivering a high energy beam of radiation to the precise location of a patient's tumor. These beams can destroy cancer cells and with careful planning, NOT kill surrounding cells. The concept is to have several beams of radiation, each of which is sub-lethal, enter the body from different directions. The only place in the body where the beam would be lethal is at the point where all the beams intersect. Before the EBT process, the patient is three-dimensionally mapped using CT scans and x-rays. The patient receives small tattoos to allow the therapist to line up the beams exactly. Alignment lasers are used to precisely locate the target. The radiation beam is usually generated with a linear accelerator. EBT is used to treat the following diseases as well as others:

- breast cancer
- colorectal cancer
- head and neck cancer
- lung cancer
- prostate cancer

Nuclear Weapons

Nuclear weapons are of two basic types; fission bombs using supercritical masses of either U-235 or Pu-239 and fusion bombs using heavy isotopes of hydrogen. The fission bombs were called **atomic bombs** (a misnomer since the energy comes from the nucleus) and fusion bombs are called **thermonuclear bombs.** Fission bombs use two or more subcritical masses of fissile material separated by enough distance that they don't become critical, and surrounded by conventional explosives. The conventional explosives are detonated to drive the subcritical masses of fissile material toward the center of the bomb and when these masses are slammed together, they form a supercritical mass and a nuclear explosion ensues. Hydrogen bombs (fusion) are detonated by using a small fission explosion to compress and heat a mass of deuterium or deuterium and tritium to the point that a fusion reaction ignites.

Figure 14: Castle-Romeo nuclear explosion.

Source: http://en.wikipedia.org/wiki/File:Castle-romeo2.jpg, *Created by:* United States Department of Energy, *License:* Public Domain)

Nuclear weapons are power-rated by comparison to the weight of conventional explosives (TNT) that would produce an equivalent explosion. For example, a nuclear device that produces an explosion equivalent to 1,000 tons (2,000,000 pounds) of TNT would be called a 1-kiloton bomb. The atomic bomb detonated at Hiroshima near the end of WWII was a 13-kiloton bomb that used 130 pounds of U-235. It has been estimated that this weapon was very inefficient and that less than 1.5% of the fissile material actually fissioned.[9] The atomic bomb detonated at Nagasaki was a 21-kiloton weapon that used 14 pounds of Pu-239. The two bombs set off in Japan would be considered very small bombs by later standards. Bombs that were tested later were measured not by kilotons but by megatons (million tons) of TNT. The largest bomb ever set off was a 50-megaton fusion weapon tested by the Soviet Union in the 1950s.

The extensive death and destruction caused by these weapons comes from four sources. The tremendous heat released by the explosion heats the air so hot and so fast that the air expansion creates a wind in excess of 200 miles/hour[11] – many times stronger than the strongest hurricane. The blast force from this wind completely destroys all but the strongest buildings for several miles from ground zero. The second source of damage is from fires ignited by the heat from the fireball at the center of the explosion. The fireball in the 50-megaton test was estimated to be four miles in diameter.[10] The third source of injury is the intense nuclear radiation (primarily gamma rays) which are instantly lethal to exposed people for several miles. The final source of injury and possibly death comes from the radioactive fall-out which may be several tons of radioactive debris and may fall up to 300 miles or more away. This fall-out can cause sickness and death for many years.

You should note that the distances given in the above material are guesses and estimates. The only actual data known are from the two (now considered small) bombs detonated in Japan and some above ground tests. The actual death and destruction from a 50-megaton bomb detonated in a heavily populated area is not known.

Lesson Summary

- The fission of U-235 or Pu-239 is used in nuclear reactors.
- The critical mass is the amount of fissile material that will maintain a chain reaction.

- Nuclear radiation also has many medical uses.

Review Questions

1. What is the primary physical difference between a nuclear electricity generating plant and a coal-burning electricity generating plant? **(Intermediate)**

2. What do the control rods in a nuclear reactor do and how do they do it? **(Intermediate)**

3. What is a breeder reactor? **(Intermediate)**

4. Name two types of particle accelerators. **(Beginning)**

5. In the medical use of radioactivity, what does EBT stand for? **(Beginning)**

6. Is it possible for a nuclear explosion to occur in a nuclear reactor? Why or why not?

Further Reading / Supplementary Links

Nuclear Power VS. Other Sources of Power, Neil M. Cabreza, Department of Nuclear Engineering, University of California, Berkeley, NE-161 Report. Available at http://www.nuc.berkeley.edu/thyd/ne161/ncabreza/sources.

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http://www.radscihealth.org/rsh/About

http://nrc.gov/reading-rm/doc-collections

http://www.world-nuclear.org/info/Chernobyl

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http://www.nuclearweaponarchive.org/Russia/Tsarbomba.html

http://www.atomicarchive.com/effects/index.shtml

http://www.en.wikipedia.org

Vocabulary

control rods	Control rods are made of chemical elements capable of absorbing many neutrons and are used to control the rate of a fission chain reaction in a nuclear reactor.
cyclotron	A cyclotron is a type of particle accelerator.

fall out	Fall out is radioactive dust hazard from a nuclear explosion, so named because it "falls out" of the atmosphere where it was spread by the explosion.
fissile	A fissile substance is a substance capable of sustaining a chain reaction of nuclear fission.
fissionable	A fissionable material is material capable of undergoing fission.
Geiger counter	A Geiger counter is an instrument used to detect radiation, usually alpha and beta radiation, but some models can also detect gamma radiation.
isotope	Nuclei with the same number of protons but different numbers of neutrons.
linear accelerator	A linear accelerator is a linear electrical device for the acceleration of subatomic particles.
moderator	A neutron moderator is a medium which reduces the velocity of fast neutrons; commonly used moderators are regular (light) water, solid graphite, and heavy water.
nuclear pile	A nuclear pile is a nuclear reactor.

Review Answers

1. In the coal-burning plant, the steam that blows through the turbines is produced from the heat of burning coal whereas in the nuclear electricity generating plant, the steam is produced by the heat from nuclear fission.

2. The control rods control the rate of the chain reaction. They do this by absorbing more or less neutrons. The more neutrons absorbed by the control rods, the slower the nuclear reaction will be.

3. A breeder reactor is a reactor than can produce fissionable fuel from non-fissionable U-238 as it runs.

4. cyclotron and linear accelerator

5. External Beam Therapy

6. The type of nuclear reactor used in the United States does not contain a critical mass of fuel and therefore, could not produce a nuclear explosion. Breeder reactors that are used in some other countries could, under extreme conditions, generate a critical mass of fuel and explode.

30. Organic Chemistry

Carbon, A Unique Element

Lesson Objectives

- Describe the allotropes of carbon.
- Describe the hybridization of carbon.
- Explain how the hybridization of carbon allows for the formation of large number of compounds containing carbon.

Introduction

Because of its unique electron dot configuration, carbon has the ability to form many types of molecules. If we were to look at the electronic configuration of carbon, we would see the following.

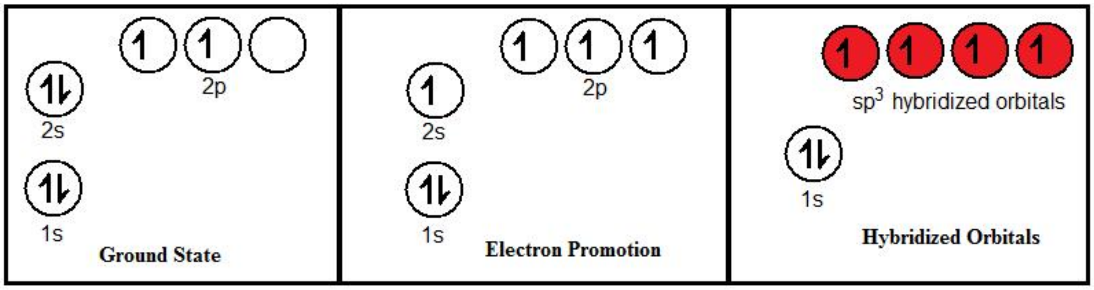


Figure 1: The electron configuration of carbon.

(*Created by:* Richard Parsons, *License:* CC-BY-SA)

Looking at the ground state electron configuration for carbon, it would seem that carbon would only form two bonds because it has only two half-filled orbitals available for overlap. Carbon, as you have learned in earlier chapters, has the ability to bond to four other atoms and thus needs to have four half-filled orbitals. Electron promotion and the hybridization of the s and p orbitals in the electron configuration of carbon is necessary in order to create these four half-filled orbitals. ***Hybridization*** is the process of combining orbitals to create new orbitals.

The electrons in the new orbitals all have equal energy and will form four identical covalent bonds. Hybridization will be investigated further in this lesson.

When bonding occurs between carbon and other atoms, the electrons can be in fixed positions or they can be free to move between two nuclei. When the carbon atom has all single bonds (sigma bonds), all of the electrons are fixed. When double and triple bonding occurs, then some of the electrons have the ability to be move around (the electrons in pi bonds). The number of fixed and free electrons associated with the structure also has an impact on the properties of the molecule.

In this lesson the three allotropes of carbon will be explored in terms of their structure. Following this the ability of carbon to have multiple arrangements of its electron configurations depending on the bonding requirements of the structure will be addressed.

Forms of Carbon

There are three forms of carbon that exist because of the unique bonding of this element. These forms are known as allotropes. ***Allotropes*** are different forms of the same element based on unique bonding arrangements. Allotropes of elements must be in the same phase. The term allotropy originally comes from the Greek words *allos* meaning other and *tropos* meaning manner thus the other manner for forming the same element. For carbon there are three main allotropes:

- diamond
- graphite
- buckyball

Diamond has a structure where carbon atoms are all bonded in a tetrahedral network so that it is in essence one large molecule. The tetrahedral network gives the molecule strength. Figure 2 below shows the structure of diamond. Notice the individual tetrahedra that join together to make the diamond structure.

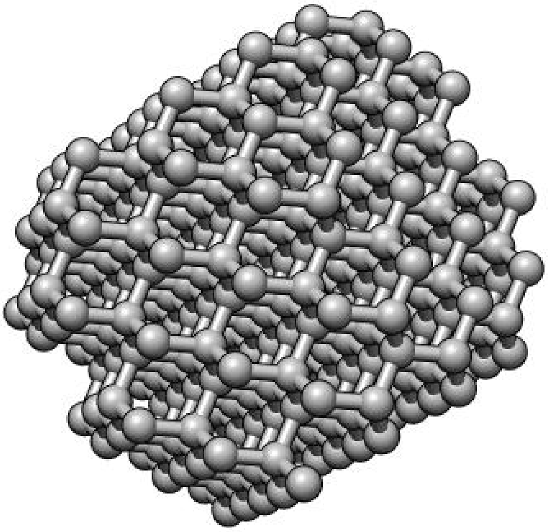


Figure 2: Diamond lattice structure.

(*Source*: http://openchemistry.co.uk/image_3, *License:* Creative Commons Attribution 3.0)

Because of this structure, diamond is extremely hard and is also known to be a poor conductor of electricity but excellent conductor of heat. With the structure of diamond, each carbon atom uses all of its four valence electrons. The interlocking structure seen in the diagram is evident of a covalent network solid and this is the reason for the structure's strength and also its high melting point. Diamond, in fact, has the highest melting point tipping the scale at 3830 Kelvin or approximately 3547ºC.

Graphite, the second allotrope of carbon, has a unique structure as well. Its soft, flaky, black appearance that we all associate with pencil lead, overshadows this beautiful covalent network.

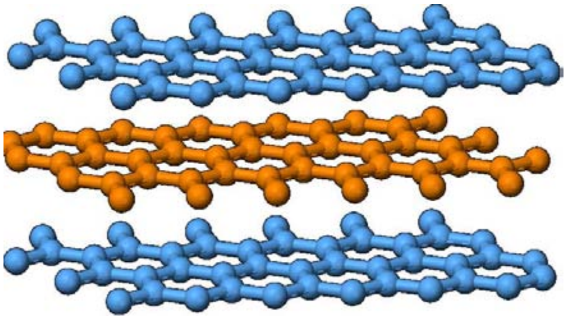


Figure 3: Graphite structure with multiple layers.

(*Source:* http:en.wikipedia.org/wiki/File:Graphite-layers-side-eD-balls, *Created by:* Benjah-bmm27, *License:* GNU Free Documentation License)

Figure 3 shows the structure of graphite. The structure consists of hexagonal carbon rings bonded together in sheets. These sheets are then layered. It is this layering that gives graphite its ability to be a lubricant. Weak intermolecular forces due to delocalized electrons hold the sheets together. With graphite, the carbon atoms in the hexagonal structures are only using three (3) of the four (4) electrons in the outer shell at any one time.

Buckyball (Buckminsterfullerene) is a combination of sixty carbon atoms arranged in hexagons and pentagons. It looks like a soccer ball! Take a look at Figure 4 at the shape of buckyball and compare it to the soccer ball.

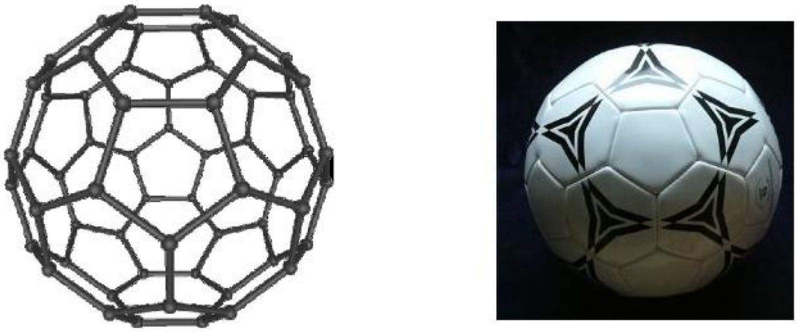


Figure 4: Buckyball structure (left) compared to soccer ball (right).

(*Source:* http://en.wikipedia.org/wiki/File:C60a, *License:* GNU Free Documentation License, *Source:* http://en.wikipedia.org/wiki/File:Fussball, *License:* GNU Free Documentation License)

Buckyball is the third allotrope of carbon discovered in soot only in the mid-1980s. The structure consists of twenty (20) hexagons and twelve (12) pentagons arranged in such a way that no two pentagons share the same edge. Each pentagon is attached to five hexagons while each hexagon is attached to three pentagons and three hexagons. For each carbon atom, there is one double bond and two single bonds.

The relatively new discovery of this allotrope of carbon has made buckyball somewhat of a mystery as to its full potential. Buckyball is very inert and one of the only allotropes of carbon soluble in organic solvents. It has been found to be a good lubricant as well as a superconductor.

Eventually, scientists intend to develop nanotechnology with the aid of this allotrope of carbon. Nanotechnology has its applications in industry, computer science, and medicine, among other disciplines.

Orbital Hybridization in Carbon

As indicated in the introduction, the electronic configuration of carbon is $1s^2 2s^2 2p^2$. We can draw the electron configuration with two valence electrons in the 2s orbital and two valence electrons in two of the 2p orbitals. We know from the discussions of the allotropes of carbon and previous learning that carbon has the ability to bond to four other atoms and therefore its valence electrons must be spread over the s and p orbitals. Look at what happens when the one s orbital and the three p orbitals combine to form four equivalent orbitals to hold electrons.

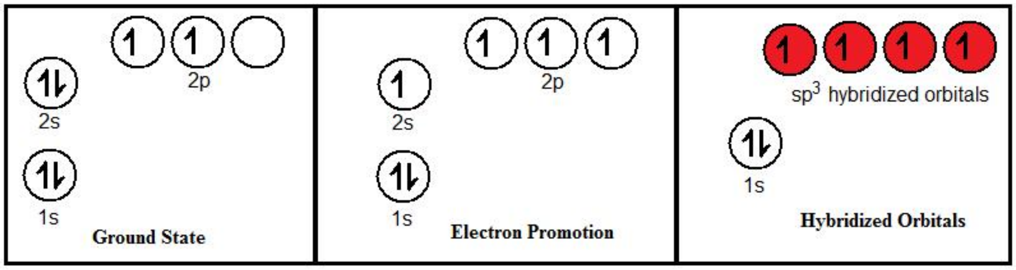


Figure 4: The electron configuration of carbon.

(*Created by:* Richard Parsons, *License:* CC-BY-SA)

When one s and three p orbitals combine to form four equivalent bonding orbitals, the electrons are said to be hybridized. Specifically for this case the electrons are sp^3 hybridized because the electrons are in an orbital where one s and three p orbitals have combined. It should be noted here that when the electrons are sp^3 hybridized for carbon, the electrons are equally distributed along the vertices of the tetrahedron. With this hybridization, carbon forms four sigma bonds. As indicated in the shape of the diamond structure above, the tetrahedron structure of this molecule gives it strength.

Consider the graphite structure from above and think about the hybridization of the electrons. The graphite molecule has double bonds and thus has electrons that are delocalized in pi bonds. How does this work?

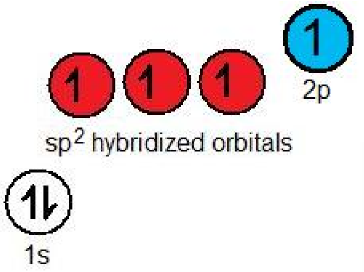


Figure 5: Only the s and two of the p orbitals are hybridized.

(*Created by:* Richard Parsons, *License:* CC-BY-SA)

In the case of graphite, and other molecules that have double bonds with carbon, the electron has been promoted from the s orbital to the p orbital, but this time only one s and two p electrons combine to form the sp^2 hybrid orbitals that house the localized electrons (sigma bonds). The third p orbital electron forms a pi bond above and below the molecule. The electron is free to move within this probability region and is therefore freer to move around.

Carbon Makes Millions of Compounds

Considering the fact that carbon can form bonds where the electrons can be localized and delocalized, carbon has the ability to form single, double, and triple bonds. With this ability, carbon, then, can make millions of compounds where it is covalently bonded to hydrogen, oxygen, nitrogen, sulfur and other nonmetals. The remainder of this chapter is devoted to the study of carbon compounds.

Lesson Summary

- Hybridization is the process of combining atomic orbitals to create new bonding orbitals. The electrons in these new orbitals will all have equal energy in and will form equivalent covalent bonds. When bonding occurs between carbon and other atoms, the electrons can be in fixed positions (sigma bonds) or they can be free to move around (pi bonds).
- Allotropes are different forms of the same element based on their bonding. There are three main allotropes of carbon: (1) diamond, (2) graphite, and (3) buckyball. sp^3 hybrid orbitals consist of one s orbital electron and three p orbital electrons. sp^2 hybrid orbitals consist of one s orbital electron and two p orbital electrons.

Review Questions

1. Carbon is considered to be unique in the periodic table. What property of the carbon atom makes it unique? **(Intermediate)**

2. What is the difference between sp, sp^2, and sp^3 hybridization? **(Intermediate)**

3. Which of the following are allotropes of carbon? **(Intermediate)**

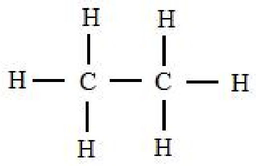
(a) diamond

(b) buckminsterfullerene

(c) graphite

(d) all of the above

4. The type of bonding in the carbon bonds of ethane (below) are: **(Intermediate)**



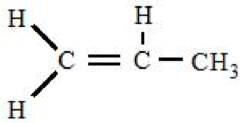
(a) sp

(b) sp^2

(c) sp^3

(d) dsp^3

5. The type of bonding in the first two carbon bonds of 1-propene (below) are: **(Intermediate)**



(a) sp

(b) sp^2

(c) sp^3

(d) dsp^3

6. The type of bonding in the first two carbon bonds of 1-propyne (below) are: **(Intermediate)**

$H - C \equiv C - CH_3$

(a) sp

(b) sp^2

(c) sp^3

(d) dsp^3

7. What characteristic is responsible for the lubrication property of graphite and buckyball? **(Intermediate)**

(a) localized electrons

(b) delocalized electrons

(c) large molecular weight

(d) carbon bonding

Further Reading / Supplemental Links

http://learner.org/resources/series61.html'"

The ***learner.org*** website allows users to view streaming videos of the Annenberg series of chemistry videos. You are required to register before you can watch the videos but there is no charge. The website has one video that relates to this lesson called ***Carbon*** .

Vocabulary

hybridization	The process of combining sublevels to create a new sublevel.
localized electrons	Electrons that are stationary (have fixed positions) between the bond.
delocalized electrons	Electrons that are free to move between the bond (in multiple bonding).

allotropes	Different forms of the same element based on their bonding.

Review Answers

1. Carbon has four bonding electrons that are capable of being localized or delocalized Carbon can therefore form strong single, double, and triple bonds with other carbon atoms in long chains, rings or chains with branches.

2. sp is a combination of one s and one p level electron. sp^2 is a combination of one s and two p level electrons. sp^3 is a combination of one s and three p level electrons.

3. (d) all of the above

4. (c) sp^3

5. (b) sp^2

6. (c) sp^3

7. (b) delocalized electrons

Hydrocarbons

Lesson Objectives

- Define alkanes as well as name and draw alkanes.
- Define alkenes as well as name and draw alkenes.
- Define alkynes as well as name and draw alkynes.
- Define structural formula.
- Define isomers and be able to draw isomers for alkanes, alkenes, and alkynes.
- Define substituted halogens as well as name and draw substituted halogens.

Introduction

In organic chemistry there are general categories of compounds that include alkanes ($C_n H_{2n+2}$), alkenes ($C_n H_{2n}$), alkynes ($C_n H_{2n-2}$), aromatics (those that contain benzene rings) and substituted halogens (or organic halides) (R - X, where X is a halogen and R is an alkyl group). There are other categories we will consider later on in this chapter including ketones, alcohols, aldehydes, ethers, carbohydrates, and proteins that are very interesting chemical compounds as well. For this section, we will focus on the alkanes, the alkenes, alkynes and the substituted halogens. The aromatics and the other special categories will be left for their own sections. During each of the sections, we will define, name compounds, draw structures, and look at isomers. All of these terms will be defined as we explore the wondrous world of organic compounds.

Alkanes

The simplest class of organic compounds is the compounds fitting into the class of alkanes. ***Alkanes*** are ***saturated*** compounds meaning that the carbon bonds are all involved in single bonding. Alkanes have a general formula of $C_n H_{2n+2}$. In the diagram below, methane has one (1) carbon atom, therefore n = 1.

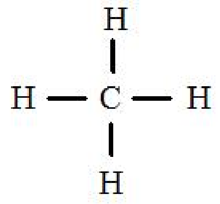


Figure 1: Methane

(*Created by*: Richard Parsons, *License*: CC-BY-SA)

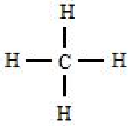
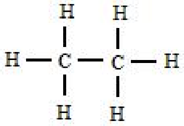
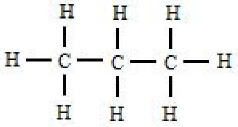
The number of hydrogen atoms would then be 2n + 2 or 2(1) + 2 or 4. In Figure 1, the number of hydrogen atoms is four (4).

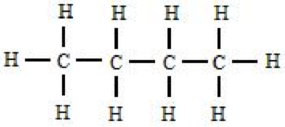
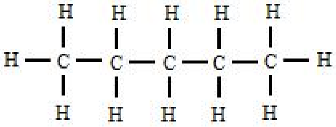
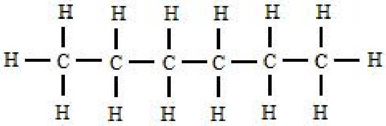
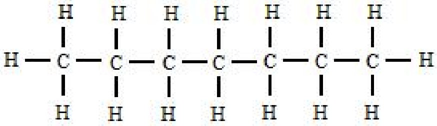
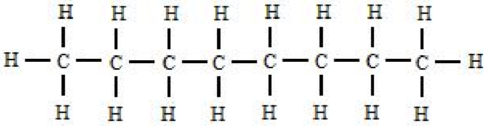
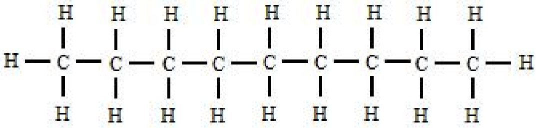
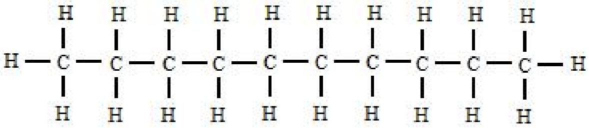
Alkanes can solids, liquids or gases depending on the number of carbon atoms. If there are between 1 and 4 carbon atoms, the alkane is a gas at room temperature. Between 5 and 16 carbon atoms, the alkane is a liquid and from 17 carbon atoms on, the alkane is a solid. Alkanes are all, however, non-polar. They are also insoluble in water but soluble in other non-polar organic liquids.

As far as reactivity, alkanes are able to be burned in combustion reactions, undergo reactions where their hydrogens are replaced by halogens, or, for larger molecules, you can break the alkanes into smaller alkanes. Alkanes have many uses, for example, crude petroleum (a mixture of C_5 to C_{18}) is used when making roads. You see them using this black sludgy material often if you see road or highway construction. However, this alkane can be broken into smaller alkanes. One of which has eight carbon atoms. This alkane is used as fuel for gasoline engines.

Carbon atoms are bonded together in straight or branched chains from very short to very long chains. The first ten alkanes are listed in Table 1. Column 1 of the table represents the name of the alkane. Column 2 represents the formula for the alkane. Notice the number of carbon atoms increases by one going down each row of the table. Column 3 represents the structural formula. The ***structural formula*** is the formula showing how the atoms are arranged in the molecule.

Table 1: First Ten Alkanes

Name	Formula	Structural Formula
methane	CH_4	
ethane	C_2H_6	
propane	C_3H_8	

butane	C_4H_{10}	
pentane	C_5H_{12}	
hexane	C_6H_{14}	
heptane	C_7H_{16}	
octane	C_8H_{18}	
nonane	C_9H_{20}	
decane	$C_{10}H_{22}$	

(*Created by*: Richard Parsons, *License*: CC-BY-SA)

When working with organic compounds, there is a need to know how to both name and draw these compounds.

Naming Alkanes

In order to name organic compounds such as alkanes, there are a number of rules to both the naming and the drawing of alkanes. First let's explore the procedures for naming alkanes.

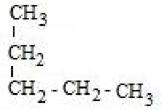
Sample Question 1: Name the following molecule

$CH_3 - CH_2 - CH_2 - CH_2 - CH_3$

Solution:

This is a straight chain hydrocarbon with all single bonds. Therefore, it is an alkane. Since the longest straight chain contains 5 carbon atoms, it is pentane.

You should recognize that the actual molecule does not look like this straight chain picture. The bonding around every carbon atom is a tetrahedron. Therefore, these molecules look more like saw teeth than they do straight chains. They are drawn in straight lines to make it easier to draw them. If the same molecule is drawn with a bend in it, it is still a straight chain (see below).



$$\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CH_2-CH_2-CH_3 \end{array}$$

This molecule is still a 5-carbon straight chain and is still pentane.

Various side chains of carbon atoms can be attached to the straight chain. When a hydrocarbon side chain is attached to the straight chain, the side chain is named according to the following table.

Table 2: Alkyl Groups Branches

Alkyl Groups	Group Name
$-CH_3$	methyl
$-CH_2CH_3$	ethyl
$-CH_2\ CH_2CH_3$	propyl
$-CH_2\ CH_2CH_2CH_3$	butyl
$-CH_2CH_2CH_2CH_2CH_3$	pentyl

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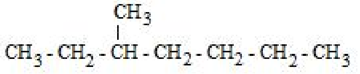
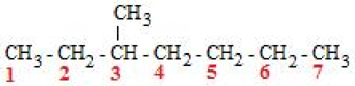
A side chain can be attached to any carbon in the straight chain except one of the end carbons. If the chain were attached to an end carbon, it would be part of the straight chain. Here is a straight chain hydrocarbon with a methyl side chain attached.

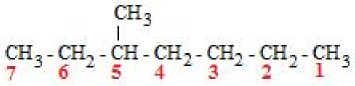


$$CH_3-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_2-CH_2-CH_2-CH_3$$

When naming this compound, we must identify both the parent straight chain and the side chain **AND** we must indicate the carbon atom to which the side chain is attached. In order to identify the carbon atom to which the side chain is attached, we number the carbon atoms in the parent straight chain. Since it is possible to begin numbering at either end of the straight chain, there is a rule about how the carbon atoms are numbered. The rule is that you must number the carbon atoms in the straight chain so that the number of the carbon atom to which the side chain is attached will be the **lowest** possible number. Here is the compound again with two possible numbering sequences.



$$\underset{1}{CH_3}-\underset{2}{CH_2}-\underset{3}{\overset{\overset{CH_3}{|}}{CH}}-\underset{4}{CH_2}-\underset{5}{CH_2}-\underset{6}{CH_2}-\underset{7}{CH_3}$$



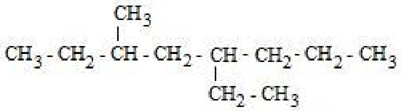
$$\underset{7}{CH_3}-\underset{6}{CH_2}-\underset{5}{\overset{\overset{CH_3}{|}}{CH}}-\underset{4}{CH_2}-\underset{3}{CH_2}-\underset{2}{CH_2}-\underset{1}{CH_3}$$

In the numbering on the left, the side chain is attached to carbon number 3, whereas on the right, the side chain is attached to carbon number 5. Therefore, the numbering sequence on the right is **WRONG**. You are required to number the carbon atoms to give the side chain or chains, the lowest possible numbers.

To name this compound, we indicate the number of the carbon atom to which the side chain is attached, insert a hyphen after the number (no spaces in between), then name the side chain (again no spaces), and finally name the parent straight chain (again no spaces). Therefore, the correct name of this compound is **3-methylheptane**.

Note, if two or more branches are present, prefixes such as di- and tri-, etc will be used. If two or more different alkyl groups are used as branches, the alkyl groups will be listed alphabetically.

Sample question 2: Name the following molecule

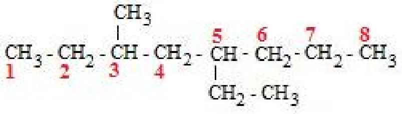


$$CH_3-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_2-\underset{\underset{\displaystyle CH_2-CH_3}{|}}{CH}-CH_2-CH_2-CH_3$$

Step 1: Find the parent chain.

The longest chain in this molecules contains 8 carbon atoms. Therefore, the parent chain is **octane**.

Step 2: Name the branches and determine the carbon numbers to which they are attached. Looking at the molecule, there are two branches that are not part of the parent chain. Using Table 2, these branches can be identified as a methyl group and an ethyl group.



$$\underset{1}{CH_3}-\underset{2}{CH_2}-\underset{3}{\overset{\overset{\displaystyle CH_3}{|}}{CH}}-\underset{4}{CH_2}-\underset{\underset{\displaystyle CH_2-CH_3}{|}}{\overset{5}{CH}}-\overset{6}{CH_2}-\overset{7}{CH_2}-\overset{8}{CH_3}$$

These branches are located as a methyl group on C_3 and an ethyl group on C_5.

Step 3: Add the name of the branches and their positions to the parent chain name.

5-ethyl-3-methyloctane

Notice there are no spaces anywhere in the name. The sequence of adding the side chain names is determined by adding them alphabetically. "e" in ethyl occurs in the alphabet before "m" in methyl.

Drawing Alkanes

To draw structures of alkanes, consider following the steps below.

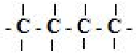
Sample question 3: Draw the structure for butane, C_4H_{10}.

Solution

Step 1: Start by drawing the four (4) carbon atoms in a straight chain with all carbon atoms bonded singularly.

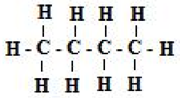
- C - C - C - C -

Step 2: Add a single bond to all remaining spaces on the carbon atom such that each carbon atom has four possible bonding sites.



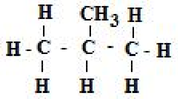
$$-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-$$

Step 3: Add one hydrogen atom to the end of each of the single bonds formed in Step 2.



Butane

There are other possible ways in which C_4H_{10} could be arranged, other than the straight chain. What could happen is that the molecule could have one carbon atom as a branch. Look at the diagram below. Notice how, in this structure, there are still four carbons and 10 hydrogens but the longest chain is only three carbon atoms. When this happens, we say the structures are structural isomers. ***Structural isomers*** are molecules that have the same formula but different arrangements of bonded atoms.

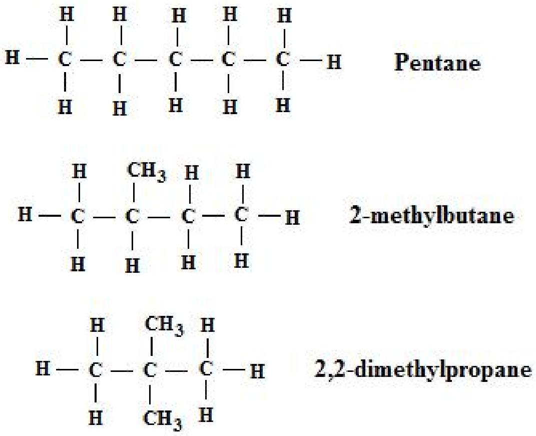


2-methylpropane

Structural isomers have the same formula, but because they have different structures they have different properties. When drawing structural isomers, as the number of carbon atoms increases, the number of isomers increases. According to Chang (2007), for a compound such as decane there are 75 isomers each with their own properties. A compound such as $C_{30}H_{62}$ has 4×10^8 isomers, each having their own possible properties (some not even isolated yet!). With this many possible compounds, you can see why carbon compounds number far more than any other element in the periodic table.

Sample question: Draw the structural isomers for pentane, C_5H_{12}.

Solution:



Alkenes

Alkenes are another group of straight chain hydrocarbons. **Alkenes** differ from alkanes in that while alkanes have all single bonds, alkenes have at least one double bond between adjacent carbon atoms. Due to this multiple bond, the alkenes are in a group of organic compounds known as ***unsaturated*** compounds. Unsaturated compounds are much more reactive than their saturated alkane counterparts.

The general formula for all alkenes with one double bond is C_nH_{2n}. The smallest alkene is ethene. There is no "methene" because in order to have a double bond between carbon atoms, you must have at least two carbon atoms. In Figure 1, ethene has two carbon atoms (n = 2). Therefore it will have 2 × 2 = 4 hydrogen atoms (or 2n hydrogen atoms).

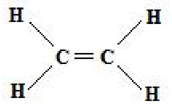


Figure 1: Ethene

In naming alkenes, the suffix is the same as in alkanes (see table 3).

Table 3: Numerical Prefixes for Straight Chain Organic Compounds

Number of C atoms in the longest chain	Numerical Prefix
1	meth-
2	eth-
3	prop-
4	but-
5	pent-
6	hex-
7	hept-
8	oct-
9	non-
10	dec-

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But in the case of alkenes, the suffix becomes -ene instead of -ane. For alkenes other than ethene, propene, and butene, you must also locate the position of the double bond since there is more than one position where the double bond could be located.

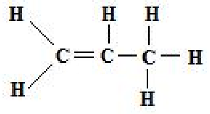


Figure 2: 1-propene

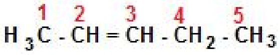
Naming Alkenes

Naming alkenes follows the same rules as with alkanes except that the position of the double bond must be indicated in the name of the molecule.

Sample question 4: Name the following compound.

$H_3C - CH = CH - CH_2 - CH_3$

Solution:



$$\overset{1}{H_3C} - \overset{2}{CH} = \overset{3}{CH} - \overset{4}{CH_2} - \overset{5}{CH_3}$$

The parent chain has five (5) carbon atoms and therefore using Table 3, the prefix is *pent-*.

There are no branches but the double bond is between C_2 and C_3. Therefore the name of the molecule is

2-pentene (using the smaller of the two numbers on the carbon atoms).

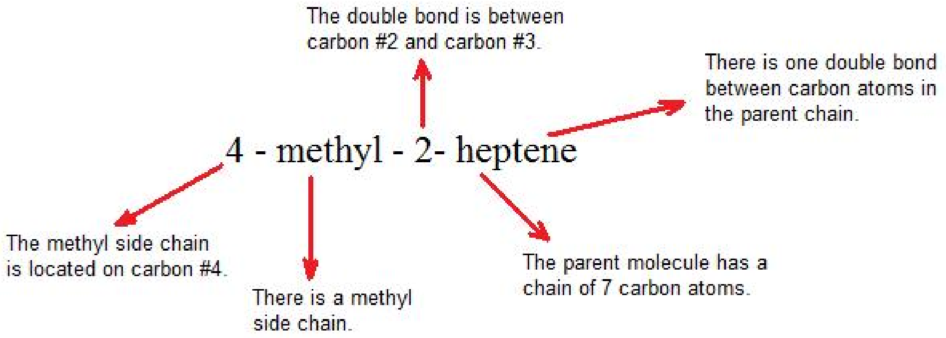
Drawing Alkenes

Drawing alkenes also follows the same rules as the alkanes. Remember to place the double bond where the name indicated its placement.

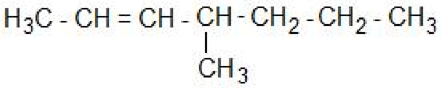
Sample question 5: Draw the structural formula for 4 – methyl – 2 – heptene.

Solution

Looking at the name reveals a great deal about how to draw the structure.



Therefore the molecule has the structure:

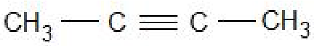


$$H_3C - CH = CH - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_2 - CH_2 - CH_3$$

When numbering alkene chains, you always begin with the carbon end nearest to the double bond regardless of what this does to the side chain number.

Alkynes

Alkynes also belong to the group of ***unsaturated*** organic compounds. ***Alkynes*** are organic compounds containing carbon and hydrogen and at least one triple bond. These compounds have the general formula C_nH_{2n-2}. In Figure 4, the structure for 2-butyne shows that there are four (4) carbon atoms (n = 4). Therefore there are (2 × 4) - 2 = 6 hydrogen atoms (or 2n - 2 hydrogen atoms).



$$CH_3 - C \equiv C - CH_3$$

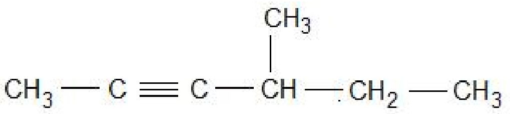
Figure 4: 2-butyne

The alkynes use the same prefixes as the other straight chain groups and the suffix -yne.

Naming Alkynes

All alkyne structures have the ending *–yne* in the name of the structural formula. In order to name alkynes, the same rules apply as were applied for alkanes and alkenes. For these compounds, the position of the triple bond is indicated in the name of the structure.

Sample question 6: Name the following structure.



$$CH_3 - C \equiv C - \overset{\overset{CH_3}{|}}{CH} - CH_2 - CH_3$$

Solution:

→ The parent chain has six (6) carbon atoms and therefore using Table 3, the prefix is *hex-*.

→ There is a triple bond, so the suffix is -yne.

→ The triple bond is between C_2 and C_3.

→ There is one branch on C_4 that is a methyl group.

Therefore the name of the molecule is ***4-methyl-2-hexyne*** (again using the smaller of the two numbers on the carbon atoms).

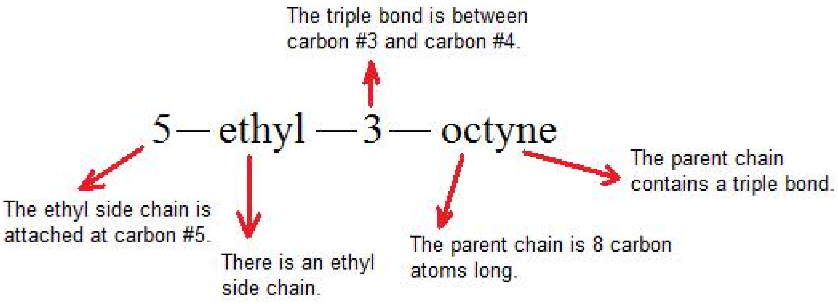
Drawing Alkynes

To draw alkynes, again follow the same rules as for alkanes and alkenes. Remember to place the triple bond where the name indicated its placement.

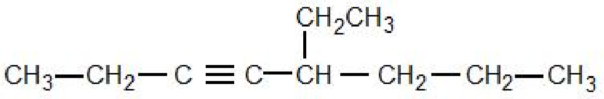
Sample question 7: Draw the structural formula for 5 – ethyl – 3 – octyne.

Solution

Looking at the name reveals a great deal about how to draw the structure.



Therefore the molecule has the structure:



$CH_3-CH_2-C\equiv C-\overset{CH_2CH_3}{\overset{|}{CH}}-CH_2-CH_2-CH_3$

Substituted Halogens

The Definition of Substituted Halogens

Substituted halogens (or alkyl halides) are another class of organic compounds that should be considered in an introduction to organic chemistry. Substituted halogen compounds involved substituting one or more halogen atoms for hydrogen atoms in alkanes, alkenes, and alkynes. These compounds play a role in fire fighting and as a propellant for medicines such as inhalers for asthma suffers.

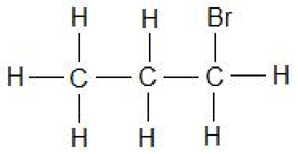
Naming Hydrocarbons With Substituted Halogens

When naming substituted halogen compounds, the rules for naming remain the same as before but now the branch name changes. Table 4 shows the branch names for the halogens in organic compounds.

Table 4: Halogen Group Substituted

Halogen	Prefix
F	fluoro-
Cl	chloro-
Br	bromo-
I	iodo-

Sample question 8: Name the following structure.



Solution :

→ The parent chain has three (3) carbon atoms and all single bonds and therefore using Table 1, the name of parent chain is propane.

→ There is one halogen on C_1 that is a bromo group.

Therefore the name of the molecule is ***1-bromopropane***

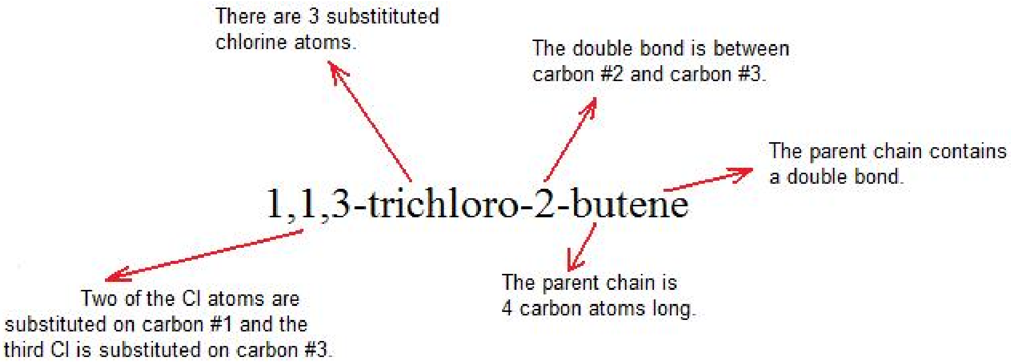
Drawing Hydrocarbons With Substituted Halogens

When drawing substituted halogen compounds, the rules for drawing remain the same as before but the substituted name changes. Using Table 4 from above and the rules for drawing we have learned already, we can draw structures for the substituted halogens.

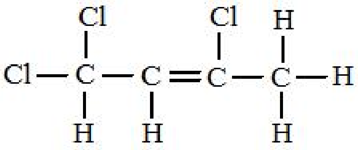
Sample question 9: Draw the structural formula for 1,1,3-trichloro – 2 - butene.

Solution

Looking at the name reveals a great deal about how to draw the structure.



Therefore the molecule has the structure:



$$\begin{array}{ccccccccc} & & \mathrm{Cl} & & & & \mathrm{Cl} & & \mathrm{H} \\ & & | & & & & | & & | \\ \mathrm{Cl} & - & \mathrm{C} & - & \mathrm{C} & = & \mathrm{C} & - & \mathrm{C} - \mathrm{H} \\ & & | & & | & & & & | \\ & & \mathrm{H} & & \mathrm{H} & & & & \mathrm{H} \end{array}$$

Lesson Summary

- Alkanes are saturated compounds meaning that the carbon bonds are all involved in single bonding. Alkanes have a general formula of C_nH_{2n+2}.
- The structural formula is the formula showing how the bonded atoms are arranged in the molecule.
- Structural isomers are molecules that have the same formula but different structures.
- Alkenes are compounds containing hydrogen and carbon but contain at least one double bonded carbon atom. Due to this multiple bond, the alkenes are in a group of organic compounds known as unsaturated compounds. Alkenes have a general formula of C_nH_{2n}.
- Alkynes are organic compounds containing carbon and hydrogen and at least one triple bond. Alkynes have a general formula of C_nH_{2n-2}.
- Substituted halogens are organic compounds where one or more of the branches are a halogen.

Review Questions

1. Define the terms alkane, alkene and alkyne. **(Beginning)**

2. What is the difference between a saturated and an unsaturated compound? **(Beginning)**

3. What is the structural formula of a compound? **(Beginning)**

4. (1) Which of the following organic compounds is unsaturated? **(Intermediate)**

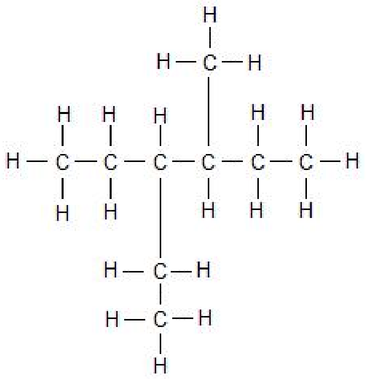
(a) ethylcyclobutane

(b) 3-ethyl-2-methyl-1-pentene

(c) 2-bromobutane

(d) 2-methyl-1-chlorohexane

5. What is the name of the compound having the following structural formula? **(Intermediate)**



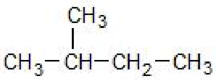
(a) 3-ethyl-4-methylhexane

(b) 4-methyl-3-ethylhexane

(c) 4-ethyl-3-methylhexane

(d) 3-methyl-4-ethylhexene

6. Which compound is a structural isomer of the compound shown below? **(Intermediate)**



$$CH_3-\overset{\overset{\large CH_3}{|}}{C}H-CH_2-CH_3$$

(a) butane

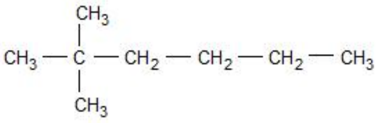
(b) methane

(c) pentane

(d) hexane

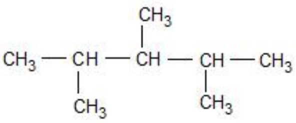
7. Which structures are isomers of the other structures? **(Intermediate)**

I.



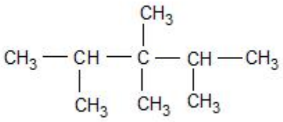
$$CH_3-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-CH_2-CH_2-CH_2-CH_3$$

II.



$$CH_3-\underset{\underset{\large CH_3}{|}}{C}H-\overset{\overset{\large CH_3}{|}}{C}H-\underset{\underset{\large CH_3}{|}}{C}H-CH_3$$

III.



$$CH_3-\underset{\underset{\large CH_3}{|}}{C}H-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-\underset{\underset{\large CH_3}{|}}{C}H-CH_3$$

IV.

$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$

(a) I, II, III

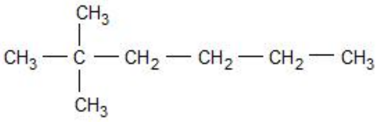
(b) II, III

(c) I, II, IV

(d) They are all isomers.

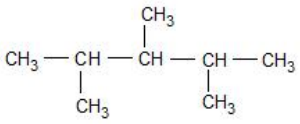
8. Which of the following structures has the shortest parent chain? **(Intermediate)**

I.



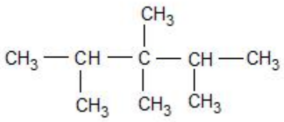
$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-CH_2-CH_2-CH_3$

II.



$CH_3-\underset{CH_3}{CH}-\overset{CH_3}{CH}-\underset{CH_3}{CH}-CH_3$

III.



$CH_3-\underset{CH_3}{CH}-\overset{CH_3}{\underset{CH_3}{C}}-\underset{CH_3}{CH}-CH_3$

IV. $CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$

9. Draw each of the following compounds. **(Intermediate)**

a. 2,3,4-trimethylpentane

b. 2-chloro-1-propene

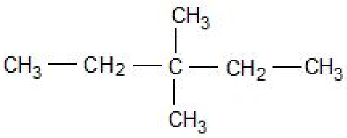
c. 1-bromo-2-methylbutane

d. Ethyne

e. 1-bromo-5,5-dimethylheptane

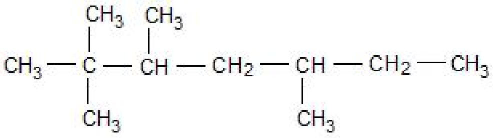
10. Name each of the following structures. **(Intermediate)**

a.



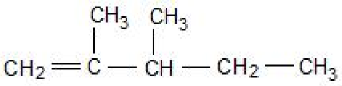
$CH_3-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-CH_3$

b.



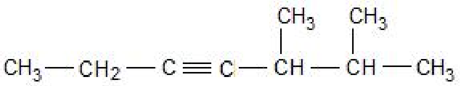
$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}-CH_2-CH_3$

c.



$CH_2=\overset{CH_3}{C}-\overset{CH_3}{CH}-CH_2-CH_3$

d.



$CH_3-CH_2-C\equiv C-\overset{CH_3}{CH}-\overset{CH_3}{CH}-CH_3$

11. Name the isomers for C_6H_{14}. **(Intermediate)**

Further Reading / Supplemental Links

http://en.wikipedia.org

Vocabulary

alkanes	Compounds containing carbon and hydrogen where the carbon bonds are all involved in single bonding.
saturated compound	Organic compound containing all single bonds.
structural formula	The formula showing how the bonded atoms are arranged in the molecule.
structural isomers	Molecules that have the same molecular formula but different structures.
alkenes	Organic compounds containing hydrogen and carbon but contain at least one double bonded carbon atom.
unsaturated compound	Organic compound that contain multiple bonding.
alkynes	Organic compounds containing carbon and hydrogen and at least one triple bond.
substituted halogens	organic compounds where one or more of the branches are a halogen.

Review Answers

1. Alkanes are saturated compounds meaning that the carbon bonds are all involved in single bonding. Alkanes have a general formula of C_nH_{2n+2}.

Alkenes are compounds containing hydrogen and carbon but contain at least one double bonded carbon atom. Alkenes have a general formula of C_nH_{2n}.

Alkynes are organic compounds containing carbon and hydrogen and at least one triple bond. Alkynes have a general formula of C_nH_{2n-2}.

2. Saturated compounds are those that contain only single bonds whereas unsaturated compounds contain double and triple bonds.

3. The structural formula is the formula showing all of the atoms in the molecule and how the bonded atoms are arranged in the molecule.

4. (b) 3-ethyl-2-methyl-1-pentene

5. (a) 3-ethyl-4-methylhexane

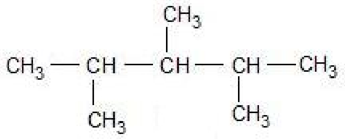
6. (c) pentane

7. (c) I, II, IV

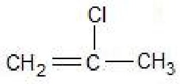
8. (b) II, III

9.

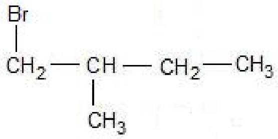
a.


$CH_3-CH(CH_3)-CH(CH_3)-CH(CH_3)-CH_3$

b.


$CH_2=C(Cl)-CH_3$

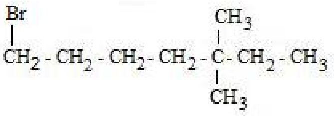
c.


$CH_2(Br)-CH(CH_3)-CH_2-CH_3$

d.

$H-C\equiv C-H$

e.


$CH_2(Br)-CH_2-CH_2-CH_2-C(CH_3)_2-CH_2-CH_3$

10.

a.) 3,3-dimethylpentane

b.) 2,2,3,5-tetramethylheptane

c.) 2,3-dimethyl-1-pentene

d.) 5,6-dimethyl-3-heptyne

11.

Hexane 2-methylpentane 3-methylpentane 2,2-dimethylbutane 2,3-dimethylbutane

Aromatics

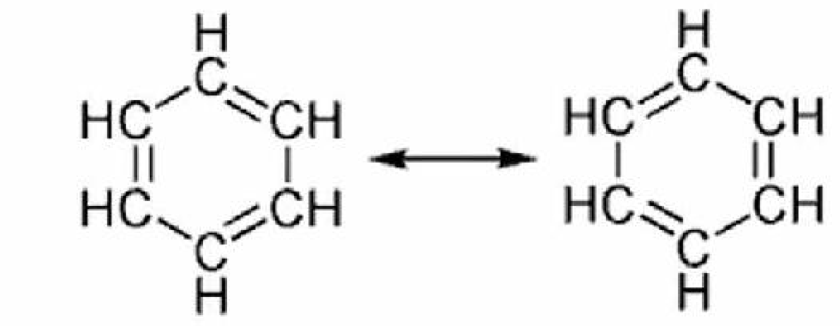
Lesson Objectives

- Describe the bonding in benzene.
- Define aromaticity.

- Name simple compounds containing benzene.
- Draw simple compounds containing benzene.

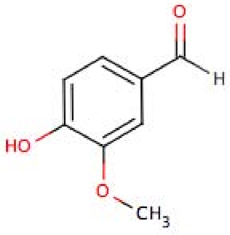
Introduction

Another category of organic compounds, and quite a large category at that, is one known as the aromatics. In each of these compounds, the common building block of the molecule is the benzene ring structure (see diagram below).

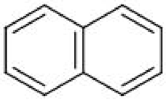


Benzene, itself was discovered in the 1820's by Michael Faraday but it took more than 40 years for the actual structure seen in the diagram above to be determined. Friedrich August Kekulé in 1865 made this amazing discovery. The legend is told that Kekulé had a dream of snakes biting the ends of their tails and from this dream he awoke with the benzene structure.

Identification as an aromatic doesn't mean that all of these have a pleasant smell even though many of them do. Vanilla, for example, is a compound made with a benzene ring as its center and has a pleasant odor. Many unpleasant odors as well have benzene rings as their centers; moth balls (naphthalene) is an example of a compound with a very unpleasant smell. In short, aromaticity has to do with structure and not smell. We shall explore this in the lesson that follows.



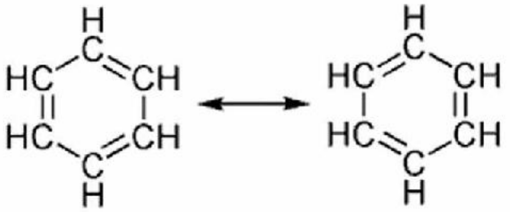
Vanilla



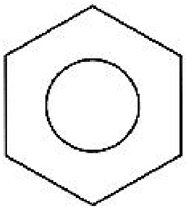
Naphthalene

Bonding and Resonance Structures for Benzene

As indicated in the introduction, there are two possible structures of the benzene molecule (C_6H_6).



Both of these structures represent resonance structures of the benzene molecule. Linus Pauling, (who received the Nobel Prize in Chemistry in 1954 but didn't receive a high school diploma until 1962) proposed the theory of ***resonance*** to explain molecules such as benzene. For example, although the structure shows alternating double and single bonds, all of the bonds have been shown to be the same length. Carbon-carbon single bonds are 154 pm long; carbon-carbon double bonds are 134 pm in length; but all of the carbon-carbon bonds in benzene are the same length: 139 pm, they are neither single nor double bonds. These can be referred to as *hybrid* structures and are often referred to as 1.5 bonds. As a less cumbersome way to write a benzene structure, it can be written as follows:

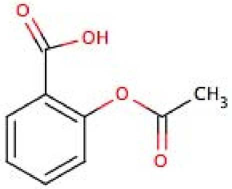


The term **resonance** is unfortunate since it implies that there is some kind of vibrating between the double and single bonds. However this is not what is occurring. Electrons are not moving between carbon atoms. Resonance is a means to represent a molecule that only one Lewis structure does not adequately describe.

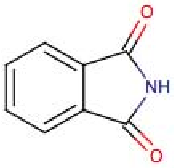
Benzene

The term ***aromatic*** means that a compound contains one or more benzene rings. A ***benzene ring*** is a structure that contains a ring represented by equivalent resonance structures. Benzene is an important compound in organic chemistry because of its properties and the vast number of compounds in which a benzene ring is an integral part of the structure.

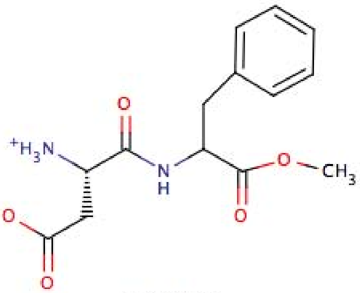
Aromatic compounds are only slightly water-soluble and most are carcinogenic depending on exposure concentration and time. Benzene is a part of many compounds that are in our everyday lives. Aspirin is a common painkiller; saccharin is an artificial sweetener as is aspartame. Aspartame is commonly used in soft drinks and diet drinks. In each of these structures, the benzene ring is an integral part of the structure.



Aspirin



Saccharin



Aspartame

As the building block of this category of organic compounds, some discussion should be made on the naming and drawing of molecules containing benzene. In this discussion, we will use the hybrid model above to represent the benzene structure.

Naming Benzene Structures

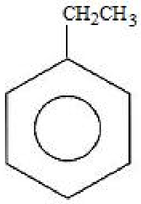
All of the carbon atoms in the benzene ring have one hydrogen atom attached. If we were to replace one of these hydrogens with a branch from Table 1 below, the naming is simply the name of the branch plus *benzene.*

Table 1: Branches

Group	Name
$-CH_3$	methyl

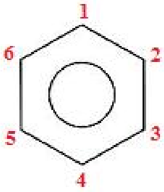
$-CH_2CH_3$	ethyl
-F	fluoro
-Cl	chloro
-Br	bromo
-I	iodo
$-NO_2$	nitro

Sample question 1: Name the following structure.



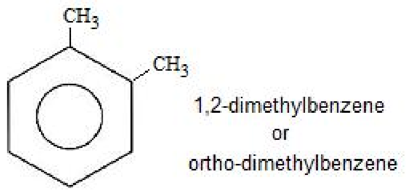
Solution: ethylbenzene

When there is more than one substituent on the benzene ring, then there has to be a way to determine the position of each branch. We number the carbon atoms the same as we had done for the alkanes, alkenes, and alkynes.



By numbering, we have a way to methodically determine the location of each branch on the benzene ring.

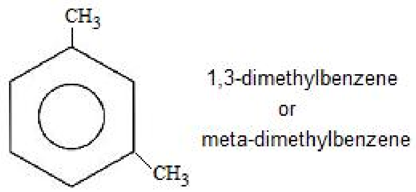
The branches are both methyl groups The locations of the methyl groups are on C_1 and C_2 The name of the molecule is **1,2-dimethylbenzene**

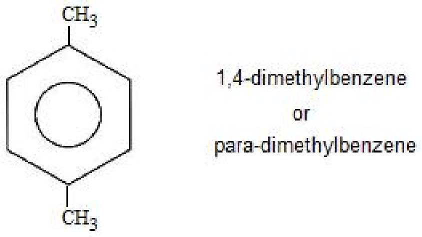


An alternate naming system is given for molecules with two substituent groups or when the benzene ring has two branches. Alternate names are provided in Table 2.

Table 2: Alternate Naming System for Disubstituted Benzene

Location of branches	prefix	Prefix symbol
C_1 and C_2	ortho-	o-
C_1 and C_3	meta-	m-
C_1 and C_4	para-	p-





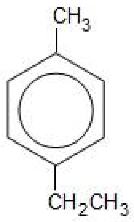
The prefix "ortho" indicates the two substituents are on adjacent carbon atoms. The prefix "meta" indicates the two substituents are on carbon atoms with one carbon atom skipped between them. The prefix "para" indicates the two substituents are on opposite carbon atoms.

1,2-dimethylbenzene could also be named ortho-dimethylbenzene

1,3-dimethylbenzene could also be named meta-dimethylbenzene

1,4-dimethylbenzene could also be named para-dimethylbenzene

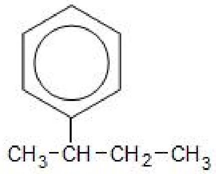
Sample question 2: Name the following structure.



Solution:

The branches are one methyl group and one ethyl group The locations of the methyl groups are on C_1 and C_4 The name of the molecule is **1-ethyl-4-methylbenzene** or , according to Table 2, **p-ethylmethylbenzene**

If you notice in Table 1, the number of alkyl groups present as branches is more limited than is found in the naming of alkanes, alkenes, and alkynes. When the alkyl group becomes larger than an ethyl group, the benzene ring is then considered the branch and the alkyl group is considered the parent chain. As a branch, benzene is known as a *phenyl* group.



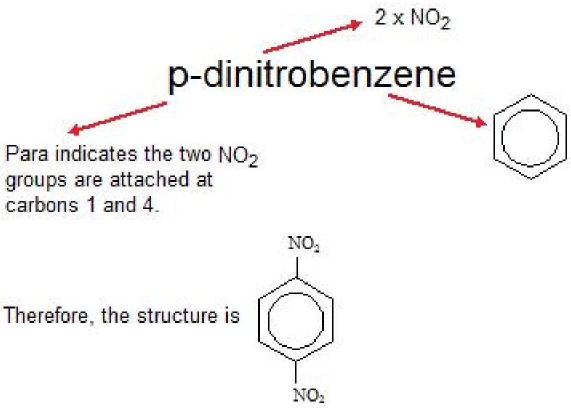
This molecule would be named **2-phenylbutane**. Butane is the parent chain and the benzene ring is a side chain. When benzene is a substituent, it is called phenyl.

Drawing Benzene Structures

Drawing benzene structures works the same as drawing alkanes, alkenes, and alkynes. Consider the following example.

Sample question 6: Draw the structure of p-dinitrobenzene.

Solution:



Lesson Summary

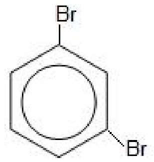
- The term aromatic means that a compound contains one or more benzene rings. A benzene ring is an organic structure that contains a 6-carbon ring with alternating double bonds.
- Resonance means to have two of more equivalent Lewis diagrams representing a particular model.
- The electrons in the pi bonds of the benzene molecule are delocalized because they are not confined to a particular pair of carbon atoms. As a substituent of a hydrocarbon chain, benzene is known as a *phenyl* group.

Review Questions

1. Define aromaticity. **(Beginning)**

2. When is the benzene ring referred to as a phenyl group? **(Intermediate)**

3. Name the following structure. **(Intermediate)**



(a) dibromocyclohexene

(b) 1,3-dibromocyclohexatriene

(c) 1,3-dibromobenzene

(d) 2,4-dibromobenzene

4. Which formula represents an aromatic compound? **(Intermediate)**

(a) C_2H_2

(b) C_6H_6

(c) C_6H_8

(d) C_6H_{14}

5. How many different possible structures of trichlorobenzene exist? **(Intermediate)**

(a) 1

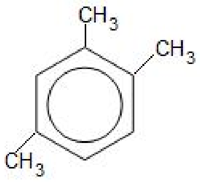
(b) 2

(c) 3

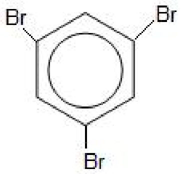
(d) 4

6. Name the following structures. **(Intermediate)**

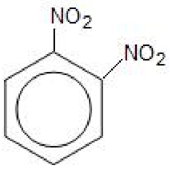
(a)



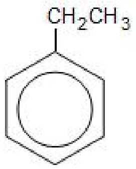
(b)



(c)



(d)



7. Draw the following structures. **(Intermediate)**

(a) fluorobenzene

(b) p-diethylbenzene

(c) 3-phenylhexane

(d) 2-methyl-1,4-diethylbenzene

Further Reading / Supplemental Links

Chemistry and Chemical Reactivity, Kotz, Truchel, Weaver; Thompson, 2006.

http://en.wikipedia.org

Vocabulary

aromatic	A compound contains one or more benzene rings.
benzene ring	Equivalent resonance structures representing a 6-carbon ring with alternating C-C double bonds.
hybrid	A species with properties in-between the properties of the parents.
resonance	To have two of more equivalent Lewis diagrams representing a particular model.

Review Answers

1. In chemistry, aromaticity is defined as an unsaturated compound containing at least one benzene ring.

2. When there are more than two carbon atoms in the alkyl branch attached to a benzene ring, the alkane becomes the parent chain, and the benzene ring becomes the branch and is called a phenyl group.

3. (c) 1,3-dibromobenzene

4. (b) C_6H_6

5. (c) 3

6. (a) 1, 2, 5 – trimethylbenzene

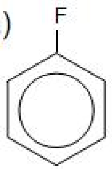
(b) 1,3,5- tribromobenzene

(c) m-dinitobenzene

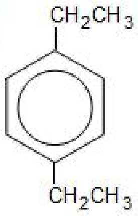
(d) ethylbenzene

7.

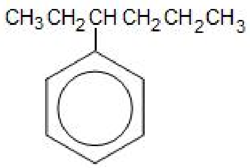
(a)



(b)



(c)



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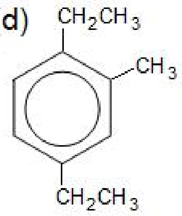


Functional Groups

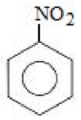
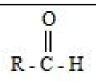
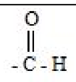
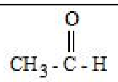
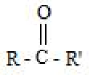
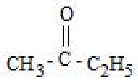
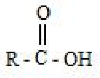
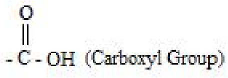
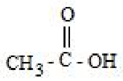
Lesson Objectives

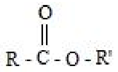
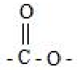
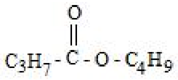
- Identify alcohols, aldehydes, ketones, ethers, organic acids, and esters based on their functional groups.
- Name and draw simple alcohols, aldehydes, ketones, ethers, organic acids, and esters.

Introduction

After the introduction to the building blocks of organic chemistry, we move into other categories of organic compounds that have a distinguishing functional group that makes them unique. In this lesson, six of these categories will be studied in terms of their functional groups to learn how to identify compounds based on these functional groups. In the table below are the categories we have studied thus far and ones we will study in this lesson. Table 1 lists the general formula and the functional groups for the alkanes, the alkenes, the alkynes, and the substituted halogens along with the aromatics. As well you will see the six new categories we are about to learn in this lesson: the alcohols, aldehydes and ketones, ethers, organic acids, and esters. An example from each category is also provided.

Table 1: Summary of the Categories of Organic Compounds

Category	**General Formula**	**Distinguishing Feature**	**Example Formula**	**Name**
Alkane	C_nH_{2n+2}	All single C-C bonds	$CH_3CH_2CH_3$	propane
Alkenes	C_nH_{2n}	One C=C bonds	$CH_2 = CH_2$	Ethene
Alkynes	C_nH_{2n-2}	One C=C bond	HC=CH	Ethyne
Aromatic	NA	Benzene ring part of structure, Benzene-like structure		Nitrobenzene (floor polish)
Substituted Halogens	R-X	One or more of halogens attached to organic compound	CH_2FCl	Chlorofluoromethane (Freon)
Alcohol	R-OH	Hydroxyl group	CH_3CH_2-OH	Ethanol
Ether	R-O-R'	C-O-C	CH_3-O-C_2H_5	Methyl ethyl ether
Aldehydes	 $\mathrm{R-\overset{\overset{O}{\|}}{C}-H}$	 $\mathrm{-\overset{\overset{O}{\|}}{C}-H}$	 $\mathrm{CH_3-\overset{\overset{O}{\|}}{C}-H}$	Ethanal
Ketone	 $\mathrm{R-\overset{\overset{O}{\|}}{C}-R'}$	 $\mathrm{-\overset{\overset{O}{\|}}{C}-}$ (Carbonyl Group)	 $\mathrm{CH_3-\overset{\overset{O}{\|}}{C}-C_2H_5}$	Butanone
Organic Acids	 $\mathrm{R-\overset{\overset{O}{\|}}{C}-OH}$	 $\mathrm{-\overset{\overset{O}{\|}}{C}-OH}$ (Carboxyl Group)	 $\mathrm{CH_3-\overset{\overset{O}{\|}}{C}-OH}$	Ethanoic acid

Ester	 $R-\overset{\overset{O}{\|}}{C}-O-R'$	 $-\overset{\overset{O}{\|}}{C}-O-$	 $C_3H_7-\overset{\overset{O}{\|}}{C}-O-C_4H_9$	Butyl butyrate (pineapple)

Alcohols

Definition of an Alcohol

Alcohols have the same general formula as an alkane except they have the functional group -OH, called the hydroxyl group. The most common alcohol, known as ethanol, is used in alcoholic drinks, as a fuel (gasohol), in thermometers, as a preservative for biological specimens, and as a solvent for paints and drugs. Alcohols have interesting properties. In terms of their solubility in water, if the number of carbon atoms is low (C_3 or below) the alcohol is soluble in water. If, however, the number of carbon atoms increases, the solubility decreases accordingly. This is an interesting property particularly if you look at one example in the car industry. In today's search for more efficient fuels, alcohols such as methanol and ethanol have been tested as additives to gasoline in vehicles (gasohol). The alcohol additives increase the octane rating and decrease the CO emissions because of the high vapor pressure. This, of course is not a new idea, it was first proposed in the early 1900s. What is known today, however, is that vehicles experience problems such as vapor lock when using these additives. Figure 1 shows the structure for ethanol. Notice the hydroxyl group on the end of the two carbon chain.

$CH_3 - CH_2 - OH$

Figure 1: Ethanol

Butanol, an alcohol with four carbon atoms, is used in the cosmetic industry as well as having applications as paint thinner! There are four isomers of butanol. Figure 2 shows the four different isomers.

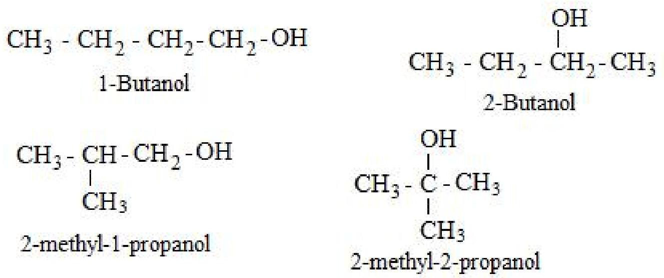


Figure 2: Isomers of Butanol

Naming Simple Alcohols

In naming alcohols, the suffix of the name is **-ol** added to the parent chain of the alkane name. The position of the -OH functional group is indicated in the name. Remember to start numbering the parent chain on the end closest to where the -OH is located.

Sample question 1: Name the following.

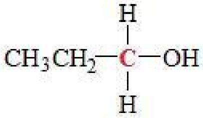
$CH_3 - CH_2 - CH_2 - OH$

Solution

The carbon chain contains 3 carbon atoms, there is an -OH group on the chain, and the -OH group is attached to an end carbon atom.

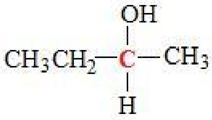
Therefore the molecule is **1-propanol.**

There are primary (1°), secondary (2°) and tertiary (3°) alcohols in the classification of alcohols. 1-propanol is a primary alcohol because the carbon atom with the hydroxyl group is also attached to only one alkyl group. In other words, if we isolate the C_1 of 1-propanol, it is attached to the OH, 2 hydrogen atoms and an ethyl group (see right).



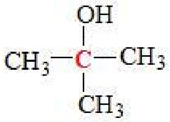
$$CH_3CH_2-\overset{\overset{\Large H}{|}}{\underset{\underset{\Large H}{|}}{C}}-OH$$

Primary Alcohol



$$CH_3CH_2-\overset{\overset{\Large OH}{|}}{\underset{\underset{\Large H}{|}}{C}}-CH_3$$

Secondary Alcohol



$$CH_3-\overset{\overset{\Large OH}{|}}{\underset{\underset{\Large CH_3}{|}}{C}}-CH_3$$

Tertiary Alcohol

1-propanol is a **(1° alcohol)**

An example of a secondary (2°) alcohol is 2-butanol. Notice in 2-butanol, the carbon atom to which the hydroxyl group is bonded is also bonded to a methyl group on the right and an ethyl group on the left.

2 - butanol is a **(2° alcohol)**

2-methyl-2-propanol is a tertiary (3°) alcohol. If you look at this structure, the carbon atom bonded to the hydroxyl group is also bonded to three methyl groups.

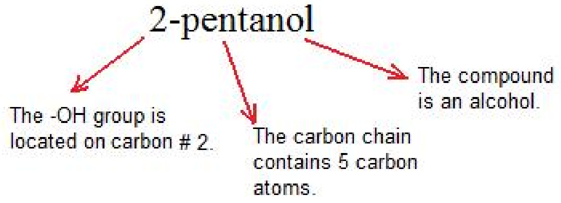
2 - methyl - 2 - propanol is a **(3° alcohol)**

Drawing Simple Alcohols

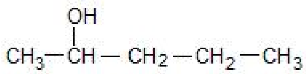
As with other organic compounds that have been named in this chapter, look at the name of the compound and analyze what the name has to tell about the structure of the compound.

Sample question 2: Draw the structure of **2 - pentanol**.

Solution:



Therefore, the structure is

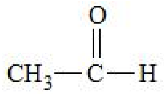


$$CH_3-\overset{\overset{\large OH}{|}}{CH}-CH_2-CH_2-CH_3$$

Aldehydes and Ketones

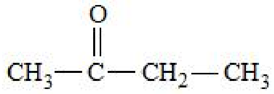
Definition of Aldehydes and Ketones

The aldehydes and ketones are the first categories in this organic chapter to contain what is known as the carbonyl group. A ***carbonyl group*** is a carbon atom double bonded to an oxygen atom (C = O) and the carbon is also bonded to two other atoms or groups. In an aldehyde, the carbonyl group is always on an **end carbon**. In a ketone, the carbonyl group is never on an end group. Aldehydes and ketones are very interesting groups and you may have had more contact with them than you think. Acetone, for example, is a ketone and is the main component in finger nail polish. Carvone is a ketone that is found in many naturally occurring products such the oils from mandarin oranges, dill seeds and spearmint. Carvone dates back to ancient Romans! Benzaldehyde is an aldehyde responsible for the baking ingredient almond extract. Look at the diagram below to see the carbonyl group in ethanal and 2-butanone (a ketone).



$CH_3-\overset{\overset{O}{\|}}{C}-H$

Ethanal



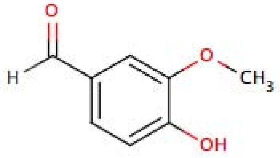
$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$

2 - butanone

Figure 3: Illustrations of Carbonyl Groups

Aldehydes

Aldehydes play an important role in our everyday lives. Those that have higher molecular masses are responsible for the very pleasant smells that you may have experienced when you clean your house. The smell of vanilla is responsible partially because of an aldehyde component in the structure (methoxybenzaldehyde).

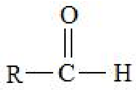


Vanilla
4-hydroxy-3-methoxybenzaldehyde

Of course, other aldehydes, such as formaldehyde, do not smell as nice. Formaldehyde is used as a preservative for organs and as an embalming fluid. Acetaldehyde is the oldest known aldehyde (more than 300 years old) and has its use in the preparation of ethanol.

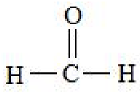
Naming and Drawing Aldehydes

In order to name aldehydes, use the parent chain name of the alkane and add the suffix *–al*. Remember that all aldehydes have the general formula shown below.



$R-\overset{\overset{O}{\|}}{C}-H$

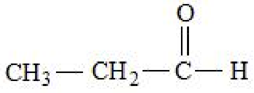
In the general formula above, R is a hydrogen atom or any alkyl group. The simplest aldehyde is methanal where R = H.



$H-\overset{\overset{O}{\|}}{C}-H$

Methanal

Sample question 3: Name the following structure.



$CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-H$

Solution:

The parent chain contains 3 carbon atoms and it has a carbonyl group on the end of the chain.

Therefore the name is **propanal.**

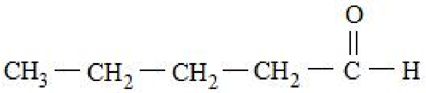
Sample question 4: Draw the structure of pentanal.

Solution:

Pentanal has the prefix *pent*- meaning it has five (5) carbon atoms.

Pentanal has the suffix –*al* meaning it has the aldehyde functional group

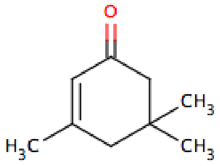
Therefore the structure is:



$CH_3-CH_2-CH_2-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-H$

Ketones

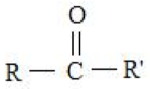
Ketones are equally as important as aldehydes in our daily lives. Ketones are present in the body when fat is broken down for energy. A buildup of ketones leads to ketoacidosis, a potentially dangerous condition. Ketones are also known to us in the form of pheromones. Pheromones are ketones that are released in the body that act as sensors or prompts that emit a response to another member of the same species. Pheromones are used extensively by insects to protect themselves, attract prey, and even for signaling other insects of the move to a new home (as in the case of some bee species). One example of a useful ketone is one that is used in paints. Isophorone or 3,5,5-trimethyl-2-cyclohene-1-one (its IUPAC name) is used in some paints to improve the flow and increase the glossiness. Isophorone has the structure shown below.



Isophorone

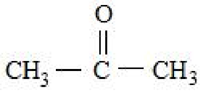
Naming and Drawing Ketones

In order to name compounds that are ketones, use the parent chain name of the alkane and add the suffix –one. For parent chains more than four carbon atoms, the position of the carbonyl group must be indicated. Remember that all ketones have the general formula shown below.



$R-\overset{\overset{\displaystyle O}{\|}}{C}-R'$

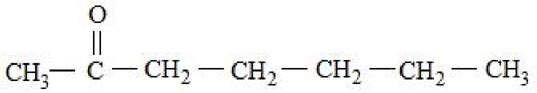
In the general formula above, R and R' are both alkyl groups and can be the same or different. The simplest ketone is propanone (acetone) where R and R'are both methyl groups. You may recognize acetone as one of the active ingredients in nail polish remover.



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3$$

Propanone (acetone)

Sample question 5: Name the following structure.



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_2-CH_2-CH_3$$

Solution:

There are alkyl groups attached on both sides of the carbonyl group, therefore the molecule is a ketone.

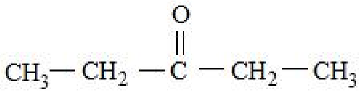
Therefore the name is **2-heptanone.**

Sample question 6: Draw the structure of 3-pentanone.

Solution:

The carbon chain will be 5 carbon atoms long and it will have a carbonyl group at carbon #3.

Therefore the structure is:



$$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$$

Ether

Ether was first publicly demonstrated as an anesthetic in 1846 at Massachusetts General Hospital. It was considered at the time to be a great breakthrough because it produced the ability for physicians to provide “painless” surgery. In old movies, you may remember seeing a villain come up behind an unsuspecting prey to put a cloth over their mouth and nose after a short time, the person falls fast asleep. Again, the cloth was supposed to give the observer the indication it was doused with ether to render the victim unconscious. Ether has other uses today, not used today as an anesthetic, but more often as a solvent for fats and oils. It is also used, sometimes, to anesthetize ticks before removing them from the skin. The harmful side effects and highly flammable nature of the compound makes its use less common today than in past eras.

But what exactly is an ether compound? All ether compounds have the general formula R - O - R', where R and R' are both alkyl groups. These alkyl groups can be the same or both different. The most common ether (like the one mentioned in paragraph one) is a compound also known as diethyl ether. It has the structure shown in Figure 3.

$CH_3 - CH_2 - O - CH_2 - CH_3$

Figure 4: Diethylether

In this structure the alkyl groups on either side of the oxygen atom are ethyl groups, hence the name diethyl ether.

In order to name ethers, one of two possibilities can be found. Ethers can be named by naming the alkyl groups on either side of the ether functional group, then adding the word *ether* on the end. The other possibility is to name the smaller alkyl group, add the suffix *–oxy*, and then giving the alkane name to the larger alkyl group. Remember to name the alkyl groups in alphabetical order.

Sample question 7: Draw the structure for ethyl methyl ether.

Solution:

The general structure is R - O - R'. Looking at the name of the structure we can determine what alkyl groups will be the R and the R'.

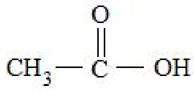
Let R = CH_3CH_2 and let R'= CH_3. Then draw the structure.

$CH_3 - CH_2 - O - CH_3$

Note this structure is also called methoxy ethane.

Organic Acid

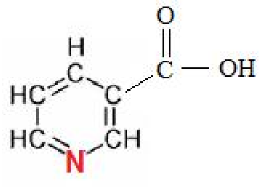
The organic acids (or carboxylic acids) contain the carboxyl group. A ***carboxyl group*** is a carbon atom double bonded to an oxygen atom (C = O) , a hydroxyl group (-OH) and also is bonded to a hydrogen atom or an alkyl group. Carboxylic acids are often found in nature and often combined with other functional groups seen in the table found in the introduction. Many of these compounds are liquids or are solids with low melting points. Carboxylic acids are also highly soluble in water and have a relatively low pH. Vinegar, a common carboxylic acid, has a pH of approximately 2.4.



$$CH_3 - \overset{\overset{\large O}{\|}}{C} - OH$$

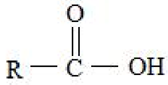
Vinegar

Another common carboxylic acid is niacin (Vitamin B_3). Niacin is found in carrots, green leafy vegetables, milk, eggs, and some fish. It is used by the body in the aid of metabolism, specifically DNA repair and the functioning of the adrenal gland.



Niacin

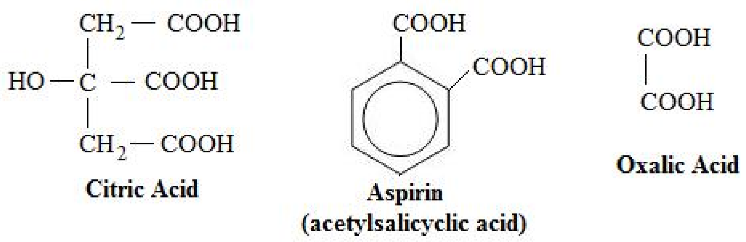
The formula for the carboxyl group is written as R-COOH, where R is a hydrogen atom or an alkyl group. The general formula for the organic acid is found in the diagram below.



$$R - \overset{\overset{\large O}{\|}}{C} - OH$$

Organic Acid

Organic acids play a key role in many aspects of our lives. Citric acid is the taste you experience when you drink citrus drinks such as orange juice or put lemon juice on fish. Aspirin (acetylsalicylic acid or ASA) is also a widely used pain killer. Oxalic acid is also a naturally occurring organic acid found in the leaves of, among other plants, rhubarb, star fruit, black pepper, and parsley.



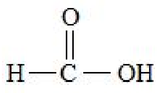
Citric Acid

Aspirin (acetylsalicyclic acid)

Oxalic Acid

Figure 5: Illustrations of Carboxyl Groups

The simplest of organic acids is one where the R group is hydrogen.

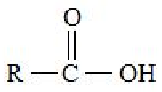


$$\mathrm{H-\overset{\overset{\displaystyle O}{\|}}{C}-OH}$$

When R = H in the general formula, the organic acid is methanoic acid. Methanoic acid (or formic acid) is commonly used in the recycling industry especially for recycling rubber. It is found in nature as the venom in bees and ants and is released when the insect bites.

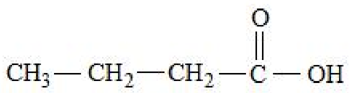
Naming and Drawing Organic Acids

When naming organic acids use the parent chain name of the alkane and add the suffix –oic acid. Remember that all organic acids have the general formula shown below. To draw organic acids, work from the formula backwards.



$$\mathrm{R-\overset{\overset{\displaystyle O}{\|}}{C}-OH}$$

Sample question 8: Name the following structure.



$$\mathrm{CH_3-CH_2-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OH}$$

Solution:

This molecule is a 4 carbon chain ending with a carboxylic acid group.

Therefore the name is **butanoic acid.**

Sample question 9: Draw the structure of 2-methyl propanoic acid.

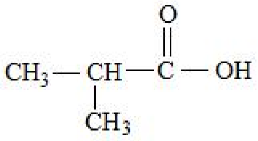
Solution:

Methyl (CH_3) is a branch and is on the C_2 position.

Propanoic has the prefix *prop-* meaning it has three (3) carbon atoms in the parent chain.

Propanoic has the suffix *–oic* acid meaning it has the organic acid functional group

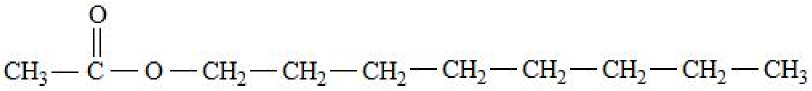
Therefore the structure is:



$$CH_3-\underset{CH_3}{\underset{|}{CH}}-\overset{O}{\overset{\parallel}{C}}-OH$$

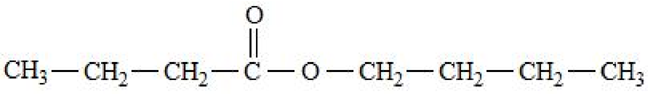
Ester

Have you ever wondered why the smell of an orange has such a wonderful aroma, or where the smell comes from when you cut a fresh pineapple? Most fruits get their rich aroma from molecules known as esters. Octyl ethanoate can take responsibility for the smell for oranges while butyl butanoate is best known for the smell of pineapple.



$$CH_3-\overset{O}{\overset{\parallel}{C}}-O-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$$

Octyl ethanoate (orange flavor)



$$CH_3-CH_2-CH_2-\overset{O}{\overset{\parallel}{C}}-O-CH_2-CH_2-CH_2-CH_3$$

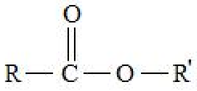
Butylbutyrate (pineapple flavor)

Actually, quite a few of the scents that we are familiar can be traced back to one ester or another. Look at the table below at some of the common scents and the ester for which the scent can be attributed to.

Table 2: Scents and Their Esters

Scent	**Ester**
Apples	Methyl butanoate
Pears	Propyl ethanoate
raspberries	2-methylpropyl ethanoate
peach	Ethyl butanoate
banana	3-Methylbutyl ethanoate
orange	Octyl acetate
jasmine	Benzyl ethanoate

The general formula for esters is found below. Notice that the general formula looks similar to the organic acid but in the case of the ester, the carboxylic acid hydrogen has been replaced with a second alkyl group. This is because esters can be produced by a reaction between an organic acid and an alcohol.

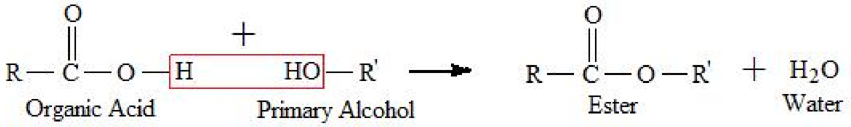


$$R-\overset{O}{\overset{\parallel}{C}}-O-R'$$

General Formula for Esters

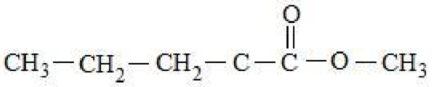
Naming and Drawing Esters

Since esters have two alkyl groups on either side of the functional group, the name of the ester will be in two pieces. As was described earlier, esters are formed from organic acids and alcohols. The alkyl group from the organic acid is R. The alkyl group from the alcohol is R'. When naming the ester, the name is the alkyl group from the alcohol then the alkyl group from the organic acid then the suffix *–oate.* A sample reaction for a general reaction and then a specific reaction to demonstrate this principal is shown below.



To draw an ester, work from the formula backwards. Remember the first alkyl group is attached to the oxygen and the alkyl group with the suffix *–oate* is part of the C = O chain.

Sample question 9: Name the following structure.



$$CH_3-CH_2-CH_2-C-\overset{\overset{O}{||}}{C}-O-CH_3$$

The name is **methyl butanoate.** (the odor of apple)

Sample question 9: Draw the structure of ethyl heptanoate. (the odor of red grape)

Solution:

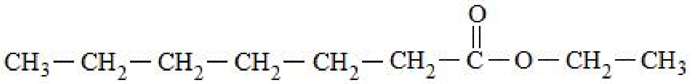
Ethyl (CH_3CH_2) is listed first and is therefore from the alcohol and will be attached to the oxygen.

Heptanoate is named second and is therefore from the organic acid.

Heptanoate has the prefix *hept-* meaning it has seven (7) carbon atoms in the parent chain.

Heptanoate has the suffix *–oate* meaning it has the ester functional group

Therefore the structure is:

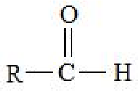


$$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-\overset{\overset{O}{||}}{C}-O-CH_2-CH_3$$

Lesson Summary

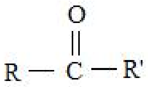
- Alcohols have the same general formula as an alkane except they have the functional group -OH, called the hydroxyl group. Primary (1°)alcohols are ones where the carbon atom is attached to the hydroxyl group and one alkyl group.

- Secondary (2°) alcohols are ones where the carbon atom is attached to the hydroxyl group and two alkyl groups. Tertiary (3°) alcohols are ones where the carbon atom is attached to the hydroxyl group and three alkyl groups.
- All aldehydes have the general formula below:



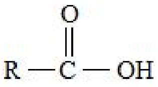
$$R-\overset{\overset{O}{\|}}{C}-H$$

- In order to name aldehydes use the parent chain name of the alkane and add the suffix *–al*.
- All ketones have the general formula below.



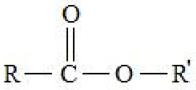
$$R-\overset{\overset{O}{\|}}{C}-R'$$

- To name ketones, use the parent chain name of the hydrocarbon with the same number of carbon atoms and add the suffix *–one*.
- A ***carbonyl group*** is a carbon atom double bonded to an oxygen atom (C = O) and the carbon is also bonded to two other atoms or groups.
- All ether compounds have the general formula R - O - R', where R and R' are alkyl groups.
- In order to name ethers, one of two possibilities can be found. Ethers can be named by naming the alkyl groups on either side of the ether functional group, then adding the word *ether* on the end. The other possibility is to name the smaller alkyl group, add the suffix *–oxy*, and then giving the alkane name to the larger alkyl group.
- The organic acids (or carboxylic acids) contain the carboxyl group.
- A ***carboxyl group*** is a carbon atom double bonded to an oxygen atom (C = O), a hydroxyl group (-OH) and also is bonded to a hydrogen atom or an alkyl group. The formula for the carboxyl group is written as R-COOH , where R is a hydrogen atom or an alkyl group.
- The general formula for the organic acid is below.



$$R-\overset{\overset{O}{\|}}{C}-OH$$

- When naming organic acids use the parent chain name of the alkane and add the suffix *–oic acid.*
- The general formula for an ester is shown below.



$$R-\overset{\overset{O}{\|}}{C}-O-R'$$

- Since esters have two alkyl groups on either side of the functional group, the name of the ester will be in two pieces. As was described earlier, esters are formed from organic acids and alcohols. The alkyl group from the organic acid is R. The alkyl group from the alcohol is R'. When naming the ester, the name is the alkyl group from the alcohol then the alkyl group from the organic acid then the suffix –*oate*.

Review Questions

1. Complete the following chart. **(Intermediate)**

Group	Distinguishing Feature	Draw Example (with name)
Alcohol		
Aldehyde		
Ketone		
Ether		
Organic Acid		
Ester		

2. What is the difference between the carbonyl group in the aldehydes and the carbonyl group in the ketones? Give an example to illustrate your answer. **(Intermediate)**

3. Which of the following compounds is an alcohol? **(Intermediate)**

(a) CH_3COOCH_3

(b) CH_3CH_2OH

(c) CH_3COOH

(d) CH_3COCH_3

4. To which family of organic compounds does $CH_3COCH_2CH_3$ belong? **(Intermediate)**

(a) alcohol

(b) aldehyde

(c) ketone

(d) carboxylic acid

5. Which class of organic compounds contains a carbon-oxygen double bond? **(Intermediate)**

I. Alcohols

II. Aldehydes

III. Ketones

IV. Ethers

V. Organic acids

VI. Esters

(a) I, III, IV only

(b) II, IV, VI only

(c) I, III, IV, V only

(d) II, III, V, VI only

6. What is the name of the compound represented below? **(Intermediate)**

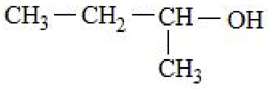
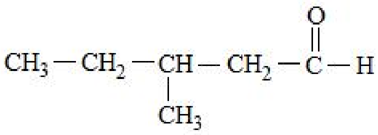
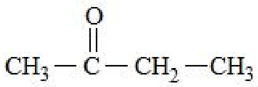
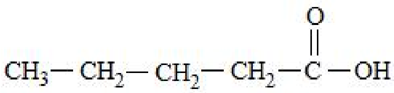
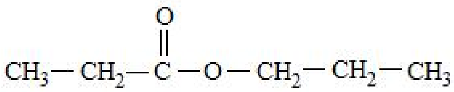
(a) heptanone

(b) 2,3-dimethyl -3-pentanone

(c) 2,3-dimethylpentanone

(d) Diisopropyl ketone

7. Name the following compounds

(a)  $CH_3-CH_2-\underset{CH_3}{\underset{\mid}{CH}}-OH$	(b)  $CH_3-CH_2-\underset{CH_3}{\underset{\mid}{CH}}-CH_2-\overset{O}{\overset{\|}{C}}-H$
(c)  $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$	(d) $CH_3-CH_2-CH_2-O-CH_2-CH_2-CH_3$
(e)  $CH_3-CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OH$	(f)  $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-CH_3$

8. (3) Draw the following compounds. **(Intermediate)**

(a) 3-ethyl – 2 - hexanol

(b) 2,2-dimethylpropanal

(c) 2-propanone

(d) Dibutyl ether

(e) methanoic acid

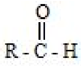
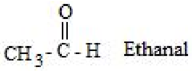
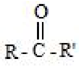
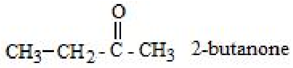
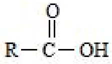
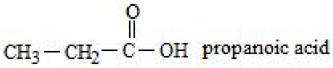
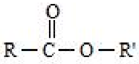
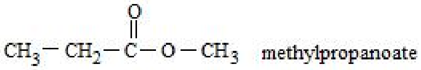
(f) methyl butanoate

Further Reading / Supplemental Links

http://en.wikipedia.org

Review Answers

1.

Group	Distinguishing feature	Draw Example (with name)
Alcohol	$\mathrm{R-OH}$	$\mathrm{CH_3-CH_2-OH}$ Ethanol
Aldehyde	 $\mathrm{R-\overset{\overset{O}{\Vert}}{C}-H}$	 $\mathrm{CH_3-\overset{\overset{O}{\Vert}}{C}-H}$ Ethanal
Ketone	 $\mathrm{R-\overset{\overset{O}{\Vert}}{C}-R'}$	 $\mathrm{CH_3-CH_2-\overset{\overset{O}{\Vert}}{C}-CH_3}$ 2-butanone
Ether	$\mathrm{R-O-R'}$	$\mathrm{CH_3-CH_2-O-CH_3}$ methoxyethane
Organic Acid	 $\mathrm{R-\overset{\overset{O}{\Vert}}{C}-OH}$	 $\mathrm{CH_3-CH_2-\overset{\overset{O}{\Vert}}{C}-OH}$ propanoic acid
Ester	 $\mathrm{R-\overset{\overset{O}{\Vert}}{C}-O-R'}$	 $\mathrm{CH_3-CH_2-\overset{\overset{O}{\Vert}}{C}-O-CH_3}$ methylpropanoate

2. The difference between the aldehydes and the ketones is that with aldehydes, the carbonyl group must have one hydrogen atom attached to the carbon atom, with ketones; both groups attached to the carbon atom are alkyl groups.

3. (b)

4. (c)

5. (d)

6. (b)

7. (a) 1-methyl -1-propanol

(b) 3-methyl pentanal

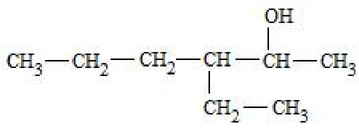
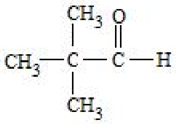
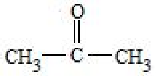
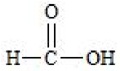
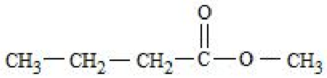
(c) 2-butanone

(d) Dipropyl ether

(e) Pentanoic acid

(f) propyl propanoate

8.

(a)  $CH_3-CH_2-CH_2-\underset{CH_2-CH_3}{CH}-\overset{OH}{CH}-CH_3$	(b)  $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{O}{\overset{\Vert}{C}}-H$
(c)  $CH_3-\overset{O}{\overset{\Vert}{C}}-CH_3$	(d) $CH_3-CH_2-CH_2-CH_2-O-CH_2-CH_2-CH_2-CH_3$
(e)  $H-\overset{O}{\overset{\Vert}{C}}-OH$	(f)  $CH_3-CH_2-CH_2-\overset{O}{\overset{\Vert}{C}}-O-CH_3$

Biochemical Molecules

Lipids

Otherwise known as fats and oils (triglycerides), **lipids** are produced for the purpose of storing energy. One of the best known lipids is cholesterol which is used in the body to construct cell membranes and as a building block for some hormones although new drugs (Lipitor^{TM}) are employed to lower its presence in the bloodstream. High levels of cholesterol are linked to coronary disease.

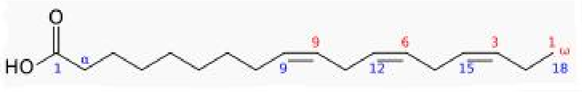
There are many categories of lipids, three of the main categories are:

(1) fatty acids

(2) steroids

(3) phospholipids

Fatty acids are molecules with a carboxylic acid group at one end while the remainder of the molecule is a hydrocarbon chain having anywhere from four (4) carbon atoms to 36 carbon atoms. They can be saturated or unsaturated and generally they occur as unbranched chains. As with all biochemical molecules, there are good fatty acids as well as bad. Omega-3 fatty acid (linolenic acid) is a beneficial fatty acid, cited as slowing the buildup of atherosclerotic plaques. It is found in seed oils, fish and also in egg yolks (shown below). Since the body cannot produce these particular fatty acids, food is the only source of this type of lipid, thus they are known as essential fatty acids.

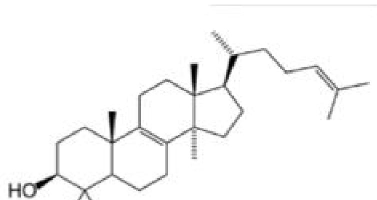


(*Source:* http://en.wikipedia.org/wiki/Omega-3_fatty_acid)

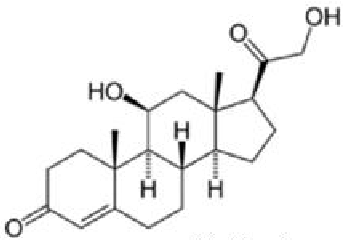
Omega-3 fatty acid has the carboxylic acid functional group on one end and the terminal methyl group on the other end with three double bonds at C_9, C_{12} and C_{15} giving this fatty acid its unique structure. Omega-

3 fatty acids have been shown to regulate the immune system and to lower blood pressure.

Steroids are compounds where four carbon rings are bonded together with branches and functional groups bonded to the rings. Depending on the combinations of the rings, branches, and functional group, different steroids form with different functions in the body. The diagram below (left) shows the structure of lanosterol. Notice the four rings, the hydroxyl group, and the number of branches from the carbon rings. Lanosterol has 30 carbon atoms in total and acts as the basic building block for all steroids.



Lanosterol



Corticosterone

In the diagram above to the right is corticosterone. Corticosterone is steroid hormone important in mobilizing the immune system to fight infection. Notice the similarity in the structures to lanosterol.

A third type of lipid is phospholipids. ***Phospholipids*** are a combination of fatty acids, glycerol and a phosphate group joined together. Phospholipids play a major role in cell membranes. The diagram below shows phosphatidyl choline which is the major component of lecithin. Lecithin is present in egg yolk and soy beans, among other foods. Notice the position of the links between the amine, the phosphate group, the glycerol, and the fatty acids.

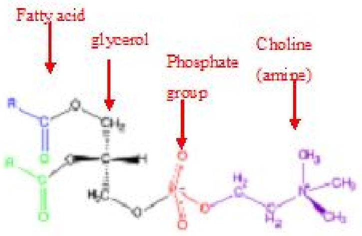


Diagram 4: Illustration of a Phospholipid.

(*Source:* http://en.wikipedia.org/wiki/Phospholipid)

Carbohydrates

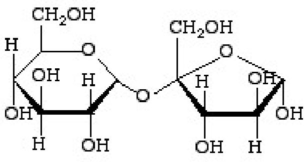
Carbohydrates supply the necessary energy living systems need to survive. All carbohydrates contain carbon, hydrogen, and oxygen and have the general formula $C_x(H_2O)_y$. These molecules are also known as sugars or sugar chains that perform specific functions depending on their structure. Carbohydrates can be classified into three different categories:

(1) Monosaccharides,

(2) Disaccharides, and

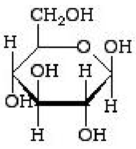
(3) Polysaccharides.

Monosaccharides and disaccharides are also known as simple sugars. Refined white sugar commonly found in the home is an example of a simple sugar. More precisely, refined white sugar is sucrose. Sucrose is a disaccharide formed when two monosaccharides (glucose and fructose) join. Diagram 1 shows an illustration of sucrose as well as glucose and fructose. Notice that the bond joining the two monosaccharide units in sucrose. The molecule on the left in sucrose is a glucose molecule; on the right is a fructose molecule. As the two monosaccharides join, both glucose and fructose will lose a hydrogen atom, and one will lose an oxygen atom also, when they join to form the disaccharide.



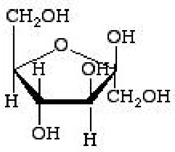
Sucrose

Sucrose: A disaccharide



Glucose

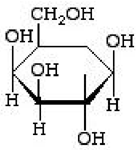
Glucose: A monosaccharide



Fructose

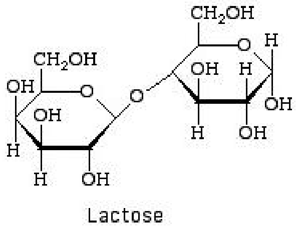
Fructose: A monosaccharide

Therefore a **monosaccharide** is a single sugar unit whereas a **disaccharide** has two sugar units. Lactose is another disaccharide made from two monosaccharides (glucose and galactose).



Galactose

Galactose: A monosaccharide



Lactose: A disaccharide

Within polysaccharides, there are numerous individual sugar units. Starches, for example, are polymers where a large number of glucose monosaccharides join together. Starches have the general formula $(C_6H_{10}O_5)_n$ where n is dependent on the type of starch formed. For example, glycogen is an animal starch, which is made up of approximately 60 000 glucose units. Glycogen is important as a source of energy storage in both the liver and in muscles; when the organism needs that energy, degradation enzymes release glucose units. Notice in the diagram below how the glucose molecules are linked together in glycogen.

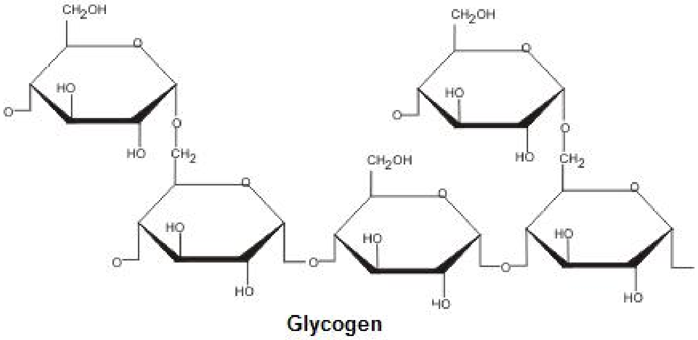


Diagram 3: Glycogen

Proteins

A **polymer** is a large organic molecule that contains hundreds or even thousands of atoms. **Amino acids** are molecules that contain an amine group ($-NH_2$) and a carboxylic acid group (-COOH). There are twenty (20) different naturally occurring amino acids that differ only in the R group that separates the amino group from the carboxyl group. When amino acids join together the link that joins them is called a peptide bond.

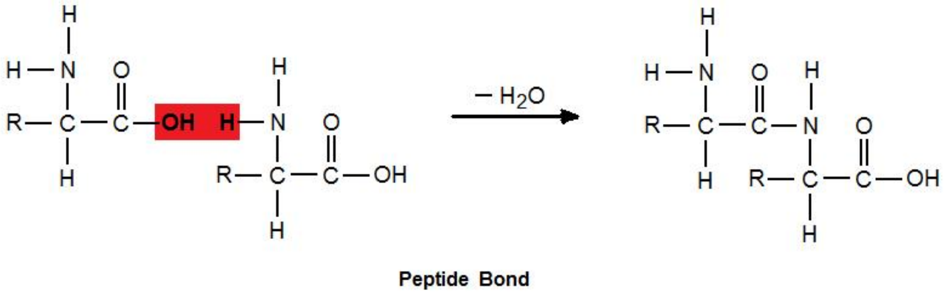


Diagram 5: Formation of the dipeptide bond.

Two amino acids joining is a **dipeptide**. When many amino acids combine together, **polypeptides** will form. A **protein** is a combination of these polypeptides or long chains of amino acids. Proteins are essential to structure and function of all biological cells. The image below shows a 3D model of the protein myoglobin which is a marker for damaged muscle tissue. It is released when muscle tissue is damaged. It is a polypeptide made from the chain of 153 linked amino acids.

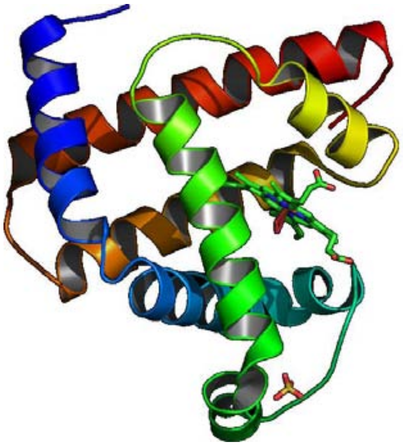


Figure 6: Representation of a 3D model of a protein.

(*Source:* http://en.wikipedia.org/wiki/File:Myoglobin, *Author:* Aza Toth, *License:* Public Domain)

Other proteins that are essential to our life include keratin, collagen, actin, myosin, hemoglobin, and many, many more. Hair and nails contain keratin, tooth enamel and bones are made from collagen, and muscle tissue contains actin and myosin. Hemoglobin is the most complex of the human proteins and is used to transport oxygen in the blood. Other proteins are present outside the body, of course. Milk and cheese contain the protein casein.

There are four different types of structures that proteins form in the body:

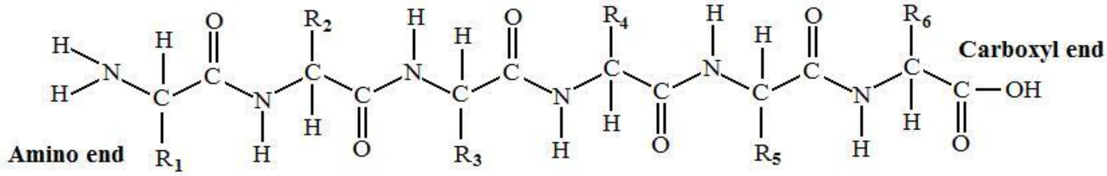
(1) Primary (1°) structures,

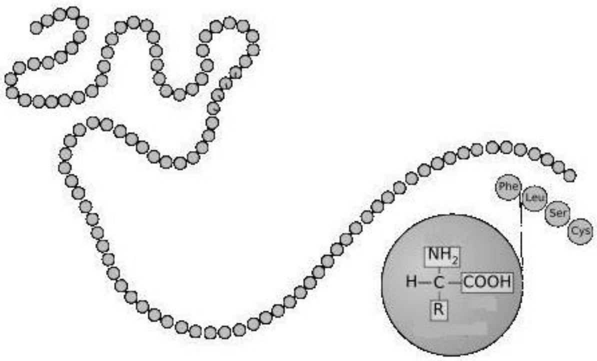
(2) Secondary (2°) structures,

(3) Tertiary (3°) structures, and

(4) Quaternary (4°) structures.

Primary (1°) structures are linear chains of amino acids where the peptide bonds link the amino acids together in long chains or sheets.





Primary structure of a protein

(*Source:* http://upload.wikimedia.org/wikipedia/commons/thumb/4/4c/Protein_primary_structure_zh.svg.png, *License:* Public Domain)

Primary structure of a protein

Secondary (2°) structures can form pleated sheets where hydrogen bonds are forming between the amine groups and the carboxylic acid groups of the amino acids in the peptide link.

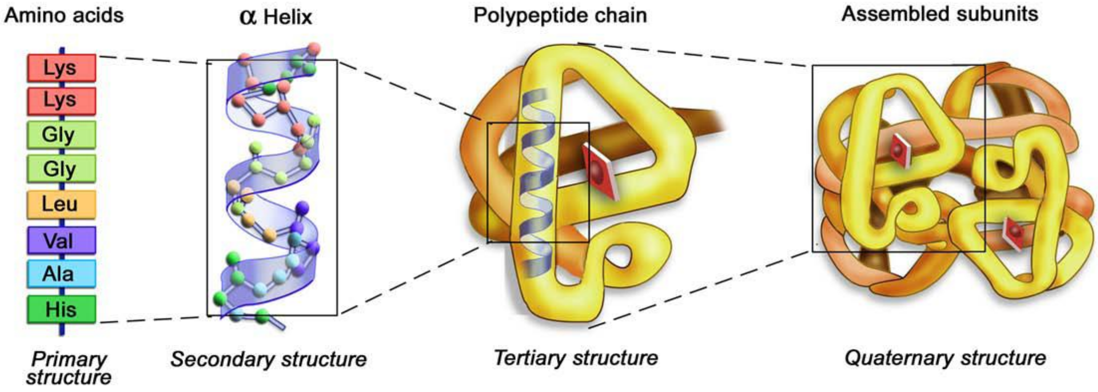


Figure 6: Secondary structure of a protein.

(*Source:* http://ocw.mit.edu/NR/rdonlyres/Materials-Science-and-Engineering/3-051JSpring-2006/lecture5.pdf , *License:* ShareAlike 3.0)

Diagram 6: Pleated Sheet of the Secondary (2°) Structure

These structures can also form alpha-helix formations where hydrogen bonds connect the amino acids in the peptide link and carboxylic acid groups in amino acids further down the protein chain. The diagram below shows the structure for the alpha helix. Notice the coiled structure versus the more straightened structure of the pleated sheet.

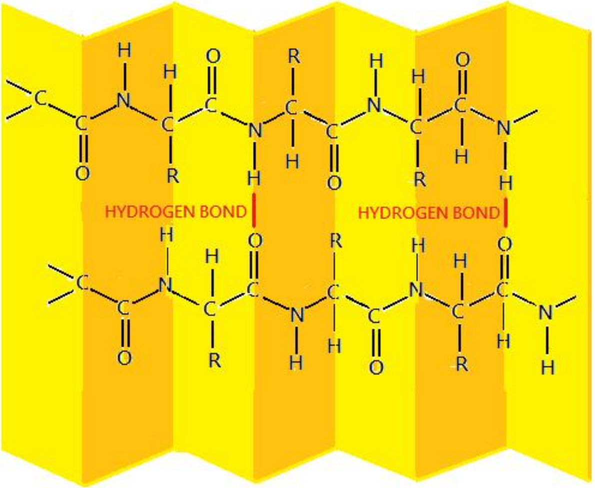
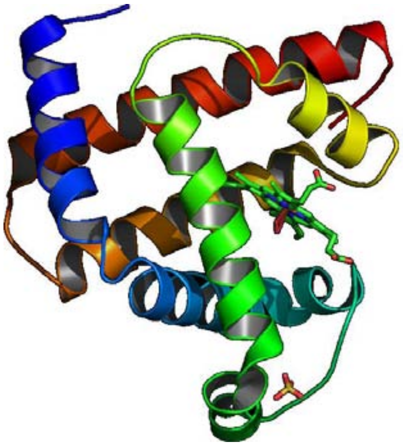


Diagram 7: Alpha-Helix Structure of the 2° Structure

Tertiary (3°) structures form helical structures as pleated sheets and alpha-helices join together in the same molecule. The structure of myoglobin shown below shows the strings of the pleated sheets and the coils of the alpha-helix structures. There is hydrogen bonding between amino hydrogen atoms and carbonyl oxygen atoms as with the secondary structures as well as bonding between the amino acids.



Myoglobin

Lastly, quaternary (4°) structures occur when two or more polypeptides join together. Therefore the quaternary structure of hemoglobin,(below) the principal oxygen-carrying protein found in red blood cells, is a combination of four structural units similar to the tertiary structure of myoglobin (above).

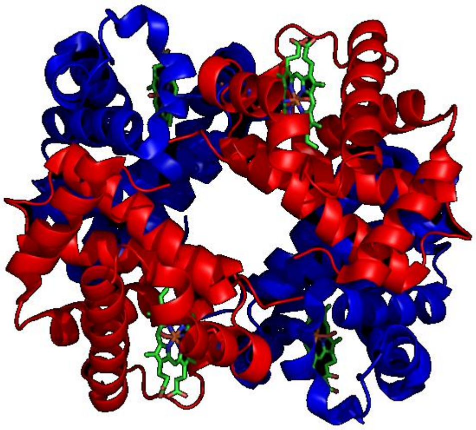


Diagram 8: Hemoglobin

(*Source:* http://en.wikipedia.org/wiki/File:1GZX_Haemoglobin.png, *Author:* Richard Wheeler, *License:* GNU Free Documentation)

Enzymes

Proteins are essential to life. There are over 100 000 different kinds of proteins in the body as well as many different enzymes. **Enzymes** are a subset of proteins. They are a specific type of protein that speed up chemical reactions, thus acting as biological catalysts. Recall that a catalyst is a substance which accelerates the rate of a chemical reaction without itself undergoing any net change. There are more than 4000 enzyme reactions that occur in biological systems. Earlier in this section, the discussion of carbohydrates included starches (Diagram 3). One of the earliest known enzymes, known as **amylase**, was first identified by Payen in 1833. This enzyme is used in digestion to convert starch to sugar in the body. If you were to chew on a cracker, after a while in your mouth you would notice it would start to taste a little sweet. This is the enzyme in the saliva beginning to do its job. The diagram below shows an illustration of amylase. Notice its similarity in structure to that of the proteins in the previous section.

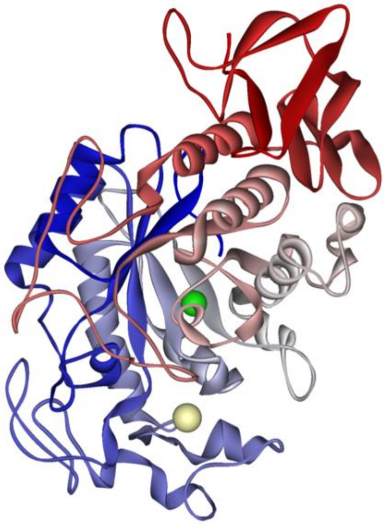


Diagram 9: Amylase

(*Source:* http://en.wikipedia.org/wiki/File:Salivary_alpha_amylase_1SMD.png, *License:* Public Domain)

DNA

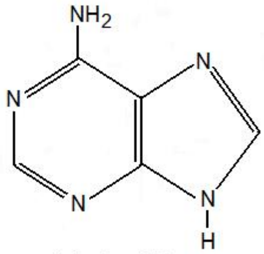
After a discussion of proteins, the next logical step is to learn about nucleic acids. DNA is deoxyribonucleic acid, a polynucleotide found primarily in the nucleus of the cell, that maintains our genetic coding. Its function is to direct the body in the synthesis of proteins. The DNA molecule is a large polynucleotide with a molecular weight in the range of 6 million amu; ribonucleic acids, like RNA are smaller with molecular weights in the realm of 20000 to 40000 amu. A nucleotide consists of one sugar (ribose for RNA and deoxyribose for DNA), a phosphate group, and one of four nitrogen bases. These four nitrogen bases are:

(1) Adenine (A)

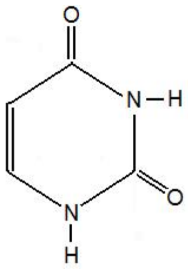
(2) Thymine (T)

(3) Guanine (G)

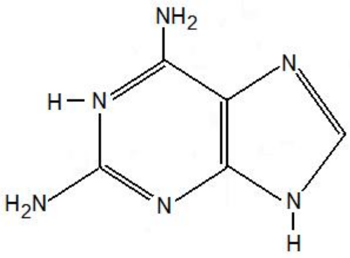
(4) Cytosine (C)



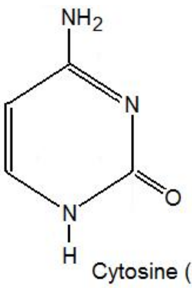
Adenine (A)



Thymine (T)



Guanine (G)



Cytosine (C)

Looking at the structure for deoxyribose (the sugar in the DNA molecule), the phosphate will react and form a link with the hydroxyl groups forming an outer layer of phosphate-deoxyribose chains. The inner structure of the DNA molecule contains the nitrogen bases. Each nitrogen base has linked to the deoxyribose via a hydroxyl group on the sugar unit but also, through hydrogen bonding, these nitrogen bases have complementary linkages to each other (A exclusively links to T, and C connects only to G).

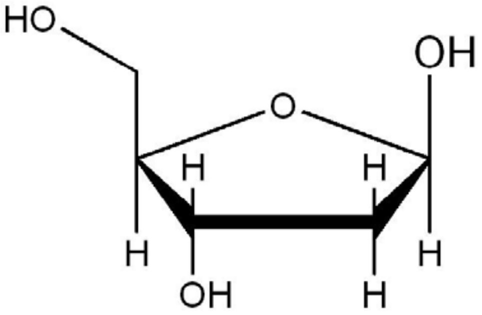


Figure 10: Deoxyribose

(*Source:* http://commons.wikimedia.org/wiki/File:Deoxygribose.png, *License:* GNU Free Documentation)

In the diagram below (left), the linkage of the deoxyribose, the phosphate groups, and the nitrogen bases are shown. It is interesting to note that the two strands, although flat in this diagram, actually form a double helix (diagram below on the right) which adds flexibility to the structure and easy storage and availability of genetic material in addition to ease in the integrity of replication. In order to copy the DNA in cell replication, the double helix unwinds, resulting in two complementary strands, each of which can construct a daughter double helical DNA structure of its own.

The structure of DNA and its unique mode of replication is an important key to understanding important processes in biological science.

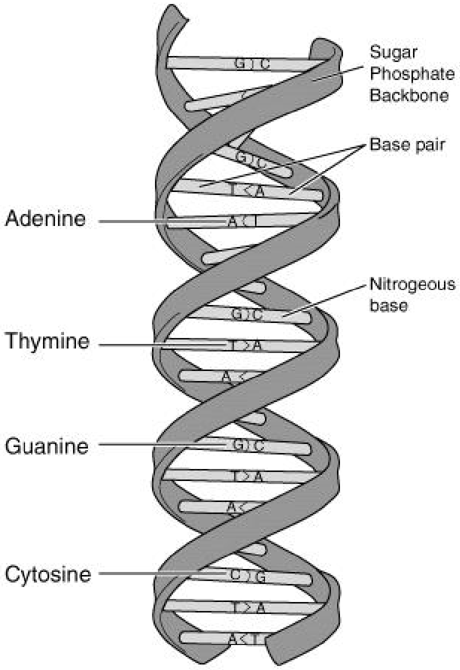


Diagram 11: DNA Illustration as a double helix.

(*Source:*http://genome.gov/Pages/DIR/VIP/Glossary/Illustration/dna.cfm?key=deoxyribonucleic%20acid, *License:* As a product of the US government, this image is in the Public Domain)

Lesson Summary

- Lipids are used for the storage of energy.
- Carbohydrates are also known as sugars or sugar chains and they supply the necessary energy for living systems.
- Amino acids are building blocks for protein.
- Enzymes are a special type of protein that speed up chemical reactions and thus act as catalysts.
- DNA contains our genetic coding, its function is to direct the body in sythesizing proteins.

Review Questions

1. Fill in the following Table. **(Intermediate)**

Compound	**Main Purpose**
Carbohydrate	
Lipid	
Protein	
Enzyme	
DNA	

1. (1) For which biochemical molecule do the triglycerides belong? **(Intermediate)**

(a) carbohydrates

(b) lipids

(c) proteins

(d) enzymes

2. (1) A primary structure is most likely part of what biochemical molecular classification? **(Intermediate)**

(a) carbohydrates

(b) lipids

(c) proteins

(d) enzymes

3. (2) This biochemical molecule is considered a subset of a larger group of molecules? **(Intermediate)**

(a) carbohydrates

(b) lipids

(c) proteins

(d) enzymes

4. (1) Starch is a member of what biochemical molecular group? **(Intermediate)**

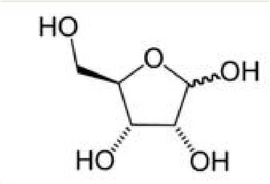
(a) carbohydrates

(b) lipids

(c) proteins

(d) enzymes

5. (3) The structure for ribose is shown below. What is the difference between this and that in the DNA molecule? **(Intermediate)**



Vocabulary

carbohydrates	Molecules that contain carbon, hydrogen, and oxygen and have the general formula $C_x(H_2O)_y$.
monosaccharide	A carbohydrate that is single sugar unit (i.e. glucose).
disaccharide	A carbohydrate that is two sugar units joined together (i.e. sucrose).

polysaccharide	A carbohydrate that is more than two sugar units joined together (i.e. starch).
lipids	Fats and oils (triglycerides) produced for the purpose of storing energy.
fatty acid	A carboxylic acid having anywhere from four(4) carbon atoms to 36 carbon atoms.
steroids	Compounds where four carbon rings are bonded together with branches and functional groups bonded to the rings.
phospholipids	A combination of fatty acids, glycerol and a phosphate group joined together.
polymer	A large organic molecule that contains hundreds or even thousands of atoms.
amino acids	Molecules that contain an amine group (-NH_2) and a carboxyl group (-COOH).
dipeptide	Two amino acids joined together.
polypeptide	Many amino acids combined together.
proteins	Polymers that are amino acids.
enzymes	A subset of proteins that function to speed up a chemical reaction.
DNA (deoxyribonucleic acid)	DNA is a polynucleotide that carries our genetic coding; its function is to direct the body in the synthesis of proteins.

Review Answers

1.

Compound	Main Purpose
Carbohydrate	supply the necessary energy living systems need to survive
Lipid	produced for the purpose of storing energy
Protein	essential functioning to every process within the cells
Enzyme	function to speed up chemical reactions
DNA	to direct the body in the synthesis of proteins

1. (b)

2. (c)

3. (d)

4. (a)

5. DNA contains deoxyribose having the structure shown below. If you look at this structure below it has one less hydroxyl group (hence deoxy).