LNC 216_CHE



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LNC 216_CHE

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Detailed Licensing

Detailed Licensing

Licensing

*A detailed breakdown of this resource's licensing can be found in **Back Matter/Detailed Licensing**.*

CHAPTER OVERVIEW

1: Introduction to Chemistry

What is chemistry? Simply put, chemistry is the study of the interactions of matter with other matter and with energy. This seems straightforward enough. However, the definition of chemistry includes a wide range of topics that must be understood to gain a mastery of the topic or even take additional courses in chemistry. Get ready for a fantastic journey through a world of wonder, delight, and knowledge. One of the themes of this book is “chemistry is everywhere,” and indeed it is; you would not be alive if it weren’t for chemistry because your body is a big chemical machine. If you don’t believe it, don’t worry. Every chapter in this book contains examples that will show you how chemistry is, in fact, everywhere. So enjoy the ride—and enjoy chemistry.

1.1: What is Chemistry?
1.2: Using the Scientific Method
1.3: Pure and Applied Research
1.4: Classification and Properties of Matter
1.5: Applying Properties - MSDS/SDS
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1.1: What is Chemistry?

Learning Objectives

- To recognize the breadth, depth, and scope of chemistry.
- Define chemistry in relation to other sciences.
- Identify the main disciplines of chemistry.
- Match a scientific project with the correct type of chemist.

Chemistry is the study of matter—what it consists of, what its properties are, and how it changes. Being able to describe the ingredients in a cake and how they change when the cake is baked is called chemistry. Matter is anything that has mass and takes up space—that is, anything that is physically real. Some things are easily identified as matter—this book, for example. Others are not so obvious. Because we move so easily through the air, we sometimes forget that it, too, is matter.

Chemistry is one branch of science. Science is the process by which we learn about the natural universe by observing, testing, and then generating models that explain our observations. Because the physical universe is so vast, there are many different branches of science (Figure **1.1.1**). Thus, chemistry is the study of matter, biology is the study of living things, and geology is the study of rocks and the earth. Mathematics is the language of science, and we will use it to communicate some of the ideas of chemistry.

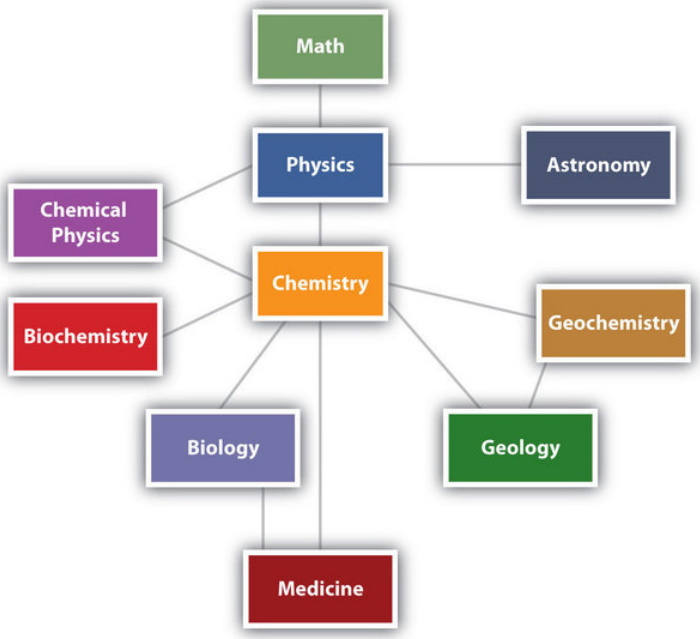


Figure **1.1.1**: The Relationships between Some of the Major Branches of Science. Chemistry lies more or less in the middle, which emphasizes its importance to many branches of science.

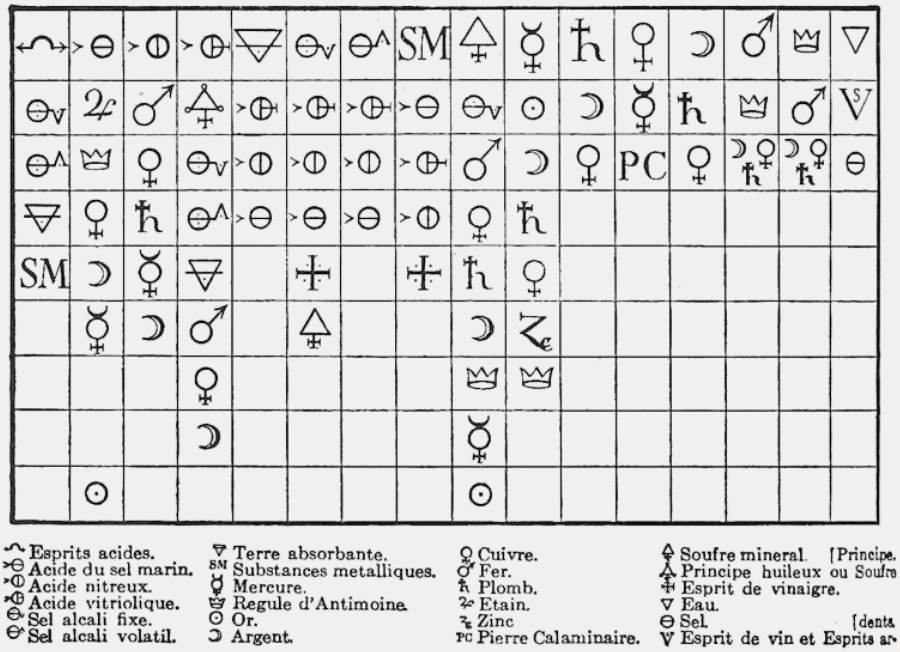
Although we divide science into different fields, there is much overlap among them. For example, some biologists and chemists work in both fields so much that their work is called biochemistry. Similarly, geology and chemistry overlap in the field called geochemistry. Figure **1.1.1** shows how many of the individual fields of science are related.

> *There are many other fields of science, in addition to the ones (biology, medicine, etc.) listed*

Alchemy Is in No way Chemistry!

As our understanding of the universe has changed over time, so has the practice of science. Chemistry in its modern form, based on principles that we consider valid today, was developed in the 1600s and 1700s. Before that, the study of matter was known as *alchemy* and was practiced mainly in China, Arabia, Egypt, and Europe.

Alchemy was a somewhat mystical and secretive approach to learning how to manipulate matter. Practitioners, called alchemists, thought that all matter was composed of different proportions of the four basic elements—fire, water, earth, and air—and believed that if you changed the relative proportions of these elements in a substance, you could change the substance. The long-standing attempts to “transmute” common metals into gold represented one goal of alchemy. Alchemy’s other major goal was to synthesize the philosopher’s stone, a material that could impart long life—even immortality. Alchemists used symbols to represent substances, some of which are shown in the accompanying figure. This was not done to better communicate ideas, as chemists do today, but to maintain the secrecy of alchemical knowledge, keeping others from sharing in it.



The first affinity table. Table of different relations observed in chemistry between different substances; Memoirs of the Royal Academy of Sciences, p. 202-212. Alchemists used symbols like these to represent substances.

In spite of this secrecy, in its time alchemy was respected as a serious, scholarly endeavor. Isaac Newton, the great mathematician and physicist, was also an alchemist.

Alchemy and the ACS (American Chemical Society)

While watching the video below and answer the following questions.



Questions

1. What was the chief goal of an alchemist according to the video?

2. What could the philosopher's stone do to urine?
3. Is Alchemy a true science?
4. When urine is boiled down to a white paste, what is the name and symbol for the element that was obtained?
5. List some properties of this element that were discussed in the video.
6. Did wealthy people produce more of this element than poorer people?
7. What types of applications (applied science) did this element lead us to?
8. Instead of collecting urine, how can one collect higher concentrations of this element?
9. The video discussed phosphoric acid (formula: H_3PO_4). Name all the elements in this compound.
10. What were the mentioned applications of phosphoric acid?
11. What are some of the organic and biochemical applications of element 13?

Areas of Chemistry

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

- **Physical chemistry:** Physical chemistry is the study of macroscopic properties, atomic properties, and phenomena in chemical systems. A physical chemist may study such things as the rates of chemical reactions, the energy transfers that occur in reactions, or the physical structure of materials at the molecular level.
- **Organic chemistry:** Organic chemistry is the study of chemicals containing carbon with hydrogen. Carbon is one of the most abundant elements on Earth and is capable of forming a tremendously vast number of chemicals (over twenty million so far). Most of the chemicals found in all living organisms are based on carbon.
- **Inorganic chemistry:** Inorganic chemistry is the study of chemicals that do not, in general, contain carbon. Inorganic chemicals are commonly found in rocks and minerals. One current important area of inorganic chemistry deals with the design and properties of materials involved in energy and information technology.
- **Analytical chemistry:** Analytical chemistry is the study of the composition of matter. It focuses on separating, identifying, and quantifying chemicals in samples of matter. An analytical chemist may use complex instruments to analyze an unknown material in order to determine its various components.
- **Biochemistry:** Biochemistry is the study of chemical processes that occur in living things. Research may cover basic cellular processes up to understanding disease states so better treatments can be developed.



Figure **1.1.2**: (left) Measurement of trace metals using atomic spectroscopy. (right) Measuring hormone concentrations.

In practice, chemical research is often not limited to just one of the five major disciplines. A particular chemist may use biochemistry to isolate a particular chemical found in the human body such as hemoglobin, the oxygen-carrying component of red blood cells. He or she may then proceed to analyze the hemoglobin using methods that would pertain to the areas of physical or analytical chemistry. Many chemists specialize in areas that are combinations of the main disciplines, such as bioorganic chemistry or physical organic chemistry.

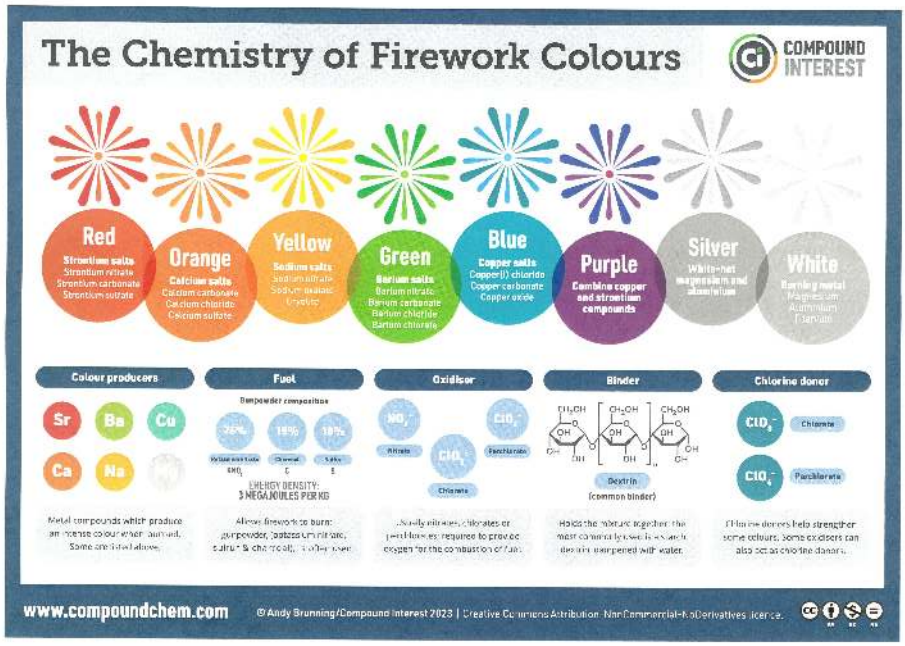


Figure **1.1.3**: The Chemistry of Firework Colours. (CC-BY-NC-ND; Andy Brunning)

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1.2: Using the Scientific Method

Learning Objectives

- To identify the components of the scientific method
- Classify measurements as being quantitative or qualitative.
- Evaluate science in the media.

The Scientific Method

Scientists search for answers to questions and solutions to problems by using a procedure called the scientific method. This procedure consists of making observations, formulating hypotheses, and designing experiments, which in turn lead to additional observations, hypotheses, and experiments in repeated cycles (Figure **1.2.1**).

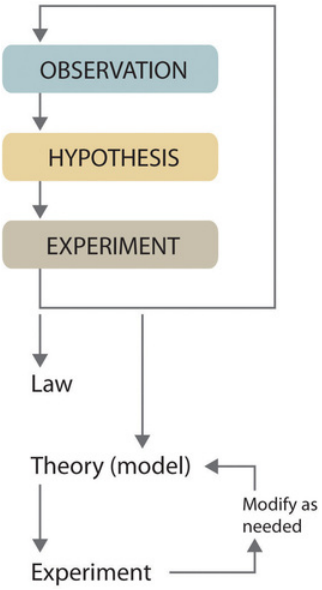


Figure **1.2.1**: The Steps in the Scientific Method. (CC BY-SA-NC; anonymous).

Step 1: Make observations

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

Step 2: Formulate a hypothesis

After deciding to learn more about an observation or a set of observations, scientists generally begin an investigation by forming a hypothesis, a tentative explanation for the observation(s). The hypothesis may not be correct, but it puts the scientist's understanding of the system being studied into a form that can be tested. For example, the observation that we experience alternating periods of light and darkness corresponding to observed movements of the sun, moon, clouds, and shadows is consistent with either of two hypotheses:

a. Earth rotates on its axis every 24 hours, alternately exposing one side to the sun, or
b. the sun revolves around Earth every 24 hours.

Suitable experiments can be designed to choose between these two alternatives. For the disappearance of the dinosaurs, the hypothesis was that the impact of a large extraterrestrial object caused their extinction. Unfortunately (or perhaps, fortunately), this hypothesis does not lend itself to direct testing by any obvious experiment, but scientists can collect additional data that either support or refute it.

Step 3: Design and perform experiments

After a hypothesis has been formed, scientists conduct experiments to test its validity. Experiments are systematic observations or measurements, preferably made under controlled conditions—that is, under conditions in which a single variable changes.

Step 4: Accept or modify the hypothesis

A properly designed and executed experiment enables a scientist to determine whether the original hypothesis is valid. In which case he can proceed to step 5. In other cases, experiments often demonstrate that the hypothesis is incorrect or that it must be modified thus requiring further experimentation.

Step 5: Development into law and/or theory

More experimental data are then collected and analyzed, at which point a scientist may begin to think that the results are sufficiently reproducible (i.e., dependable) to merit being summarized in law, a verbal or mathematical description of a phenomenon that allows for general predictions. A law simply says what happens; it does not address the question of why.

One example of a law, the law of definite proportions, which was discovered by the French scientist Joseph Proust (1754–1826), states that a chemical substance always contains the same proportions of elements by mass. Thus, sodium chloride (table salt) always contains the same proportion by mass of sodium to chlorine, in this case, 39.34% sodium and 60.66% chlorine by mass, and sucrose (table sugar) is always 42.11% carbon, 6.48% hydrogen, and 51.41% oxygen by mass.

Whereas a law states only what happens, a theory attempts to explain why nature behaves as it does. Laws are unlikely to change greatly over time unless a major experimental error is discovered. In contrast, a theory, by definition, is incomplete and imperfect, evolving with time to explain new facts as they are discovered.

Because scientists can enter the cycle shown in Figure **1.2.1** at any point, the actual application of the scientific method to different topics can take many different forms. For example, a scientist may start with a hypothesis formed by reading about work done by others in the field, rather than by making direct observations.

A Real-World Application of the Scientific Method

In 2007, my husband and I journeyed to China to adopt our daughter. Upon arrival in Beijing, I became violently ill. Due to her visa paperwork, my husband, daughter, and I were required to stay in China for two weeks. Unfortunately, I was ill the entire time. Once the two-week period was up, the three of us flew back to the United States where I continued to be sick. For the next year, I remained ill and lost a total of 30 pounds. The picture below shows me holding my daughter eight months after we returned home from China.



Figure **1.2.2**: Mother and child. (CC BY-SA-NC; Elizabeth R. Gordon).

I would like you to attempt to perform the scientific method on my situation described above. List the steps of the scientific method along with some plausible explanations. * **Please have this ready to discuss in class**.*

Exercise \(\PageIndex{2}\)

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

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

Answer a

experiment

Answer b

law

Answer c

theory

Answer d

hypothesis

Answer e

qualitative observation

Answer f

quantitative observation

Evaluating Science in the Media

A Rough Guide to

SPOTTING BAD SCIENCE

Being able to evaluate the evidence behind a scientific claim is important. Being able to recognise bad science reporting, or faults in scientific studies, is equally important. These 12 points will help you separate the science from the pseudoscience.

1. SENSATIONALISED HEADLINES

Article headlines are commonly designed to entice viewers into clicking on and reading the article. At times, they can over-simplify the findings of scientific research. At worst, they sensationalise and misrepresent them.

2. MISINTERPRETED RESULTS

News articles can distort or misinterpret the findings of research for the sake of a good story, whether intentionally or otherwise. If possible, try to read the original research, rather than relying on the article based on it for information.

3. CONFLICTS OF INTEREST

Many companies will employ scientists to carry out and publish research - whilst this doesn't necessarily invalidate the research, it should be analysed with this in mind. Research can also be misrepresented for personal or financial gain.

4. CORRELATION & CAUSATION

Be wary of any confusion of correlation and causation. A correlation between variables doesn't always mean one causes the other. Global warming increased since the 1800s, and pirate numbers decreased, but lack of pirates doesn't cause global warming.

5. UNSUPPORTED CONCLUSIONS

Speculation can often help to drive science forward. However, studies should be clear on the facts their study proves, and which conclusions are as yet unsupported ones. A statement framed by speculative language may require further evidence to confirm.

6. PROBLEMS WITH SAMPLE SIZE

In trials, the smaller a sample size, the lower the confidence in the results from that sample. Conclusions drawn can still be valid, and in some cases small samples are unavoidable, but larger samples often give more representative results.

7. UNREPRESENTATIVE SAMPLES USED

In human trials, subjects are selected that are representative of a larger population. If the sample is different from the population as a whole, then the conclusions from the trial may be biased towards a particular outcome.

8. NO CONTROL GROUP USED

In clinical trials, results from test subjects should be compared to a 'control group' not given the substance being tested. Groups should also be allocated randomly. In general experiments, a control test should be used where all variables are controlled.

9. NO BLIND TESTING USED

To try and prevent bias, subjects should not know if they are in the test or the control group. In 'double blind' testing, even researchers don't know which group subjects are in until after testing. Note, blind testing isn't always feasible, or ethical.

10. SELECTIVE REPORTING OF DATA

Also known as 'cherry picking', this involves selecting data from results which supports the conclusion of the research, whilst ignoring those that do not. If a research paper draws conclusions from a selection of its results, not all, it may be guilty of this.

11. UNREPLICABLE RESULTS

Results should be replicable by independent research, and tested over a wide range of conditions (where possible) to ensure they are consistent. Extraordinary claims require extraordinary evidence - that is, much more than one independent study!

12. NON-PEER REVIEWED MATERIAL

Peer review is an important part of the scientific process. Other scientists appraise and critique studies, before publication in a journal. Research that has not gone through this process is not as reputable, and may be flawed.

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1.3: Pure and Applied Research

Learning Objectives

- Distinguish between basic and applied chemistry
- Review the basics of the videos within in this section.

In science, we usually talk about two types of research: pure and applied. **Pure research** focuses on answering basic questions such as, "how do gases behave?" **Applied research** would be involved in the process of developing specific preparation for a gas in order for it to be produced and delivered efficiently and economically. This division sounds like it would be easy to make, but sometimes we cannot draw a clear line between what is "pure" and what is "applied".

Examples of "Pure" Research

A lot of "pure" research is of the "what is this?" or "how does it work?" variety. The early history of chemistry contains many examples. The ancient Greek philosophers debated the composition of matter (earth? air? fire? water? all of the above?). They did not intend to apply the knowledge gained from exploring the matter. Instead, they choose to focus on understanding the nature of matter.



Figure **1.3.1**: Ancient Greek philosophers."A Greek Philosopher and His Disciples", Antonio Zucchi

Applied Research (Technology)

There is a great deal of "applied" research taking place today. In general, no new science principles are discovered, but existing knowledge is used to develop a new product. A good example of this type of research is the application of x-rays in medicine. In the later part of the 1800s, Wilhelm Röentgen discovered how to produce x-rays by using a cathode ray. He noted that this new ray could go through the body. Immediately, Röentgen believed that x-rays would be very helpful in diagnosing and determining disease and injury in the body.

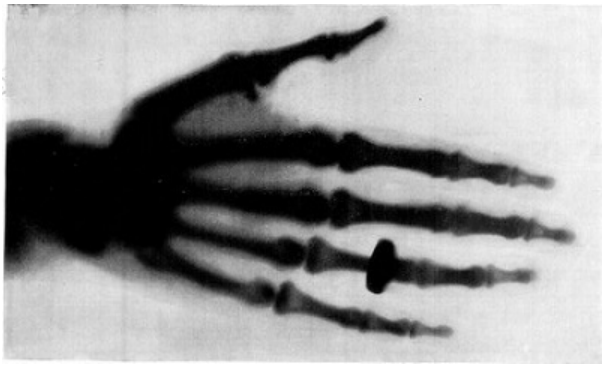


Figure **1.3.2**: Röentgen is the father of the X-ray. while working with experiments and procedures of previous scientists, Röentgen noticed that even through secured chambers for light, an unknown energy was emitted that reacted with phosphorescent materials he was using in his experiments. his discovery and subsequent papers earned him the Nobel Prize in Physics in 1901. He used his wife's hand to determine if the new rays could pass through the body.

The Conversion of Basic Research to Applied Research

Scientists and engineers desire to understand how the universe works. Many times, this leads to unimaginable applications for their works. During the early 20th century, physicists and engineers performed experiments probing atoms with electricity and/or magnets. This research led to the identification of the three subatomic particles of the atom- electron, proton, and neutron. After determining these particles, physical chemists and physicists began experimenting on the central core of atoms (called nuclei). By bombarding a nucleus with other particles (beta, alpha, or neutron), they were able to transform one element into another.



Artificial transmutation can only occur in the nuclear lab. Large pieces of equipment are needed to change the nucleus. This discovery of altering the nucleus led to the production of new isotopes (atoms of the same element that differ in mass and neutron count). These new isotopes now are used in nuclear medicine (diagnosing and treating disease), nuclear weapons (producing fuel for bombs), sanitizing food, spices, and cosmetics, and nuclear energy.



Video **1.3.1**: Click on the video to explore applications of nuclear science

Undergraduate Research at Furman University

All chemistry majors at our university are required to participate in undergraduate research. During the summertime, many of these students remain on campus to work in our laboratories. Students will join a group and research in one of the following areas: organic, inorganic, analytical, biochemistry, or physical chemistry. Some continue on their research in the calendar year. Upon graduation, all of our majors could enter industry immediately. Others will continue their chemical education by enrolling in Ph.D. programs. Lastly, many of our majors will continue on to become educators, patent attorneys, medical doctors, pharmacists, or physical therapists.

Application: Dr. Raychelle Burks

Listen to this 11-minute episode of the Shortwave Podcast. Answer the questions below about how Dr. Raychelle Burks distinguishes between good and bad science in the media.



1. Did Dr. Burks always dream of becoming a scientist?
2. How did Dr. Burks become interested in science?
3. Before exploring academia, what kind of work did Dr. Burks do?
4. Briefly explain the field of forensic science.
5. According to Dr. Burks which shows get the science correct? Which shows are inaccurate?
6. Provide some examples as to how the CSI shows have reported inaccurate science.
7. How are machines over-glorified in crime based television shows?
8. On the show, "Madam Secretary," what type of information did Dr. Burks provide to the show's, producers.
9. List the two WMD chemicals that were mentioned by Dr. Burks. How should scientists be dressed when they encounter them?
10. What type of chemist (recall the five types) is Dr. Burks?

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1.4: Classification and Properties of Matter

Learning Objectives

- Use physical and chemical properties, including phase, to describe matter.
- Distinguish between physical and chemical changes.
- Identify a sample of matter as an element, a compound, or a mixture (homogeneous/heterogeneous).
- Distinguish between organic and inorganic chemicals.
- Label all atoms within an organic or inorganic compound.
- Recognize physical methods used to separate mixtures.

Physical and Chemical Properties

The properties that chemists use to describe matter fall into two general categories. Physical properties are characteristics that **describe** matter. They include characteristics such as size, shape, color, and mass. Many of these properties can be quantitative in nature. For example, quantitative physical properties of water would be the boiling point (100 °C / 212 °F), melting point (0°C / 32 °F) and density (1.00 g/ml at 4.0°C.

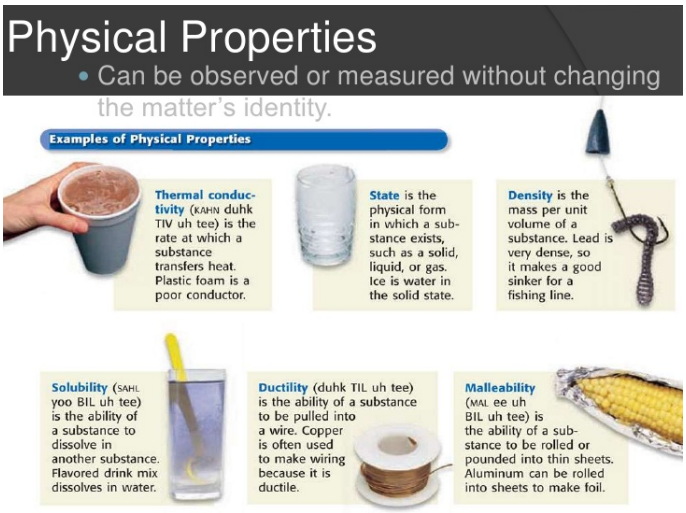


Figure 1.4.1: Physical Properties. (Copyright;https://www.slideshare.net/cfoltz/ph...cal-properties)

Chemical properties are characteristics that describe how matter **changes** its chemical structure or composition. An example of a chemical property is flammability—a material's ability to burn—because burning (also known as combustion) changes the chemical composition of a material. Oxidation, rusting, decomposition, and inertness (not reactive) are chemical properties as well. Click on this video and record the physical and chemical properties of the element sodium.

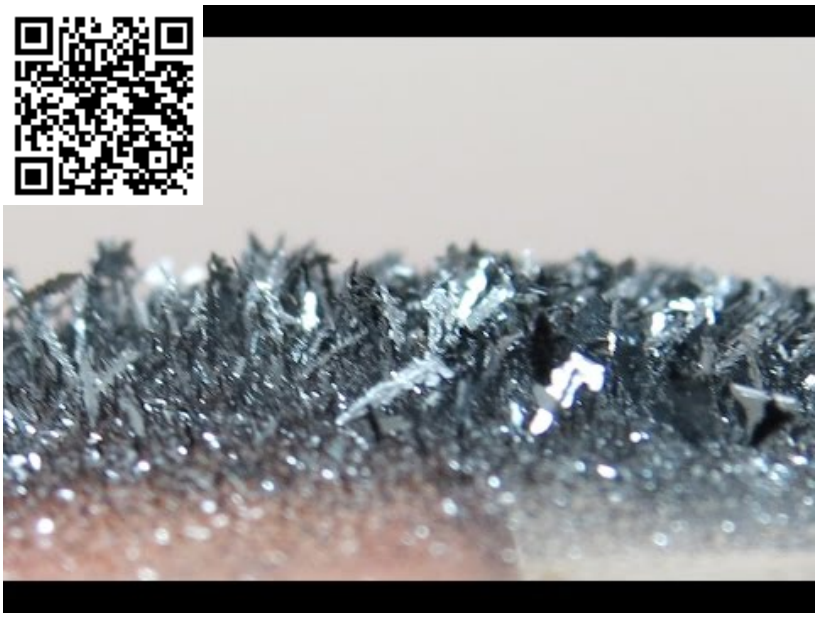


Figure 1.4.2: Port Royal, South Carolina oxidation of iron. Image courtesy of Elizabeth R. Gordon.

States of Matter (phases)

Another way to classify matter is to describe it as a solid, a liquid, or a gas, which was done in the examples of solutions. These three descriptions, each implying that the matter has certain physical properties, represent the three phases of matter. A solid has a

definite shape and a definite volume. Liquids ordinarily have a definite volume but not a definite shape; they take the shape of their containers. Gases have neither a definite shape nor a definite volume, and they expand to fill their containers. We encounter matter in each phase every day; in fact, we regularly encounter water in all three phases: ice (solid), water (liquid), and steam (gas).



Video**1.4.1**: Sublimation and deposition of Iodine.

We know from our experience with water that substances can change from one phase to another if the conditions are right. Typically, varying the temperature of a substance (and, less commonly, the pressure exerted on it) can cause a phase change, a physical process in which a substance goes from one phase to another (Figure **1.4.3**). Phase changes have particular names depending on what phases are involved, as summarized in Table **1.4.1**.

Table **1.4.1**: Phase Changes

Change	Name
solid to liquid	melting, fusion
solid to gas	sublimation
liquid to gas	boiling, evaporation
liquid to solid	solidification, freezing
gas to liquid	condensation
gas to solid	deposition

Classification of Matter

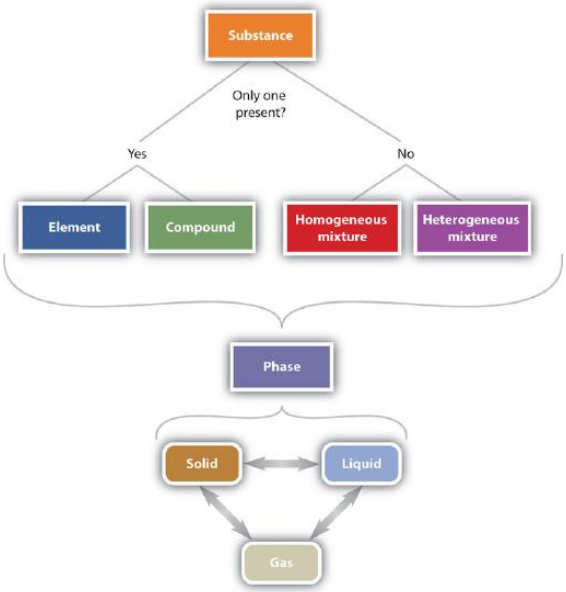


Figure **1.4.3**: The Classification of Matter. Matter can be classified in a variety of ways, depending on its properties. (Cc BY-NC-SA; anonymous)

Elements and Compounds

Any sample of matter that has the same physical and chemical properties throughout the sample is called a substance. There are two types of substances. A substance that cannot be broken down into chemically simpler components is an element. Aluminum, which is used in soda cans, is an element. A substance that can be broken down into chemically simpler components (because it has more than one element) is a compound . Water is a compound composed of the elements hydrogen and oxygen. Today, there are 118 elements in the known universe. In contrast, scientists have identified tens of millions of different compounds to date.

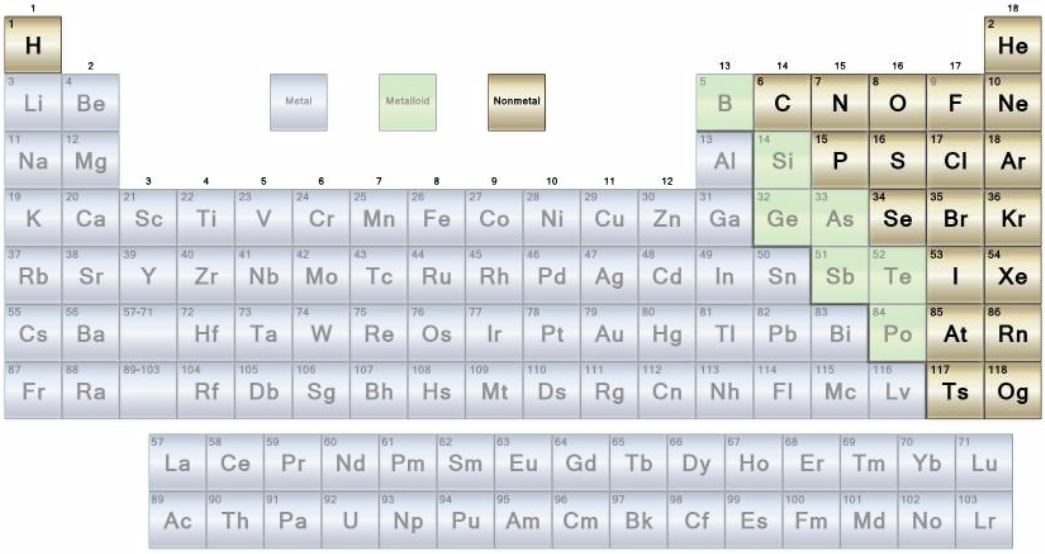


Figure **1.4.4**: Periodic-Table-Metals.jpg. (CC-BY-SA-4.0), https://commons.wikimedia.org/w/inde...edit&redlink=1.

Sometimes the word *pure* is added to a substance, but this is not absolutely necessary. By definition, any single substance is pure.

The smallest part of an element that maintains the identity of that element is called an atom. Atoms are extremely tiny; to make a line 1 inch long, you would need 217 million iron atoms. The smallest part of a compound that maintains the identity of that compound is called a molecule. Molecules are composed of atoms that are attached together and behave as a unit. Scientists usually work with millions and millions of atoms and molecules at a time. When a scientist is working with large numbers of atoms or molecules at a time, the scientist is studying the macroscopic view of the universe.

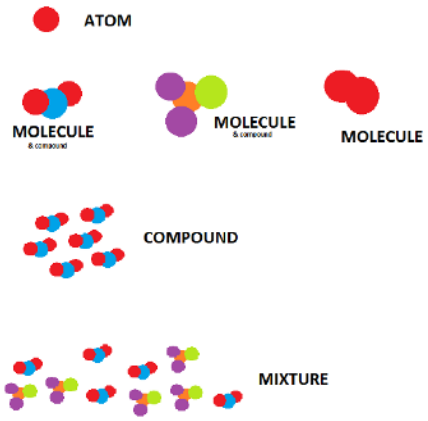


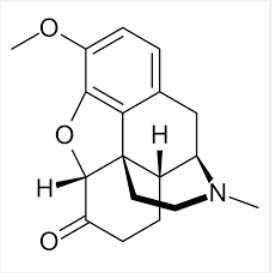
Figure **1.4.5**: Appreciating elements, molecules and compounds.

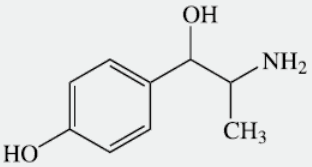
Inorganic and Organic Compounds

Compounds can be further classified as being inorganic or organic. Organic compounds contain carbon, hydrogen, and usually another element from the right side of the periodic table. Be careful when thinking about organic chemicals. In the real world, the term "organic" is typically used to describe products that have natural ingredients. In the world of science, the word "organic" is used to denote compounds that have carbon and hydrogen connections. Look at some of the structures below to get an appreciation of organic chemical structures.

Organic structures

The two molecules shown below are heavily used in the pharmaceutical industry. The compound on the left is known as hydrocodone. This is an opioid painkiller that is extremely addictive. It is regularly dispensed for surgical and chronic pain. The compound on the right is Adderall. This medication is used to treat ADHD and narcolepsy. Both of these medications are controlled by the DEA (Drug Enforcement Agency) and are illegal to possess unless you have a valid prescription.





Mixtures

A material composed of two or more substances is a mixture. In a mixture, the individual substances maintain their chemical identities. Many mixtures are obvious combinations of two or more substances, such as a mixture of sand and water. Such mixtures are called **heterogeneous mixtures**. In some mixtures, the components are so intimately combined that they act like a single

substance (even though they are not). Mixtures with a consistent composition throughout are called **homogeneous mixtures** (or **solutions**). Sugar dissolved in water is an example of a solution. A metal alloy, such as steel, is an example of a solid solution. Air, a mixture of mainly nitrogen and oxygen, is a gaseous solution.

✔ Exercise 1.4.1

How would a scientist categorize each type of matter?

a. saltwater
b. soil
c. water
d. oxygen

Solution

a. Saltwater acts as if it were a single substance even though it contains two substances—salt and water. Saltwater is a homogeneous mixture, or a solution.
b. Soil is composed of small pieces of a variety of materials, so it is a heterogeneous mixture.
c. Water is a substance; more specifically, because water is composed of hydrogen and oxygen, it is a compound.
d. Oxygen, a substance, is an element.

? Exercise 1.4.2

How would a chemist categorize each example of matter?

a. coffee
b. hydrogen
c. an egg

Answer a

Coffee could be a heterogeneous or homogeneous mixture. If insoluble parts are able to be identified, then it would be classified as being heterogeneous. If not, then coffee would be a homogeneous mixture or a solution.

Answer b

Hydrogen is an element. It can be located on the periodic table.

Answer c

An egg (assume raw) would be a heterogeneous mixture. The yolk and egg white are two different substances that can be easily seen.

? Exercise 1.4.3

a. Classify each as being element, compound, heterogeneous mixture, or homogeneous mixture (solution): air at Furman University, Furman Lake water, copper wire, and Furman tap water.
b. What is the difference between a heterogeneous mixture and a homogeneous mixture? Give an example of each.
c. Which is/are physical change(s): burning of fuel, digestion of food, salt dissolving in water, copper conducting electricity, and water boiling.

Answer a

Hopefully, Furman air is a homogenous mixture (solution). If there is no burning or dust build-up in the area, this is safe to assume. Furman Lake is definitely a heterogeneous mixture (in some areas it can get a bit swampy). Copper wire is an element. There are very few elements in nature. Lastly, Furman tap water is usually a homogeneous mixture. Natural and

man-made chemicals are in our tap water (trust me, you want the chlorine). Our toilets do use greywater which can look heterogeneous (ok for sewer but not to drink).

Answer b

A heterogeneous mixture is obviously a mixture, such as dirt; a homogeneous mixture behaves like a single substance, such as saltwater.

Answer c

The physical changes are salt dissolving water, copper conducting, and water boiling. If composition is not changed, then this is a physical change. If there is a method to physically separate the components (like boiling, evaporation, distillation, magnetism, or filtration), then a physical change has occurred.

Contributors and Attributions

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1.5: Applying Properties - MSDS/SDS

Learning Objectives

- Review physical and chemical properties.
- Know the purpose of a MSDS/SDS.
- Explain the bolded words on this page.

What is a MSDS/SDS?

A Material Safety Data Sheet (MSDS) or Safety Data Sheet (SDS) is designed to provide both workers and emergency personnel with the proper procedures for handling or working with a particular substance. MSDS's include information such as physical data (melting point, boiling point, flash point, etc.), toxicity, health effects, first aid, reactivity, storage, disposal, protective equipment, and spill/leak procedures. These are of particular use if a spill or other accident occurs.

The MSDS's are available from many sources such as the chemistry store, health and safety offices, material producing companies, etc. Any business or industry that has chemicals on site is required to have access to MSDS files for employers to be able to access at any time. If an employee is concerned about their exposure to chemicals, they can peruse an MSDS to obtain helpful information. Likewise, one could research household chemicals that could be dangerous to humans and animals. Many substances found around the home (pesticides, fuels, and cleaners) can be hazardous or harmless.

Safety Data Sheets Requirement Summary		
1	Identification	Product identifier, recommended use and restrictions on use, supplier contact information, emergency phone number
2	Hazard Identification	Classification (hazard class and category), label elements (including hazard pictogram, signal word, hazard statement and precautionary statements) and other hazards (e.g. thermal hazards).
3	Composition / Ingredients Information	For a hazardous product that is a substance: the chemical name, synonyms, CAS No. and the chemical name of impurities, stabilizing solvents and stabilizing additives where classified and that contribute to the classification of the product. For a hazardous product that is a mixture: for ingredients that present a health hazard, the chemical name, synonyms, CAS No. and concentration. Note: Confidential Business Information Rules may apply.
4	First Aid Measures	First-aid measures by route of exposure as well as most important symptoms/effects.
5	Fire Fighting Measures	Suitable (and unsuitable) extinguishing media, specific hazards, special equipment and precautions for fire fighters.
6	Accidental Release Measures	Protective equipment, emergency procedures, methods and materials for containment and clean up.
7	Handling and Storage	Precautions for safe handling, conditions for storage, including any incompatibilities.
8	Exposure Controls / Personal Protection	Exposure limits, engineering controls, personal protective equipment.
9	Physical and Chemical Properties	Appearance, odour, odour threshold, pH, melting/freezing point, boiling point and range, flash point, upper and lower flammable or explosive limits.
10	Stability and Reactivity	Reactivity, chemical stability, possible hazardous reactions, conditions to avoid, incompatible materials, hazardous decomposition products.
11	Toxicological Information	Description of various toxic effects by route of entry, including effects of acute or chronic exposure, carcinogenicity, reproductive effects, respiratory sensitization.
12	Ecological Information	Aquatic and terrestrial toxicity (if available), persistence and degradability, bioaccumulative potential, mobility in soil
13	Disposal Considerations	Safe handling and methods of disposal, including contaminated packaging.
14	Transport Information	UN number and proper shipping name, hazard classes, packing group.
15	Regulatory Information	Safety, health and environmental regulations specific to the product.
16	Other Information	Other information, including date of the latest revision of the SDS.

Figure 1.5.1: Categories of a MSDS/SDS document.

Other Terms Used in MSDS/SDS

Aspects of toxicity and how chemicals will affect a body can also be found in this resource. **Along with physical and chemical properties, you should be familiar with the terms below that could also be found in an MSDS/SDS document.**

- **Mutagen:** able to alter DNA and could result in carcinogenesis (a chemical example would be nitrosamine)
- **Carcinogen:** able to cause cancer (this can get complicated, animal and human carcinogens both exist). There are very few chemicals classified as being human carcinogens. (benzene, radon, asbestos)
- **Neurotoxin:** affects the nervous system (chemical examples include lead and mercury)

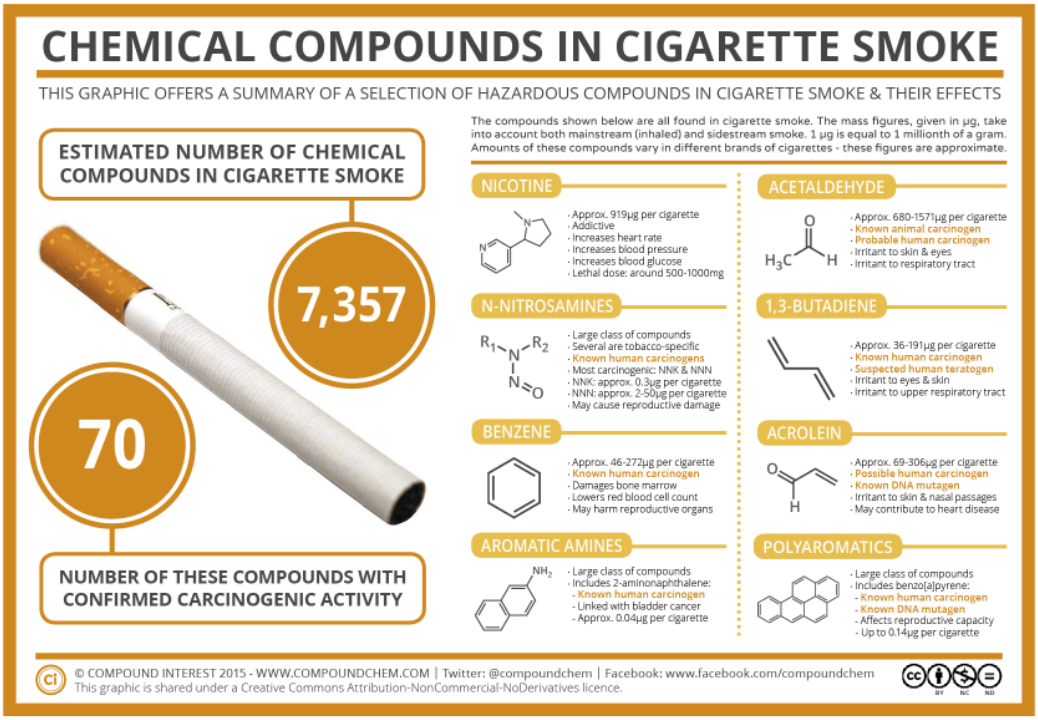


Figure **1.5.2**: Chemical Compounds in Cigarette Smoke. (CC-BY-NC-ND; Andy Brunning).

- **Teratogen**: affects developing fetus or embryo (pharmaceutical examples would be thalidomide and Accutane)
- **Corrosive**: can chemically destroy things easily (acids/bases are examples)
- **Flammable/Combustible**: able to catch on fire (examples would include gasoline and acetone)
- **Volatile**: a liquid that can transform into gas easily (examples would include gasoline and acetone)
- **LD50:** lethal dose (ingest,inhale, or inject) to kill 50% of a studied population (toxicology terminology)

MSDS/SDS's can be several pages long. A complete MSDS/SDS guide for acetic acid (also known as vinegar) can be viewed by clicking on this here. Although this chemical might appear dangerous, it used in the production of vinegar, ketchup, and barbeque sauce. *After looking over vinegar's entire MSDS/SDS sheet, write down any questions for your instructor regarding unfamiliar terminology.*

Exercise 1.5.1

After looking at the MSDS for acetic acid, answer the questions below:

a. Is this chemical a carcinogen?
b. Does acetic acid react with metals?
c. What odor does acetic acid produce?
d. If this chemical is ingested, should you induce vomiting to remove it from the body?
e. Does this chemical have a color?

Answer a

Acetic acid is not a carcinogen. It will not alter cause cancer.

Answer b

Acetic acid reacts with metals. This is a chemical property of this substance.

Answer c

Acetic acid smells like vinegar.

Answer d

Acetic acid is very corrosive and will eat biological tissues. If swallowed, vomiting should not be induced.

Answer e

This chemical is colorless



Figure 1.5.3: IARC's carcinogenic classifications. (CC-BY-NC-ND, Andy Brunning)

? Exercise 1.5.1

Read over the cigarette infographic and write down all the chemicals listed that are known human carcinogens. Research chemicals used in vapes and record these on a sheet of paper. Using the MSDS/SDS toxicological section for each chemical, record all known human carcinogens in vapes.

Answer

For traditional cigarettes, aromatic amines, nitrosamines, benzene, acetaldehyde, 1,3-butadiene, and polyaromatics. For vapes, this will vary and we will discuss this in class.

Contributors and Attributions

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1.6: All About the Elements

Learning Objectives

- Identify groups and periods on the periodic table.
- Provide an element that was named after a person and an element named after a place.
- Identify all atoms within a compound.
- Classify a compound as being organic or inorganic.
- Research an element using the link provided below.

Basic Arrangement of Periodic Table

In Chapter 3, we will delve more into the initial construction and modifications of today's periodic table. For now, you need to be aware that the periodic table has columns (known as **families**/**groups**). Horizontal rows are called **periods**. On the table below, the element symbols are either one or two letters. Previously, some of the newly discovered elements (see period seven on other tables) used three-letter symbols. These three-letter symbols corresponded to a Latin numbering system until the elements were given official names.

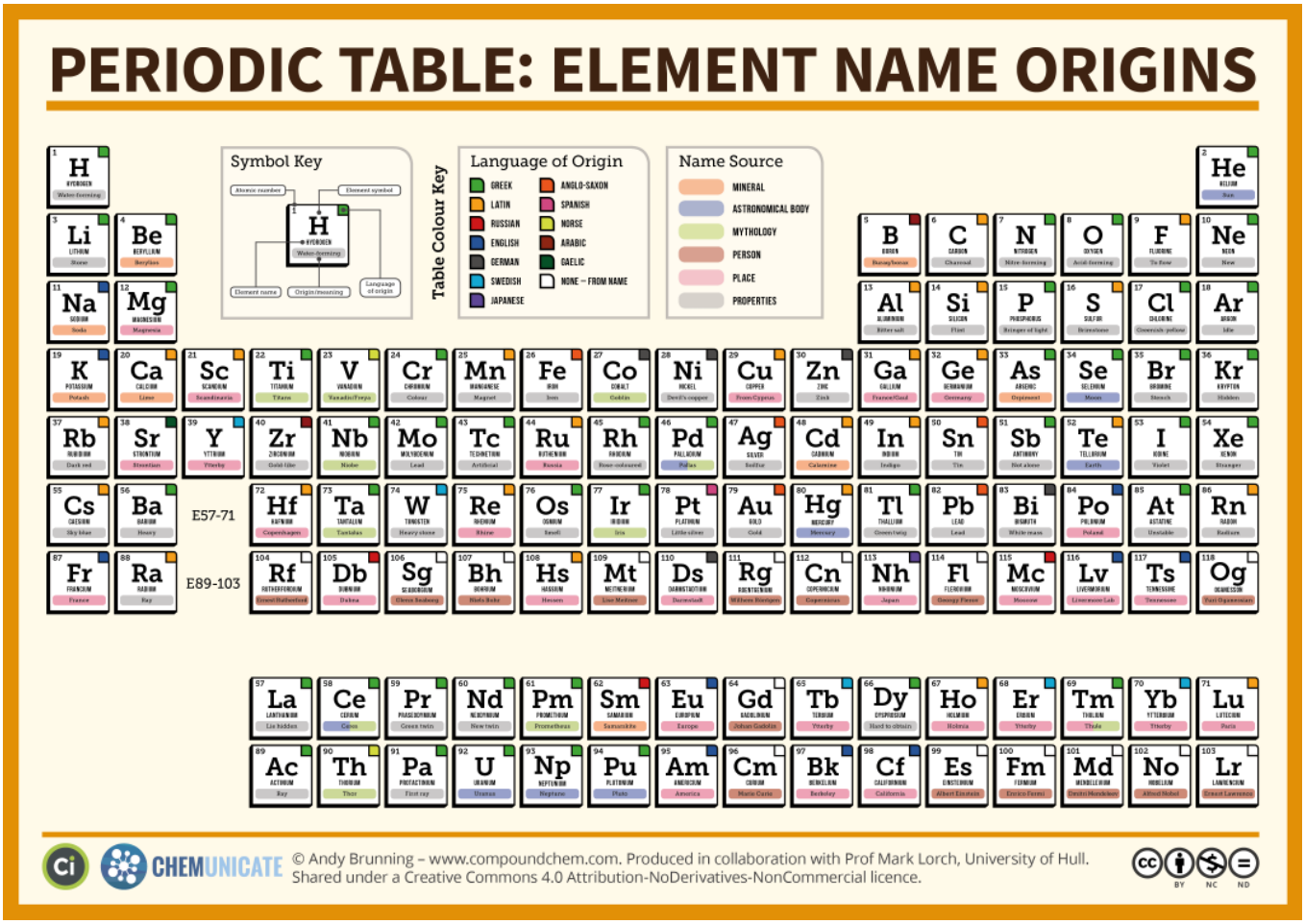
Languages of Element Names

Interestingly, different languages are used on the periodic table. Depending on your background, you might be more familiar with some elemental symbols than others. *For* example, Hydrogen is represented by the symbol H. This element's name is derived from the Greek hydro, and genes which means to generate water. Other elemental symbols like copper (which has a symbol of Cu) are not so predictable. This particular element's name originated from the Latin *cuprum* (from the island of Cyprus). A variety of languages are displayed on the periodic table. For example, Swiss roots are present in the element Tungsten. The symbol for this element is W which corresponds to the Swedish word, wolfram. **For this particular class, you will find a list of required elements/symbols that need to be memorized. Please locate this document on the moodle page for this course.**

Meanings of Element Names

Many elements are named in honor of people. Some familiar names you might see are curium (Marie and Pierre Curie), einsteinium (Albert Einstein), and mendelevium (Dimitri Mendeleev). IUPAC (International Union of Pure and Applied Chemistry) requires these types of names to be done posthumously. In other words, the scientist who discovered the element could not name it after her/himself or anyone who is still currently living. Over the years, there have been two exceptions. The elements of seaborgium (Sg) and oganesson (Og) were named while Glen Seaborg and Yuri Oganessian were still living. Seaborgium was named in honor of an American nuclear chemist who synthesized the element plutonium. He is also credited with assisting the discovery of other elements like c, americium (element 95), curium (element 96), and fermium (element 100). His accomplishments encouraged his fellow researcher, Albert Ghiorso, to name Seaborgium in honor of him. As for element 118 (oganessian), a joint research commission of Russian and American scientists named this element for Russian physicist, Yuri Oganessian. As of 2017, Oganessian is still living and is responsible for the discovery of superheavy elements. **For midterm, please research an element that has not been mentioned on this page or on your list to be memorized. By accessing this link, information about a selected element can be obtained. You will need to provide the symbol and interesting factoid for five-point question.**

It is acceptable to name an element in honor of a geographical location. Some notable Earth locations would include Am (americium, American continent), Ge (germanium, Germany), Fr (francium, France), and Eu (europium, European continent). Some scientists have ventured past Earth to name their elements in honor of other places. Examples of these would include Pu (plutonium, Pluto), U (uranium, Uranus), and Np (neptunium, Neptune).



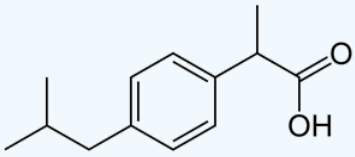
Example 1.6.1

List the element names contained in the compounds below. Classify each compound as being organic or inorganic.

a. Na_2SO_4

b. HCl

c. $Cu(NO_3)_2 \cdot H_2O$

d. 

e. CO_2

Solution

a. sodium, sulfur, and oxygen. This compound is inorganic.

b. hydrogen and chlorine. This compound is inorganic

c. copper, nitrogen, oxygen, and hydrogen. This compound is inorganic.

d. The corners of each line drawing represent carbons. You can assume for the single lines, the carbons have hydrogens attached (organic chemists tend not to draw all atoms). This compound is organic and contains carbon, hydrogen, and oxygen.

e. carbon and oxygen. This compound is inorganic.

Example 1.6.2

Locate and name all the elements you see below in the compounds that are given below. Circle the organic compounds.

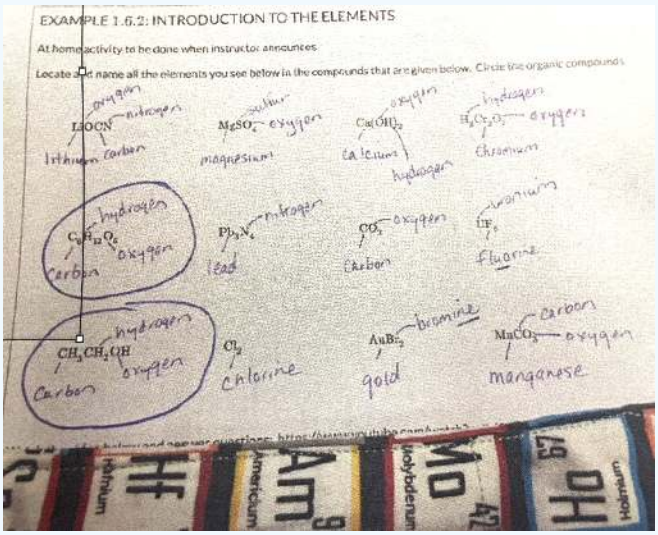
$LiOCN$	$MgSO_4$	$Ca(OH)_2$	$H_2Cr_2O_7$
$C_6H_{12}O_6$	Pb_3N_4	CO_2	UF_6
CH_2CH_2OH	Cl_2	$AuBr_2$	$MnCO_3$

Recently, elements 113-118 received their official names. Watch this ACS video and answer the questions below.

a. How were the last four elements made?
b. How many total elements do we have now?
c. How many elements are named in honor of female scientists?
d. What would you name your new element and what would its symbol be?

Answer

(elements only)



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CHAPTER OVERVIEW

2: The Mathematics of Chemistry

Mathematics is used widely in chemistry and are absolutely necessary to explore important concepts in chemistry. Without some basic mathematics skills, these calculations, and therefore chemistry itself, will be extremely difficult. However, with a basic knowledge of some of the mathematics that will be used in your chemistry course, you will be well prepared to deal with the concepts and theories of chemistry.

2.1: Measuring Matter

2.2: Dimensional Analysis

2.3: Density

2.4: Temperature

2.E: The Mathematics of Chemistry (Exercises)

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2.1: Measuring Matter

Learning Objectives

- Connect basic glassware and equipment with metric units.
- Provide SI units for mass, temperature, and length.
- Practice scientific notation and calculator skills (entering powers of ten).
- Memorize or place the bolded conversion factors on your reference card.

A variety of instruments are available for making direct measurements of the macroscopic properties of a chemical substance. For example, we usually measure the **volume** of a liquid sample with pipettes, burets, graduated cylinders, and volumetric flasks (Figure **2.1.1**), whereas we usually measure the mass of a solid or liquid substance with a balance (Figure **2.1.2**).

Instruments that Measure Volume

Many academic scientists report their volume measurements with the milliliter unit. On the other hand, analytical chemists tend to work with much smaller volumes, and they would use nanoliter and microliter samples in their laboratory. When considering the industrial realm, scientists work with larger volumes and would thus employ the liter unit of measurement. Scientists use beakers and flasks to contain liquids. For measuring this type of matter, graduated cylinders and pipettes are utilized.

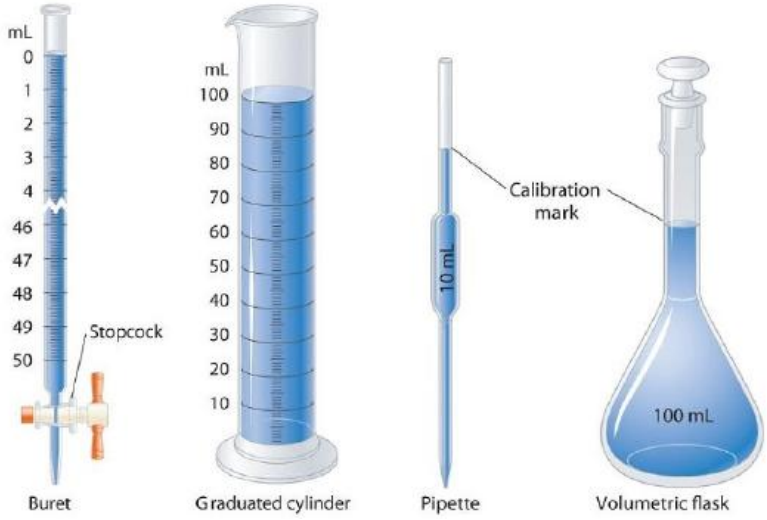


Figure **2.1.1**: (left two) Graduated glassware is used to deliver variable volumes of liquid. (right two) Volumetric glassware is used to deliver (pipette) or contain (volumetric flask) a single volume accurately when filled to the mark. (CC BY-SA-NC 3.0; anonymous).

Instruments that Measure Mass

Balances are utilized to measure the **mass** of matter. Typically, high school and middle schools will use triple beam balances for laboratory activities. Colleges will rely on digital balances. For larger quantities of materials, top-loading digital balances are employed. For higher sensitivity and accuracy, some chemists use analytical balances.



Figure 2.1.2: Triple beam balance (image from: upload.wikimedia.org/wikiped...m_balance2.JPG. Digital top-loading balance (upload.wikimedia.org/wikiped...00-2M_-_01.jpg) and an analytical balance (upload.wikimedia.org/wikiped...-NaCl-1mol.jpg)

In the academic laboratory (like Furman University's), a chemist will commonly use the gram, or the even smaller unit, the milligram. Industrial chemists making larger quantities of material would work with kilograms of materials. Analytical chemists (industrial or academic), environmental scientists, and toxicologists are typically more concerned with the smaller units of the metric system. For example, many chemicals found in drinking water and air are regulated in concentrations like nanograms and or micrograms.

Tools that Measure Length

Length is measured using a metric stick or a metric ruler marked in millimeters and centimeters. Most devices used to measure length (in the United States) contain both English and metric markings.

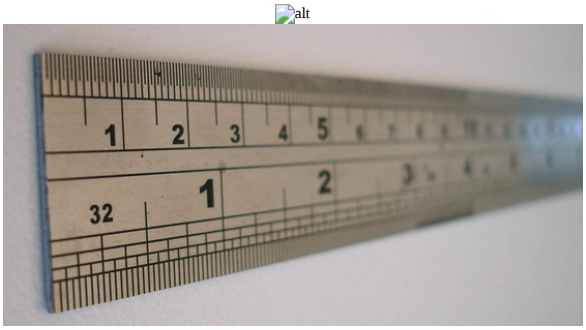


Figure 2.1.3: Metric and English measuring devices. (CC BY-SA 4.0; Ejay).

SI Units

All reported measurements must include an appropriate unit of measurement. To say that a substance has "a mass of 10" does not tell whether the mass was measured in grams, pounds, tons, or some other unit. For example, a nurse giving morphine to a patient needs to be specific in the unit dosages. A volume of liters would kill a patient quickly while a milliliter amount would provide sufficient pain relief. To establish worldwide standards for the consistent measurement of significant physical and chemical properties, an international body called the General Conference on Weights and Measures devised the Système Internationale d'unités (or SI). The International System of Units is based on metric units and requires that measurements be expressed in decimal form. Table 2.1.1 lists the seven base units of the SI system; all other SI units of measurement are derived from them.

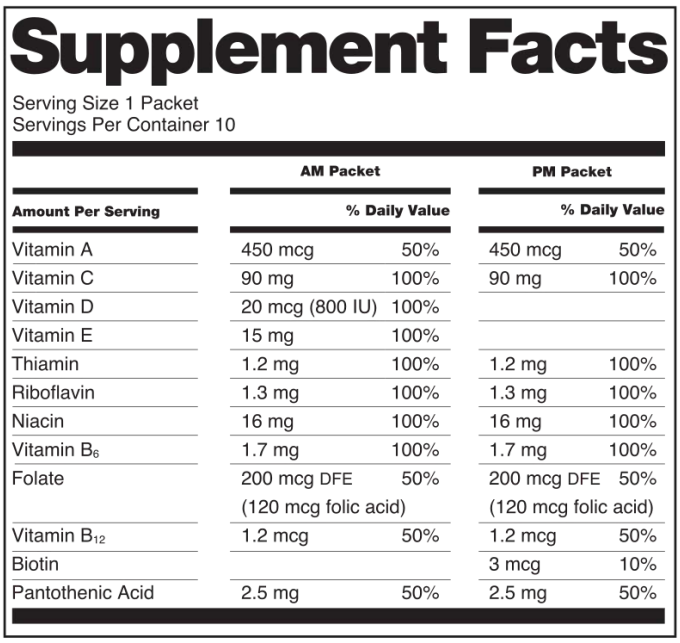
Table 2.1.1: *SI Units*

Base Quantity	Unit Name	Abbreviation
mass	**kilogram**	**kg**
length	**meter**	**m**
time	**second**	**s**
temperature	**Kelvin**	**K**
amount of substance	mole	mol
intensity of light	candela	cd

The Metric System

Table **2.1.2**: *Prefixes Used with metric bases of meter, liter, and gram*

Prefix	Symbol	Value	Power of 10	Meaning
tera	T	1,000,000,000,000	10^{12}	trillion
giga	**G**	**1,000,000,000**	**10^{9}**	**billion**
mega	**M**	**1,000,000**	**10^{6}**	**million**
kilo	**k**	**1000**	**10^{3}**	**thousand**
hecto	h	100	10^{2}	hundred
deca	da	10	10^{1}	ten
—	—	1 (this is base unit which could be gram, liter, or meter)	10^{0}	one
deci	d	0.1	10^{-1}	tenth
centi	**c**	**0.01**	**10^{-2}**	**hundredth**
milli	**m**	**0.001**	**10^{-3}**	**thousandth**
micro	**μ (medical community uses mcg)**	**0.000001**	**10^{-6}**	**millionth**
nano	**n**	**0.000000001**	**10^{-9}**	**billionth**
pico	p	0.000000000001	10^{-12}	trillionth
femto	f	0.000000000000001	10^{-15}	quadrillionth



Supplement Facts

Serving Size 1 Packet
Servings Per Container 10

	AM Packet		PM Packet	
Amount Per Serving		**% Daily Value**		**% Daily Value**
Vitamin A	450 mcg	50%	450 mcg	50%
Vitamin C	90 mg	100%	90 mg	100%
Vitamin D	20 mcg (800 IU)	100%		
Vitamin E	15 mg	100%		
Thiamin	1.2 mg	100%	1.2 mg	100%
Riboflavin	1.3 mg	100%	1.3 mg	100%
Niacin	16 mg	100%	16 mg	100%
Vitamin B_6	1.7 mg	100%	1.7 mg	100%
Folate	200 mcg DFE (120 mcg folic acid)	50%	200 mcg DFE (120 mcg folic acid)	50%
Vitamin B_{12}	1.2 mcg	50%	1.2 mcg	50%
Biotin			3 mcg	10%
Pantothenic Acid	2.5 mg	50%	2.5 mg	50%

Ingredients: Sodium ascorbate, ascorbic acid, calcium pantothenate, niacinamide, dl-alpha tocopheryl acetate, microcrystalline cellulose, dextrin, starch, mono- and diglycerides, vitamin A acetate, magnesium stearate, gelatin, FD&C Blue #1, FD&C Red #3, artificial colors, thiamin mononitrate, pyridoxine hydrochloride, citric acid, lactose, sorbic acid (preservative), tricalcium phosphate, sodium benzoate (preservative), sodium caseinate, preservatives (methylparaben, potassium sorbate, BHA, BHT), ergocalciferol, cyanocobalamin, and artificial flavors.

Figure **2.1.4**: Example of Supplement Facts by the FDA. (Public Domain, FDA.gov)

Two methods of Memorization for the Metric System

Using negative exponents (see above) is the traditional way to memorize the metric system. Many students who have been taught outside of the United States approach the metric system this way. For their conversion factors, students who have been taught the metric system in the United States tend to use positive exponents. Either method is fine, pick one method and use it consistently.

Two different ways to memorize the metric systems (be sure to know all bolded conversion factors listed in section 2.1 of this OER)

1 gigabase = 1 x10^9 base
1 megabase = 1x10^6 base
1 kilobase = 1x10^3base

- **1 centibase = 1x10^{-2}base** **or 1x10^2 centibase = 1 base**
- **1 millibase = 1x10^{-3}base** **or 1x10^3 millibase = 1 base**
- **1 microbase = 1x10^{-6}base** **or 1x10^6 microbase = 1 base**
- **1 nanobase = 1x10^{-9}base** **or 1x10^9 nanobase = 1 base**

Note: A base unit can be gram (mass), meter (length), volume (liter), and joules (energy).

Additional Units

When traveling to different regions of the globe, it is helpful to be able to convert from English to Metric units. **Please be sure to commit the bolded conversions below to memory**.

Unit Conversion
2.21 pounds = 1.00 kilograms
1 mile = 1.61 kilometers
1.00 inch = 2.54 centimeters
1.00 mL = 1.00 cc (cubic centimeters) = 1.00 cm^3
1 teaspoon (tsp) = 5.00 mL
12 in = 1.00 ft.
16 oz. = 1.00 pounds

Scientific Notation

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

$$N \times 10^n$$

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

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

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

Another way to remember this is to recognize that as the number N decreases in magnitude, the exponent increases, and vice versa. The application of this rule is illustrated in Example **2.1.1**.

Example 2.1.1: scientific notation

Convert each number to scientific notation.

a. 637.8
b. 0.0479
c. 7.86
d. 12,378
e. 0.00032
f. 61.06700
g. 2002.080
h. 0.01020

Solution

Explanation	Solution
To convert 637.8 to a number from 1 to 10, we move the decimal point two places to the left: 6.378 Because the decimal point was moved two places to the left, n = 2.	$637.8 = 6.378 \times 10^{2}$
To convert 0.0479 to a number from 1 to 10, we move the decimal point two places to the right: 4.79 Because the decimal point was moved two places to the right, n = −2.	$0.0479 = 4.79 \times 10^{-2}$
This is usually expressed simply as 7.86. (Recall that $10^{0} = 1$).	7.86×10^{0}
Move the decimal point four places to the left and note a positive exponent.	1.2378×10^{4}
Move the decimal place four places to the right a note a negative exponent.	3.2×10^{-4}
Move the decimal place one space to the left and note a positive exponent.	6.106700×10^{1}
Move the decimal place three places to the left and note a positive exponent.	2.002080×10^{3}
Move the decimal place two places to the right and note a negative exponent.	1.020×10^{-2}

Using the Scientific Calculator

Please be sure to obtain a calculator that has an exponent button on it. It will either say "exp" or have an "ee" key indicating this function. This key represents the function of 10^{x}. You do not need to enter a 10 for an exponent when using this particular function. Read the steps below and practice on your calculator.

Use of Calculator

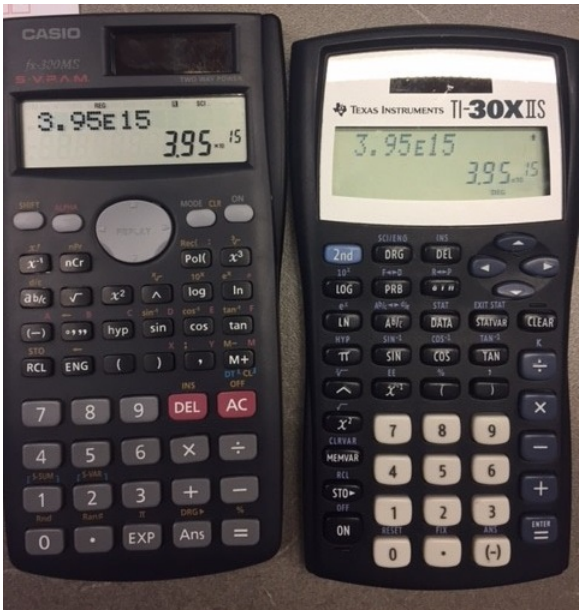
To input powers of ten:

1. Locate the ee or exp button on your calculator. Do not use the carrot (looks like the ^ button).
2. Put the coefficient number in and then hit "ee" or "exp."
3. If you need to have a negative "exp," then locate the +/- or small - button.
4. Lastly, input your power of ten. You do not need to put the actual number ten in for the exponent.

Table **2.1.3**: *Examples*

Number	**How to Input in a calculator**
3.95×10^{15}	Put 3.95 in as the coefficient number. Hit the "ee" or "exp" button. Lastly, enter the 15 for the exponent. Your calculator should say $3.95e^{15}$.
9.26×10^{-4}	Put 9.26 in as the coefficient number. Hit the "ee" or "exp" button. Locate the small +/- button for negative (not minus function). Next, enter the number four. Your calculator should say $9.26e^{-4}$.

This is an image of suggested calculators for CHM101. You will need a non-programmable, scientific calculator that does not have metric conversion functions. In this picture, you will see the correct way to input one of the numbers shown in the example above. Please take time to practice with your calculator before tests and quizzes.



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2.2: Dimensional Analysis

Learning Objective

- Convert metric and English based units.
- Report converted values in correct scientific notation with the corresponding units.
- Master using your calculator.

Conversion Factors

We have an expression,

$$\frac{3\,ft}{1\,yd} = 1 \tag{2.2.1}$$

Equation 2.2.1 is a strange way to write 1, but it makes sense: 3 ft equal 1 yd, so the quantities in the numerator and denominator are the same quantity, just expressed with different units. The expression in Equation 2.2.1 is called a conversion factor and it is used to formally change the unit of a quantity into another unit. (The process of converting units in such a formal fashion is sometimes called *dimensional analysis* or the *factor label method*.)

To see how this happens, let us start with the original quantity: $4\,yd$ and let us multiply this quantity by 1. Rather than multiplying by just 1, let us write 1 as

$$1 = \frac{3\,ft}{1\,yd}$$

When you multiply anything by 1, you don't change the value of the quantity.

$$\begin{aligned} 4\,yd &= 4\,yd \times 1 \\ &= 4\,yd \times \frac{3\,ft}{1\,yd} \end{aligned}$$

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

$$4\,\cancel{yd} \times \frac{3\,ft}{1\,\cancel{yd}}$$

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

$$\frac{4 \times 3\,ft}{1} = \frac{12\,ft}{1} = 12\,ft$$

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

How many millimeters are in 14.66 m? To answer this, we need to construct a conversion factor between millimeters and meters and apply it correctly to the original quantity. One method would entail using the conversion factor of $1\,mm = 1 \times 10^{-3}\,m$

$$14.66\,\cancel{m} \times \frac{1\,mm}{10^{-3}\,\cancel{m}} = 14660\,mm \tag{2.2.2}$$

$$= 1.46 \times 10^{4}\,mm \tag{2.2.3}$$

Which conversion factor do we use? The answer is based on *what unit you want to get rid of in your initial quantity*. The original unit of our quantity is meters, which we want to convert to millimeters. Because the original unit is assumed to be in the numerator, to get rid of it, we want the meter unit in the *denominator*; then they will cancel. Using the positive metric exponents, we have an alternative method to calculate the same answer as shown previously. Canceling units and performing the mathematics, we get:

$$14.66 \cancel{m} \times \frac{1000\,mm}{1\,\cancel{m}} = 14660\,mm \tag{2.2.4}$$

$$= 1.46 \times 10^4\,mm \tag{2.2.5}$$

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

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

Example 2.2.1

a. Convert 35.9 kL to liters.
b. Convert 555 nm to meters.

Solution

a. We will use the fact that 1 kL = 1,000 L. Of the two conversion factors that can be defined, the one that will work is 1000L/1kL. Applying this conversion factor, we get:

$$35.9 \cancel{kL} \times \frac{1000\,L}{1\,\cancel{kL}} = 35,900\,L$$

b. We will use the fact that 1 nm = 1/1,000,000,000 m, which we will rewrite as 1,000,000,000 nm = 1 m, or 10^9 nm = 1 m. Of the two possible conversion factors, the appropriate one has the nm unit in the denominator:

$$\frac{1\,m}{10^9\,m}$$

Applying this conversion factor, we get

$$555 \cancel{nm} \times \frac{1\,m}{10^9\,\cancel{nm}} = 0.000000555\,m$$

$$= 5.55 \times 10^{-7}\,m$$

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

Exercise 2.2.1

a. Convert 67.08 µL to liters.
b. Convert 56.8 m to kilometers.

Answer a

6.708×10^{-5} L

Answer b

5.68×10^{-2} km

Exercise 2.2.2

How many milliliters are in 607.8 kL?

Answer

This problem involves multiple steps that require going through the metric base of liters. Think of a pathway of a conversion before setting up these types of problems. The suggested pathway would be mL ⇒ L ⇒ kL

$$607.8\,kL \times \frac{1000\,L}{1\,kL} = 6.08 \times 10^5\,L$$
$$= 6.08 \times 10^5\,L \frac{1000\,mL}{1\,L}$$
$$= 608000000\,mL$$
$$= 6.08 \times 10^8\,mL$$

? Exercise 2.2.3

Kathleen Hsu Barron (Furman University, Class of 2011) is exploring Switzerland with her husband Patrick Barron (Furman University, Class of 2011). The sign she is pointing to is a typical speed in km/hr. Convert this distance to miles/hr and feet/hr.



Figure **2.2.1**: Kathleen Hsu Barron standing by speed limit sign. (CC-BY-NC-ND, Patrick Barron)

Answer

Again, this problem is a multi-step problem. There are multiple ways that one could proceed to solve this problem. With the conversion factors in this course, the suggested round would be miles ⇒ kilometers ⇒ meters ⇒ centimeters ⇒ inches ⇒ feet. Another method could utilize miles ⇒ feet.

18.6 miles/hr, 9.8 x 10^4 ft/hr

In this course, we will not use significant figures. You will need to read the directions on your assignment, quiz, or test and round accordingly.

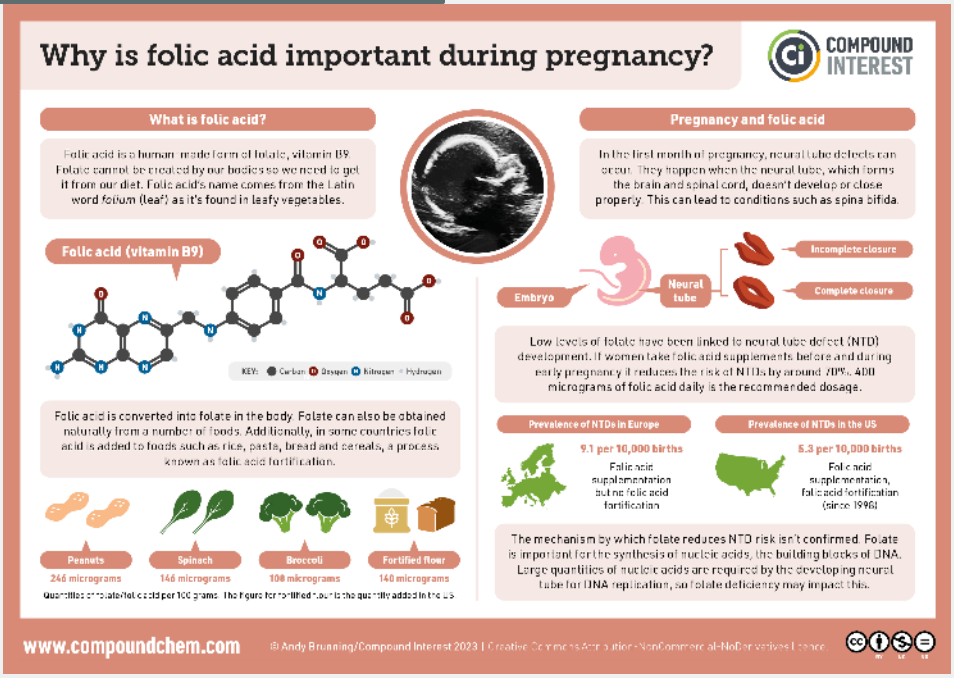


Figure **2.2.2**: Why is folic acid important in pregnancy. (CC-BY-NC-ND, Andy Brunning).

Question: The FDA recommends taking 0.400 mg of folic acid a day before pregnancy. How many micrograms is this dosage? Hint- think of the pathway mg⇒? ⇒μg

Need More Practice?

- Turn to Section 2.E of this OER and work problems #1, #3, #5, #6, and #8.

Contributors and Attributions

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2.3: Density

Learning Objectives

- Calculate density, mass, or volume when given 2 of these three variables.
- Identify what units are required for the density equation.
- Review metric conversions.
- Compare densities of different chemical substances.
- Classify a substance as being a heterogeneous or homogeneous mixture if solubility date is provided.
- Identify where a chemical would appear in water if solubility and density data are provided.
- Compare any chemical substance's density to the density of water (please memorize this value).

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

$$\text{density} = \frac{\text{mass}}{\text{volume}} \tag{2.3.1}$$

$$d = \frac{m}{V} \tag{2.3.2}$$

Density is usually a measured property of a substance, so its numerical value affects the significant figures in a calculation. Notice that density is defined in terms of two dissimilar units, mass and volume. That means that density overall has *derived units*, just like velocity. Common units for density include g/mL, g/cm^3, g/L, kg/L, and even kg/m^3. Densities for some common substances are listed in Table **2.3.1**. **Memorize the density of water with its appropriate units**.

Table **2.3.1**: Densities of Some Common Substances

Substance	Density (g/mL or g/cm^3)
water	**1.0**
gold	19.3
mercury	13.6
air	0.0012
cork	0.22–0.26
aluminum	2.7
iron	7.87



Figure **2.3.1**: Separatory Funnel containing oil and colored water to display density differences. (CC BY-SA 3.0; PRHaney via Wikipedia).

Because of how it is defined, density can act as a conversion factor for switching between units of mass and volume. For example, suppose you have a sample of aluminum that has a volume of 7.88 cm^3. How can you determine what mass of aluminum you have without measuring it? You can use the volume to calculate it. If you multiply the given volume by the known density (Table **2.3.1**), the volume units will cancel and leave you with mass units, telling you the mass of the sample:

Start with Equation 2.3.1

$$\text{density} = \frac{m}{V}$$

and insert the relevant numbers

$$\frac{2.7g}{cm^3} = \frac{m}{7.88\,cm^3}$$

Cross multiplying both sides (right numerator x left denominator = left numerator x right denominator), we get the following expression with answer and appropriate unit.

$$7.88\,\cancel{cm^3} \times \frac{2.7\,g}{\cancel{cm^3}} = 21g \text{ of aluminum}$$

Example 2.3.1: Mercury

What is the mass of 44.6 mL of mercury? If you need to review how to isolate variables, please click here for a short tutorial.

Solution

Use the density value for mercury from Table **2.3.1** and the definition of density (Equation 2.3.1)

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

$$\frac{13.6g}{mL} = \frac{m}{44.6\,mL}$$

Remember to cross multiply here in order to isolate variable. Then, report answer with correct units.

$$44.6\,\cancel{mL} \times \frac{13.6\,g}{\cancel{mL}} = 607\,g$$

The mass of the mercury is 607 g.

? Exercise 2.3.1

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

Answer

Use the density value for iron from Table 2.3.1

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

$$\frac{7.87g}{cm^3} = \frac{m}{25.0\,cm^3}$$

Cross multiplying both sides (right numerator x left denominator = left numerator x right denominator), we get the following expression with answer and appropriate unit.

$$25.0\,\cancel{cm^3} \times \frac{7.87\,g}{\cancel{cm^3}} = 197g \text{ of iron}$$

Another way of looking at density (some students choose to perform calculations using this method)

Density can also be used as a conversion factor to convert mass to volume—but care must be taken. We have already demonstrated that the number that goes with density normally goes in the numerator when density is written as a fraction. Take the density of gold, for example:

$$d = 19.3\,g/mL = \frac{19.3\,g}{mL}$$

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

$$d = 19.3\,g/mL = \frac{19.3\,g}{mL}$$

That is, the density value tells us that we have 19.3 grams for every 1 milliliter of volume, and the 1 is an exact number. When we want to use density to convert from mass to volume, the numerator and denominator of density need to be switched—that is, we must take the *reciprocal* of the density. In so doing, we move not only the units but also the numbers:

$$\frac{19.3\,\cancel{g}}{mL} = \frac{45\,\cancel{g}}{V}$$

Cross multiplying denominators with numerators, we obtain the following algebraic equation.

$$19.3V = 45.9\,mL$$

then you will need to isolate the variable (volume)

$$V = \frac{45.9\,mL}{19.3}$$

After multiplication, the answer would be

$$V = 2.38\,mL$$

✔ Example 2.3.2: Wine Cork

A cork stopper from a bottle of wine has a mass of 3.78 g. If the density of cork is 0.22 g/mL, what is the volume of the cork? *Regardless of the method that is used, you should still be able to obtain the same (and correct) answer.*

Solution

To use density as a conversion factor, we need to take the reciprocal so that the mass unit of density is in the denominator. Taking the reciprocal, we find

$$\frac{0.22\ \cancel{g}}{mL} = \frac{3.78\ \cancel{g}}{V}$$

Cross multiplying denominators with numerators, we obtain the following algebraic equation.

$$0.22V = 3.78\,mL$$

then you will need to isolate the variable (volume)

$$V = \frac{3.78\,mL}{0.22}$$

so, the volume of the cork is 17.2 mL.

? Exercise 2.3.2

What is the volume of 3.78 g of gold?

Answer

Before attempting this question, be sure to obtain the density of gold in the table above. If you were to need this value on a quiz or a test, then it would be provided. Once you have this value, plug it into the density equation. Next, you will need to isolate the volume variable (basic algebra). The final answer should be 0.196 cm^3.

Care must be used with density as a conversion factor. Make sure the mass units are the same or the volume units are the same, before using density to convert to a different unit. Often, the unit of the given quantity must be first converted to the appropriate unit before applying density as a conversion factor.

Using Density in Environmental Applications

Along with solubility, density can help determine how a contaminant could affect an aquatic system. For example, imagine mercury has been spilled in Furman Lake. Looking at this element's density value and comparing it to liquid water, one could determine the location of the insoluble (you would be given solubility information) mercury layer. The more dense mercury layer would reside on the bottom of Furman Lake. If one were to take a cross-section of the lake, you could see that a heterogeneous mixture would result.

In contrast, spilling ethanol (density = 0.789g/mL) would result in the formation of a homogeneous mixture. Ethanol (grain alcohol) is soluble in water. This would make it miscible (mixable to form a solution) in water and one would not be able to denote separate layers. According to the density, an alcohol layer would remain on top, but would ultimately dissolve.

Applications

What difficulties would arise from the separation and removal of contaminants?

1. Hg in Furman Lake
2. Ethanol in Furman Lake
3. oil (less dense, insoluble) in Furman Lake

Watch this video and record your observations.

1. What component was different in the two types of beverages (mass or volume)?
2. How does the above-mentioned difference affect the density equation?
3. Which beverage is denser than water?

Need More Practice?

- Turn to Section 2.E of this OER and work problems #2 and #9.

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2.4: Temperature

Learning Objectives

- Learn about the various temperature scales that are commonly used in chemistry and other cultures.
- Memorize temperature equations for **Celsius, Kelvin, and Fahrenheit conversions**.
- Differentiate between various thermometers (alcohol or mercury-based).
- Understand how body temperature can vary.
- Provide some examples of how cryogenics is used in the real-world.

Temperature Scales

One of the fundamental quantities in science is temperature, which is a measure of the average amount of energy of motion, or *kinetic energy*, a system contains. Temperatures are expressed using scales that use units called degrees. There are three scales used for reporting temperatures. Figure **2.4.1** compares the three temperature scales.

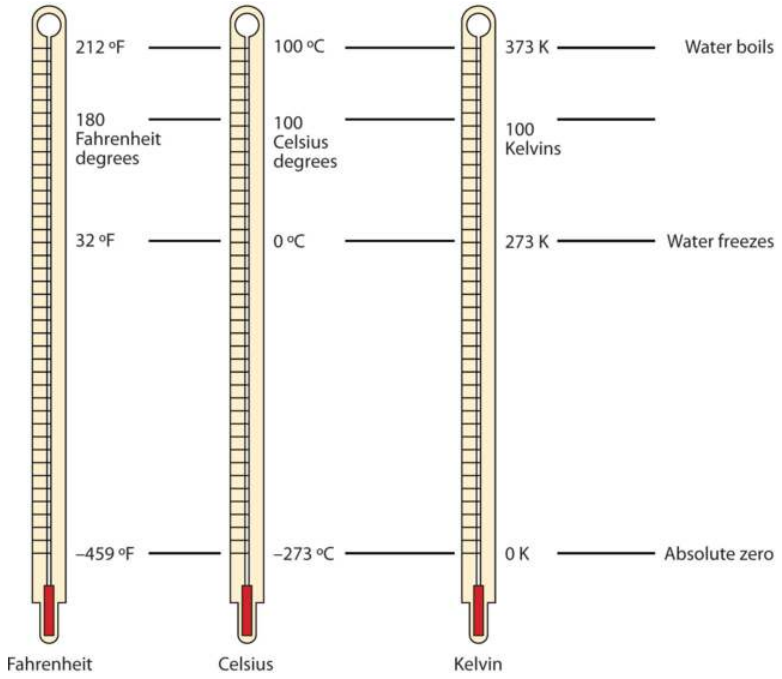


Figure **2.4.1**: Fahrenheit, Celsius, and Kelvin Temperatures. A comparison of the three temperature scales. These thermometers have a red-colored liquid which contains alcohol and food coloring. Silver looking thermometers contain mercury, which is a neurotoxin.

In the United States, the commonly used temperature scale is the *Fahrenheit scale* (symbolized by °F and spoken as “degrees Fahrenheit”). On this scale, the freezing point of liquid water (the temperature at which liquid water turns to solid ice) is 32 °F, and the boiling point of water (the temperature at which liquid water turns to steam) is 212 °F.

Science also uses other scales to express temperature. For example, the Celsius scale (symbolized by °C and spoken as “degrees Celsius”) defines 0°C as the freezing point of water and 100 °C as the boiling point of water. This scale is divided into 100 divisions between these two landmarks and extended higher and lower as well. By comparing the Fahrenheit and Celsius scales, a conversion between the two scales can be determined:

$$^{\circ}C = (^{\circ}F - 32) \times \frac{5}{9} \tag{2.4.1}$$

$$^{\circ}F = \left(^{\circ}C \times \frac{9}{5}\right) + 32 \tag{2.4.2}$$

Note that science uses the Celsius and Kelvin scales almost exclusively; virtually no practicing chemist expresses laboratory-measured temperatures with the Fahrenheit scale. (In fact, the United States is one of the few countries in the world that still uses the Fahrenheit scale on a daily basis. People driving near the borders of Canada or Mexico may pick up local radio stations on the other side of the border that express the daily weather in degrees Celsius, so do not get confused by their weather reports.)

Example 2.4.1: Conversions

a. What is 98.6°F in degrees Celsius?
b. What is 25.0°C in degrees Fahrenheit?

Solution

a. Using Equation 2.4.1, we have

$$\begin{aligned} ^\circ C &= (98.6 - 32) \times \frac{5}{9} \\ &= 66.6 \times \frac{5}{9} \\ &= 37.0^\circ C \end{aligned}$$

b. Using Equation 2.4.2, we have

$$\begin{aligned} ^\circ F &= (25.0 \times \frac{9}{5}) + 32 \\ &= 45.0 + 32 \\ &= 77.0^\circ F \end{aligned}$$

For more examples of how to perform these types of problems, click on this video to see your professor in action.

Exercise 2.4.1

a. Convert 0°F to degrees Celsius.
b. Convert 212°C to degrees Fahrenheit.

Answer a

−17.8°C

Answer b

414°F

The fundamental unit of temperature in SI is the Kelvin (K). The Kelvin temperature scale (note that the name of the scale capitalizes the word *Kelvin*, but the unit itself is lowercase) uses degrees that are the same size as the Celsius degree, but the numerical scale is shifted up by 273.15 units. That is, the conversion between the Kelvin and Celsius scales is as follows:

$$K =^\circ C + 273.15 \tag{2.4.3}$$

For most purposes, it is acceptable to use 273 instead of 273.15 in Equation 2.4.3.

Note that the Kelvin scale does not use the word *degrees*; a temperature of 295 K is spoken of as “two hundred ninety-five kelvin” and not “two hundred ninety-five degrees Kelvin.”

The reason that the Kelvin scale is defined this way is that there exists a minimum possible temperature called absolute zero (zero Kelvin). The Kelvin temperature scale is set so that 0 K is absolute zero, and the temperature is counted upward from there. Normal room temperature is about 295 K, as seen in the following example.

Example 2.4.2: Room Temperature

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

Solution

First, we use Equation 2.4.1 to determine the temperature in degrees Celsius:

$$\begin{aligned} ^{\circ}C &= (72.0 - 32) \times \frac{5}{9} \\ &= 40.0 \times \frac{5}{9} \\ &= 22.2^{\circ}C \end{aligned}$$

Then we use Equation 2.4.3 to determine the temperature in the Kelvin scale:

$$\begin{aligned} K &= 22.2^{\circ}C + 273.15 \\ &= 295.4K \end{aligned}$$

So, room temperature is about 295 K.

Health APPlication: Body temperature

Normal body temperature is defined as being 98.6°F (+/- 1.0°F). To determine body temperature, thermometers can be placed inside or on the surface of the body. The two best methods of obtaining body temperature are placing the thermometer either under the tongue or inside the rectum. Typically, children are capable of holding a thermometer in their mouths around the age of four (have fun before that age).

Fever is defined as body temperature being above 100°F (adults). High fever status occurs at and above 104°F. For adults, these adults should seek medical attention immediately if the fever exceeds 104°F. For children, these values are much lower.

Hyperthermia (inability of the body to regulate heat) occurs when normal body temperature is exceeded. Conditions that can cause hyperthermia are fever (infection), heat stroke, thyroid disorders, heart attack, or traumatic injury. Medications for cancer, arthritis, and thyroid patients can cause the body temperature to rise. Symptoms of hyperthermia include sweating, confusion, nausea, and dizziness.

Hypothermia (exposure to cold environments) occurs when normal body temperature dips below 95.0°F. When this occurs, the affected person(s) should seek immediate medical attention. During hypothermia, the body has problems producing heat. Medical conditions like diabetes, infection, and thyroid dysfunction can cause hypothermia. Watch this video of American Marines attempting to survive extreme environments. Symptoms of this condition involve shivering, confusion, and sluggish behavior.

Treating hyperthermia could involve hydrating a patient. If a fever is due to infection, analgesics (like Tylenol, Advil, aspirin, or Aleve) can help alleviate fever. Placing someone in a cool bath can also relieve symptoms.

To combat hypothermia, one must remove wet clothing, redress in warm materials, and participate in physical movement.

The Science of Cryogenics

Cryogenics is branch of physics that incorporates the production and effects of substances at temperatures ranging between -150ºC to -273°C. In the late 1870's, cryogenic science began with the cooling of gaseous oxygen. At -183ºC, O_2 condensed from a clear gas into a blue liquid. Changing the state of oxygen enables it to be transported easier. Both the aircraft and medical industries rely on the liquid form of this molecule to provide breathable oxygen for pilots, travelers, and patients.



Figure **2.4.2**: Liquid oxygen (O_2) exhibits a bluish hue.

Besides oxygen, other gases have been condensed as well. These permanent gases, meaning these substances normally exist in the gaseous state, include nitrogen (N_2), hydrogen (H_2), chlorine (Cl_2), and helium (He). By manipulating pressure and/or temperature, many chemists and physicists have attempted to produce the lowest, theoretical temperature possible. At absolute zero (-273°C or 0 K), the particles of a material have a minimum kinetic energy. Click on this video to determine if scientists can ever reach absolute zero in their laboratories.

Investigating a Cryogenic material: N_2 (l)

With a boiling point of -196°C (-321°F), liquid nitrogen has a variety of cryogenic uses. This clear, odorless liquid is used widely in the field of dermatology. For patients that have warts, skin tags (see image below), or precancerous moles, physicians can spray a selected area of skin. Typically, the unwanted skin lesion will fall off the body after being exposed to this cryogenic material. If this does not occur, then the dermatologist will use a scalpel to remove the frozen area of skin.



Figure **2.4.1**: Liquid nitrogen is stored in insulated flasks called Dewars. Image courtesy of Elizabeth R. Gordon

Liquid N_2 is also utilized to freeze biological samples. Fertility clinics freeze semen, eggs, and embryos that can be used at a later date for couples who chose to undergo InVitro Fertilization (IVF). Umbilical cord blood and stem cells can be preserved in liquid nitrogen for future applications.

Culinary Arts employ liquid nitrogen for preparing various dishes and interesting cocktails. In the following video, chefs are freezing components of salads and desserts for their customers. When using liquid nitrogen for any application, chemists, chefs, and other individuals should protect their skin and eyes from the extremely cold (-196ºC) temperature. Wearing thick rubber gloves and goggles can prevent frostbite. When ingesting materials that have been frozen with liquid nitrogen, there is

concern that internal burns can occur. Lastly, indoor use of liquid nitrogen could induce asphyxiation. Kitchens and labs should have adequate ventilation to ensure sufficient oxygen remains in the atmosphere.



Video **2.4.2**: At the Bazaar restaurant: Cooking with liquid nitrogen, more

References

- https://www.bbc.com/news/magazine-19870668
- https://ehs.research.uiowa.edu/liqui...rogen-handling

Need More Practice?

- Turn to Section 2.E of this OER and work problems #4, #7, and #10.

Contributors and Attributions

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2.E: The Mathematics of Chemistry (Exercises)

End of Chapter Exercises

1) Convert 45.0 cm^3 to L.

2) Acetone (CH_3COCH_3) has a density of .791g/mL. Assuming this compound is soluble in water, how many grams are present in 3.0 L of acetone. If acetone was spilled in Furman Lake, what would you expect to see and how would this be classified in the matter scheme (element,compound, heterogeneous, or homogeneous mixture?

3) Convert the distance from Greenville, South Carolina to Atlanta, Georgia. The measured length of the trip is approximately 235 kilometers. Convert this distance to meters and miles.

4) In January, the average temperature of eastern Siberia is -50°C. Calculate this temperature in Fahrenheit and Kelvin. Of the three temperature units, which one is the SI unit for temperature. (Kelvin temperature answer is incorrect on answer key should be 223.15K)

5) The mass of an adult human eyeball is 7.5 grams. Convert this value to kilograms and ounces. What type of lab equipment is used to measure mass?

6) How many milliliters and gallons are contained in a 2.0L Coca-Cola drink? (1 gallon = 3.79 L)

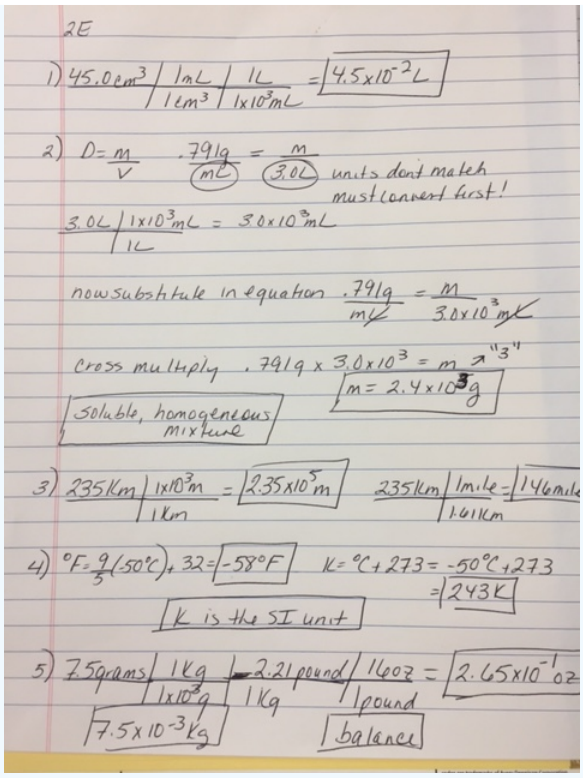
7) Convert your body temperature to °F and K.

8) Your cat needs .5 tsp of Tylenol. How many milliliters is this dosage?

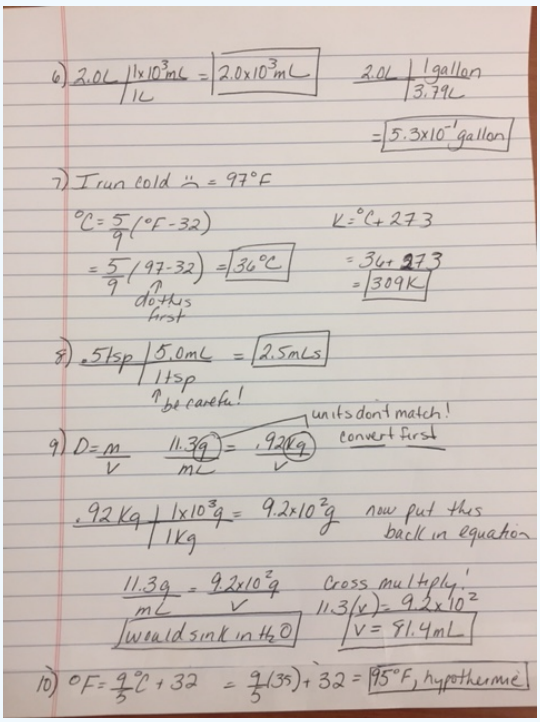
9) The density of lead is 11.3g/mL. If you measured out .92 kg, how many milliliters would this mass displace? Based upon density only, would you expect lead to sink or float in water?

10) If you have a body temperature of 35°C, are you hypothermic or hyperthermic?

Solutions



*** #4 should be 223K***



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CHAPTER OVERVIEW

3: Atoms and the Periodic Table

3.1: Basic Atomic Theory

3.2: Development of the Modern Periodic Table

3.3: Subatomic Particles - Electrons, Protons, and Neutrons

3.4: Atomic Mass and Atomic Number

3.5: Isotopes

3.6: The Importance of Ions to a Chemist

3.E: Atoms and the Periodic Table (Exercises)

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3.1: Basic Atomic Theory

Learning Objectives

- Give a short history of the concept of the atom.
- Describe the contributions of Democritus and Dalton to atomic theory.
- Summarize Dalton's atomic theory and explain its historical development.

Democritus and the Greek Philosophers

Around 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 substances were connected as a single, big, unchangeable "thing." Democritus was one of the first people to propose the term "atoms." As an alternative to the beliefs of the Greek philosophers, he suggested that **atomos**, or atomon - tiny, indivisible, solid objects - make up all matter in the universe.



Figure **3.1.1**: Democritus by Hendrick ter Brugghen, 1628. Democritus was known as the "laughing philosopher." It was a good thing he liked to laugh, because most other philosophers were laughing at his theories.

Early Greek philosophers tried to understand the nature of the world through reason and logic, 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 many 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 many discoveries that they could have made otherwise. Greek philosophers dismissed Democritus' theory entirely. Unfortunately, it took over two millennia before the theory of atomos (or "atoms," as they're known today) was fully accepted.



Video **3.1.1**: Since ancient Greek times, philosophers and scientists have tried to figure out what an atom looks like. For a couple thousand years, humans could only speculate on the structure and other properties of the smallest unit of matter. It wasn't until the 1980s that chemists could see individual atoms. Bestselling author Sam Kean takes us through the nearly 2,400-year quest to see the atom in a new episode of the "Legends of Chemistry" series.

While it must be assumed that many more scientists, philosophers, and others studied composition of matter after Democritus, a major leap forward in our understanding of the composition of matter took place in the 1800's with the work of the British

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

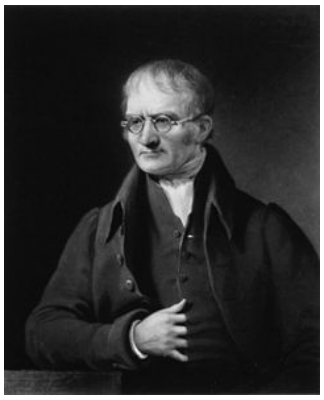


Figure **3.1.3**: British physicist and chemist John Dalton (1766-1844). Unlike the greek philosophers, John Dalton believed in both logical thinking and experimentation.

Dalton studied the weights of various elements and compounds. He noticed that matter always combined in fixed ratios based on weight, or volume in the case of gases. Chemical compounds always contain the same proportion of elements by mass, regardless of amount, which provided further support for Proust's law of definite proportions. Dalton also observed that there could be more than one combination of two elements.

From his experiments and observations, as well as the work from peers of his time, Dalton proposed a new theory of the atom (1803). This later became known as Dalton's **atomic theory**. The published (1808) tenets of this theory were as follows:

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

Dalton's Eyes

As a scientist, John Dalton was also interested in colorblindness. Both he and his brother suffered from red/green colorblindness. At this time (1794), no other scientist had explored this medical issue. He devised theories (although not correct) as to why he could not differentiate between red and green. In addition, he named this medical condition "Daltonism." Upon his death (1844), he donated his eyes to a medical research facility in Manchester, England. Today, his eyes are still on display at the Museum of Science and Industry in Manchester, England.



Figure **3.1.3**: Image taken from: https://c1.staticflickr.com/3/2823/1...37dd23af_b.jpg

The evidence for atoms is so great that few doubt their existence. In fact, individual atoms are now routinely observed with state-of-the art technologies. Moreover, atoms can even be used for making pretty images or as IBM research demonstrate in Video **3.1.2**, control of individual atoms can be use used create animations. A Boy and His Atom is a 2012 stop-motion animated short film released by IBM Research. The movie tells the story of a boy and a wayward atom who meet and become friends. It depicts a boy playing with an atom that takes various forms. It was made by moving carbon monoxide molecules viewed with a scanning tunneling microscope, a device that magnifies them 100 million times. These molecules were moved to create images, which were then saved as individual frames to make the film.



Video **3.1.2**: A Boy And His Atom: The World's Smallest Movie

Dalton was not completely correct

Dalton's atomic theory has been largely accepted by the scientific community, with the exception of three changes. We know now that:

1. An atom is composed of smaller particles (electrons, protons, and neutrons).
2. All atoms of an element are not identical. The existence of isotopes illustrates this phenomena.
3. Through the use of nuclear reactions, atoms of one element can be changed into atoms of another element.

The first two will be be discussed later in this chapter, while the last requires introducing "nuclear chemistry" and will be discussed in a different chapter.

References

1. https://pubs.acs.org/subscribe/archi...3chemchron.pdf

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3.2: Development of the Modern Periodic Table

Learning Objectives

- Appreciate how the modern periodic table was constructed.
- Explain how elements are organized into the periodic table.
- Describe how some characteristics of elements relate to their positions on the periodic table.
- Distinguish between the A (atomic mass) value and the Z (atomic number) value when viewing the periodic table.
- Compare and contrast Mendeleev's and Moseley's ordering of the periodic table.

In 1864, Julius Lothar Meyer, a German chemist, organized the elements by atomic mass and grouped them according to their chemical properties. Later that decade, Dmitri Mendeleev, a Russian chemist, organized all the known elements according to similar properties. He left gaps in his table for what he thought were undiscovered elements, and he made some bold predictions regarding the properties of those undiscovered elements. When elements were discovered whose properties closely matched Mendeleev's predictions, his version of the table gained favor in the scientific community. Because certain properties of the elements repeat regularly throughout the table (that is, they are periodic), it became known as the periodic table.

	4 werthig	3 werthig	2 werthig	1 werthig	1 werthig	2 werthig
	-	-	-	-	Li = 7,03	(Be =9,3?)
Differenz =	-	-	-	-	16,02	(14,7)
	C = 12,0	N = 14,04	O = 16,00	Fl = 19,0	Na = 23,05	Mg = 24,0
Differenz =	16,5	16,96	16,07	16,46	16,08	16,0
	Si = 28,5	P = 31,0	S = 32,07	Cl = 35,46	K = 39,13	Ca = 40,0
Differenz =	89,1 /2 = 44,55	44,0	46,7	44,51	46,3	47,6
	-	As = 75,0	Se = 78,8	Br = 79,97	Rb =85,4	Sr = 87,6
Differenz =	89,1 /2 = 44,55	45,6	49,5	46,8	47,6	49,5
	Sn = 117,6	Sb = 120,6	Te = 128,3	J =126,8	Cs = 133,0	Ba = 137,1
Differenz =	89,4 = 2*44,7	87,4 = 2*43,7	-	-	(71 = 2*35,5)	-
	Pb = 207,0	Bi = 208,0	-	-	(Tl = 204?)	-

Figure **3.2.1**: Copy of table on page 137 of (Julius) Lothar Meyer: "Die modernen Theorien der Chemie" (1864). (Copyright;By Kawarayaki - Own work, CC BY-SA 4.0, https://commons.wikimedia.org/w/inde...curid=75552705)

Dimitri Mendeleev (1834–1907)

The father of the modern periodic table, Dmitri Mendeleev was born in Siberia. He was the youngest of fourteen living children. Shortly after Dmitri's birth, his father lost his sight. When Dmitri was thirteen, his father died suddenly. His mother was left to manage the family's glass factory to support the family. In 1848, their glass factory burned down leaving the family with little resources. Dmitri's mother chose to take her son to St. Petersburg, Russia. Here, he would study chemistry at his father's alma mater (Main Pedagogical Institute which is not called St. Petersburg University). After several illnesses and his mother's death, he would earn his doctorate in chemistry in 1865.

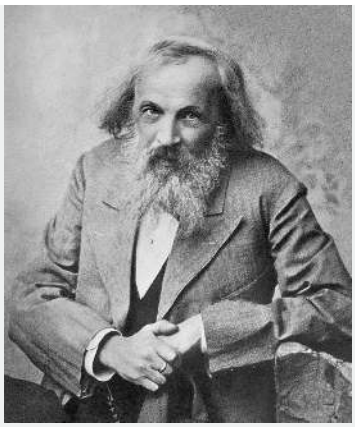


Figure **3.2.2**: Dmitri Mendeleev, the father of the modern periodic table.

From 1867 to 1890, Dmitri served as a professor of general chemistry at St. Petersburg University. In his lifetime, he published more than 400 articles and books. Two of these works were noted in textbooks of general and organic chemistry.

As for his personal life, Dmitri Mendeleev married twice (his first marriage ended in a controversial divorce). Dmitri fathered a total of six children from both marriages. In 1907, he passed away from influenza complications. He was honored for his works by having element 101 (Mendelevium) named for him. Watch the video below to see how Mendeleev ordered his table of elements.



Mendeleev's Periodic Table

Mendeleev, who first published his periodic table in 1869 (Figure **3.2.1**), is usually credited with the origin of the modern periodic table. The key difference between his arrangement of the elements and that of Meyer and others is that Mendeleev did not assume that all the elements had been discovered (actually, only about two-thirds of the naturally occurring elements were known at the time). Instead, he deliberately left blanks in his table at atomic masses 44, 68, 72, and 100, in the expectation that elements with those atomic masses would be discovered. Those blanks correspond to the elements we now know as scandium, gallium, germanium, and technetium.

Reihen	Gruppe I. — R^2O	Gruppe II. — RO	Gruppe III. — R^2O^3	Gruppe IV. RH^4 RO^2	Gruppe V. RH^3 R^2O^5	Gruppe VI. RH^2 RO^3	Gruppe VII. RH R^2O^7	Gruppe VIII. — RO^4
1	H=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	— =44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63.
5	(Cu=63)	Zn=65	— =68	— =72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	— =100	Ru=104, Rh=104, Pd=106, Ag=108.
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Ce= 40	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199.
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	
12	—	—	—	Th=231	—	U=240	—	— — — —

Figure **3.2.3**: Mendeleev's Periodic Table, as Published in the German Journal Annalen der Chemie und Pharmacie in 1872. The column headings "Reihen" and "Gruppe" are German for "row" and "group." Formulas indicate the type of compounds formed by each group, with "R" standing for "any element" and superscripts used where we now use subscripts. Atomic masses are shown after equal signs and increase across each row from left to right.

The groups in Mendeleev's table are determined by how many oxygen or hydrogen atoms are needed to form compounds with each element. For example, in Group I (referred to as Gruppe 1), two atoms of each element (hydrogen, lithium, potassium) bond with one atom of oxygen to form compounds. In Group VII (Gruppe VI), one atom of fluorine, F, chlorine, Cl, and bromine, Br, reacts with one atom of hydrogen to form respective compounds. According to Mendeleev, elements in the same column of the periodic table produced similar types of compounds. This trend could not predict the types of hydrogen/oxygen-based compounds resulting from the middle section of the periodic table. Mendeleev had difficulty explaining the chemical nature of this part of the table now referred to as the transition metals.

The most convincing evidence in support of Mendeleev's arrangement of the elements was the discovery of two previously unknown elements whose properties closely corresponded with his predictions (Table **3.2.1**). Two of the blanks Mendeleev had left in his original table were below aluminum and silicon, awaiting the discovery of two as-yet-unknown elements, eka-aluminum and eka-silicon (from the Sanskrit eka, meaning "one," as in "one beyond aluminum"). The observed properties of gallium and germanium matched those of eka-aluminum and eka-silicon so well that once they were discovered, Mendeleev's periodic table rapidly gained acceptance.

When the chemical properties of an element suggested that it might have been assigned the wrong place in earlier tables, Mendeleev carefully reexamined its atomic mass. He discovered, for example, that the atomic masses previously reported for beryllium, indium, and uranium were incorrect. The atomic mass of indium had originally been reported as 75.6, based on an assumed stoichiometry of InO for its oxide. If this atomic mass were correct, then indium would have to be placed in the middle of the nonmetals, between arsenic (atomic mass 75) and selenium (atomic mass 78). Because elemental indium is a silvery-white *metal*, however, Mendeleev postulated that the stoichiometry of its oxide was really In_2O_3 rather than InO. This would mean that indium's atomic mass was actually 113, placing the element between two other metals, cadmium, and tin.

Table **3.2.1**: Comparison of the Properties Predicted by Mendeleev in 1869 for eka-Aluminum and eka-Silicon with the Properties of Gallium (Discovered in 1875) and Germanium (Discovered in 1886)

Property	*eka*-Aluminum (predicted)	Gallium (observed)	*eka*-Silicon (predicted)	Germanium (observed)
atomic mass	68	69.723	72	72.64
element	metal	metal	dirty-gray metal	gray-white metal
	low mp*	mp = 29.8°C	high mp	mp = 98°C
	d = 5.9 g/cm^3	d = 5.91 g/cm^3	d = 5.5 g/cm^3	d = 5.323 g/cm^3
oxide	E_2O_3	Ga_2O_3	EO_2	GeO_2
	d = 5.5 g/cm^3	d = 6.0 g/cm^3	d = 4.7 g/cm^3	d = 4.25 g/cm^3
chloride	ECl_3	$GaCl_3$	ECl_4	$GeCl_4$
	volatile	mp = 78°C bp* = 201°C	bp < 100°C	bp = 87°C

*mp = melting point; bp = boiling point.

One group of elements absent from Mendeleev's table is the noble gases, all of which were discovered more than 20 years later, between 1894 and 1898, by Sir William Ramsay (1852–1916; Nobel Prize in Chemistry 1904). Initially, Ramsay did not know where to place these elements in the periodic table. Argon, the first to be discovered, had an atomic mass of 40. This was greater than chlorine's and comparable to that of potassium, so Ramsay, using the same kind of reasoning as Mendeleev, decided to place the noble gases between the halogens and the alkali metals.

The Role of the Atomic Number in the Periodic Table

Despite its usefulness, Mendeleev's periodic table was based entirely on empirical observation supported by very little understanding. It was not until 1913, when a young British physicist, H. G. J. Moseley (1887–1915), while analyzing the frequencies of x-rays emitted by the elements, discovered that the underlying foundation of the order of the elements was by the *atomic number*, not the atomic mass. Moseley hypothesized that the placement of each element in his series corresponded to its atomic number Z, which is the number of positive charges (protons) in its nucleus. Argon, for example, although having an atomic mass greater than that of potassium (39.9 amu versus 39.1 amu, respectively), was placed *before* potassium in the periodic table. While analyzing the frequencies of the emitted x-rays, Moseley noticed that the atomic number of argon is 18, whereas that of potassium is 19, which indicated that they were indeed placed correctly. Moseley also noticed three gaps in his table of x-ray frequencies, so he predicted the existence of three unknown elements: technetium (Z = 43), discovered in 1937; promethium (Z = 61), discovered in 1945; and rhenium (Z = 75), discovered in 1925.

H. G. J. Moseley (1887–1915)

Moseley left his research work at the University of Oxford to join the British army as a telecommunications officer during World War I. He was killed during the Battle of Gallipoli in Turkey.



Figure **3.2.4**:G.J. Moseley

Features of the Periodic Table

Elements that have similar chemical properties are grouped in columns called groups (or families). As well as being numbered, some of these groups have names—for example, *alkali metals* (the first column of elements), *alkaline earth metals* (the second column of elements), *halogens* (the next-to-last column of elements), and *noble gases* (the last column of elements). The word *halogen* comes from the Greek for "salt maker" because these elements combine with other elements to form a group of compounds called salts.

Each row of elements on the periodic table is called a **period**. Periods have different lengths; the first period has only 2 elements (hydrogen and helium), while the second and third periods have 8 elements each. The fourth and fifth periods have 18 elements each, and later periods are so long that a segment from each is removed and placed beneath the main body of the table.

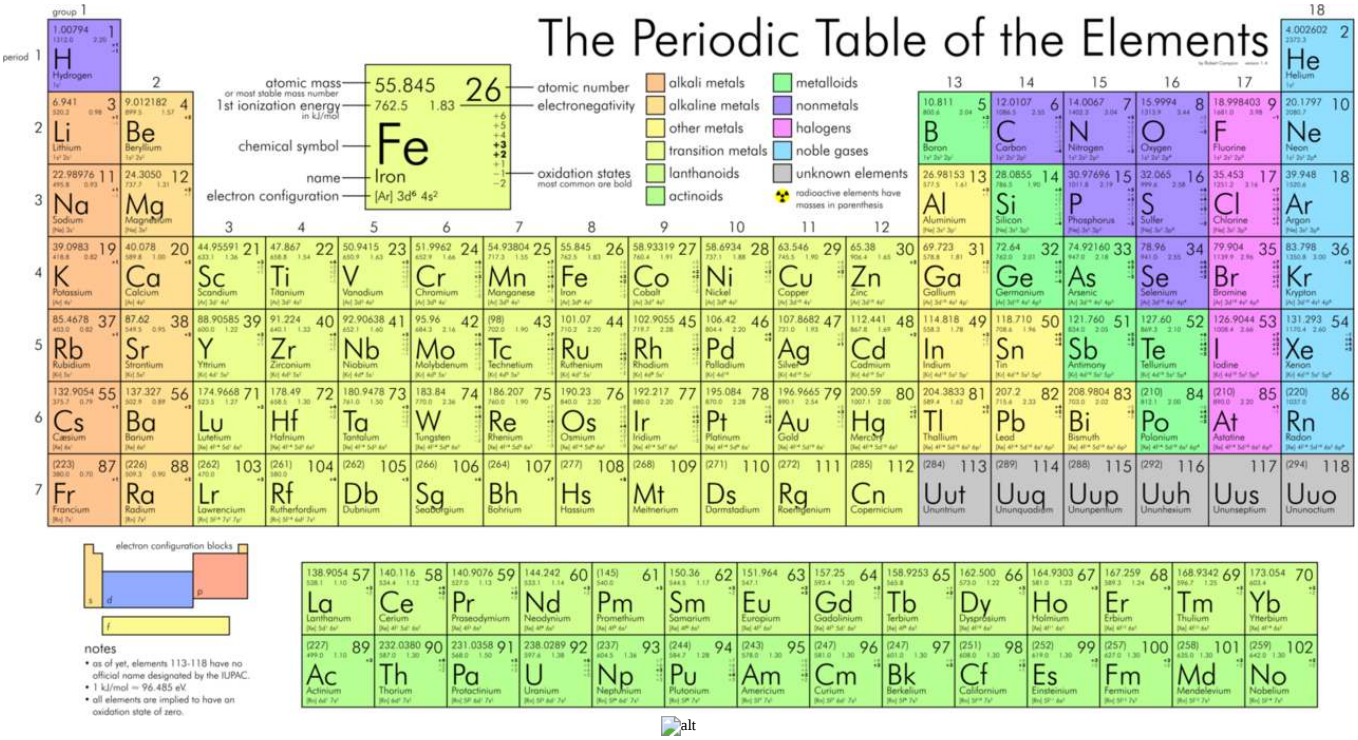


Figure **3.2.5**: Types of Elements. Elements are either metals, nonmetals, or metalloids. Each group is located in a different part of the periodic table. An interactive Periodic table can be found here. (Public Domain; 2012rc).

Certain elemental properties become apparent in a survey of the periodic table as a whole. Every element can be classified as either a metal, a nonmetal, or a metalloid (or semi-metal), as shown in Figure **3.2.5**. A **metal** is a substance that is shiny, typically (but not always) silvery in color, and an excellent conductor of electricity and heat. Metals are also malleable (they can be beaten into thin

sheets) and ductile (they can be drawn into thin wires). A **nonmetal** is typically dull and a poor conductor of electricity and heat. Solid nonmetals are also very brittle. As shown in Figure **3.2.5**, metals occupy the left three-fourths of the periodic table, while nonmetals (except for hydrogen) are clustered in the upper right-hand corner of the periodic table. The elements with properties intermediate between those of metals and nonmetals are called **metalloids**. Elements adjacent to the bold line in the right-hand portion of the periodic table have semimetal properties.

Example 3.2.1

Based on its position in the periodic table, classify each element below as metal, a nonmetal, or a metalloid.

a. Se
b. Mg
c. Ge

Solution

a. In Figure **3.2.5**, selenium lies above and to the right of the diagonal line marking the boundary between metals and nonmetals, so it should be a nonmetal.
b. Magnesium lies to the left of the diagonal line marking the boundary between metals and nonmetals, so it should be metal.
c. Germanium lies within the diagonal line marking the boundary between metals and nonmetals, so it should be a metalloid.

The first two columns on the left and the last six columns on the right are called the main group elements. The ten-column block between these columns contains the **transition metals**. The two rows beneath the main body of the periodic table display the **inner transition metals**. The elements in these two rows are also referred to as, respectively, the **lanthanide metals** and the **actinide metals**.

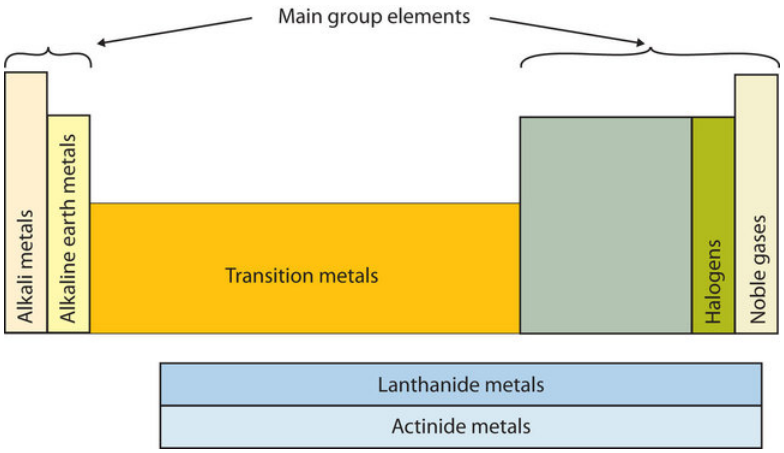


Figure **3.2.6**: Some sections of the periodic table have specific names. Be sure to know the section names for quizzes and tests.

Descriptive Names

As previously noted, the periodic table is arranged so that elements with similar chemical behaviors are in the same group. Chemists often make general statements about the properties of the elements in a group using descriptive names with historical origins. To watch a video of your instructor presenting these groups and periods, access your Moodle class chapter 3 documents.

Group 1: The Alkali Metals

The alkali metals are lithium, sodium, potassium, rubidium, cesium, and francium. Hydrogen is unique in that it is generally placed in Group 1, but it is not a metal. The compounds of the alkali metals are common in nature and daily life. One example is table salt (sodium chloride); lithium compounds are used in greases, in batteries, and as drugs to treat patients who exhibit manic-depressive, or bipolar, behavior. Although lithium, rubidium, and cesium are relatively rare in nature, and francium is so unstable and highly radioactive that it exists in only trace amounts, sodium and potassium are the seventh and eighth most abundant elements in Earth's crust, respectively.

Group 2: The Alkaline Earth Metals

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

Group 17: The Halogens

The halogens are fluorine, chlorine, bromine, iodine, and astatine. The name halogen is derived from the Greek words for "salt-forming," which reflects that all the halogens react readily with metals to form compounds, such as sodium chloride and calcium chloride (used in some areas as road salt). Compounds that contain fluorine ions (fluoride) are added to toothpaste and the water supply to prevent dental cavities. Fluorine is also found in Teflon coatings on kitchen utensils. Although chlorofluorocarbon propellants and refrigerants are believed to lead to the depletion of Earth's ozone layer and contain both fluorine and chlorine, the latter is responsible for the adverse effect on the ozone layer. Bromine and iodine are less abundant than chlorine, and astatine is so radioactive that it exists in only negligible amounts in nature.

Group 18: The Noble Gases

The noble gases are helium, neon, argon, krypton, xenon, and radon. Because noble gases are composed of only single atoms, they are called monatomic. At room temperature and pressure, they are unreactive gases. Because of their lack of reactivity, for many years they were called inert gases or rare gases. However, the first chemical compounds containing noble gases were prepared in 1962. Although the noble gases are relatively minor constituents of the atmosphere, natural gas contains substantial amounts of helium. Because of its low reactivity, argon is often used as an unreactive (inert) atmosphere for welding and in light bulbs. The red light emitted by neon in a gas discharge tube is used in neon lights.

Example 3.2.2: Groups

Provide the family/group names and period numbers (horizontal values)of each element.

a. Li
b. Ar
c. Ra

Solution:

a. Lithium is an alkali metal. It is located in period two.
b. Argon is a noble gas. It is located in period three.
c. Radium is an alkaline metal. It is located in period seven.

Example 3.2.3: Classification of Elements

Provide elemental names for the following combinations:

a. The alkali metal in period three.
b. The halogen in period two
c. A metalloid in period four
d. A transition metal in period three

Solution:

a. Sodium
b. Fluorine
c. Germanium or Arsenic
d. There are no transition metals in period three (gotcha!)

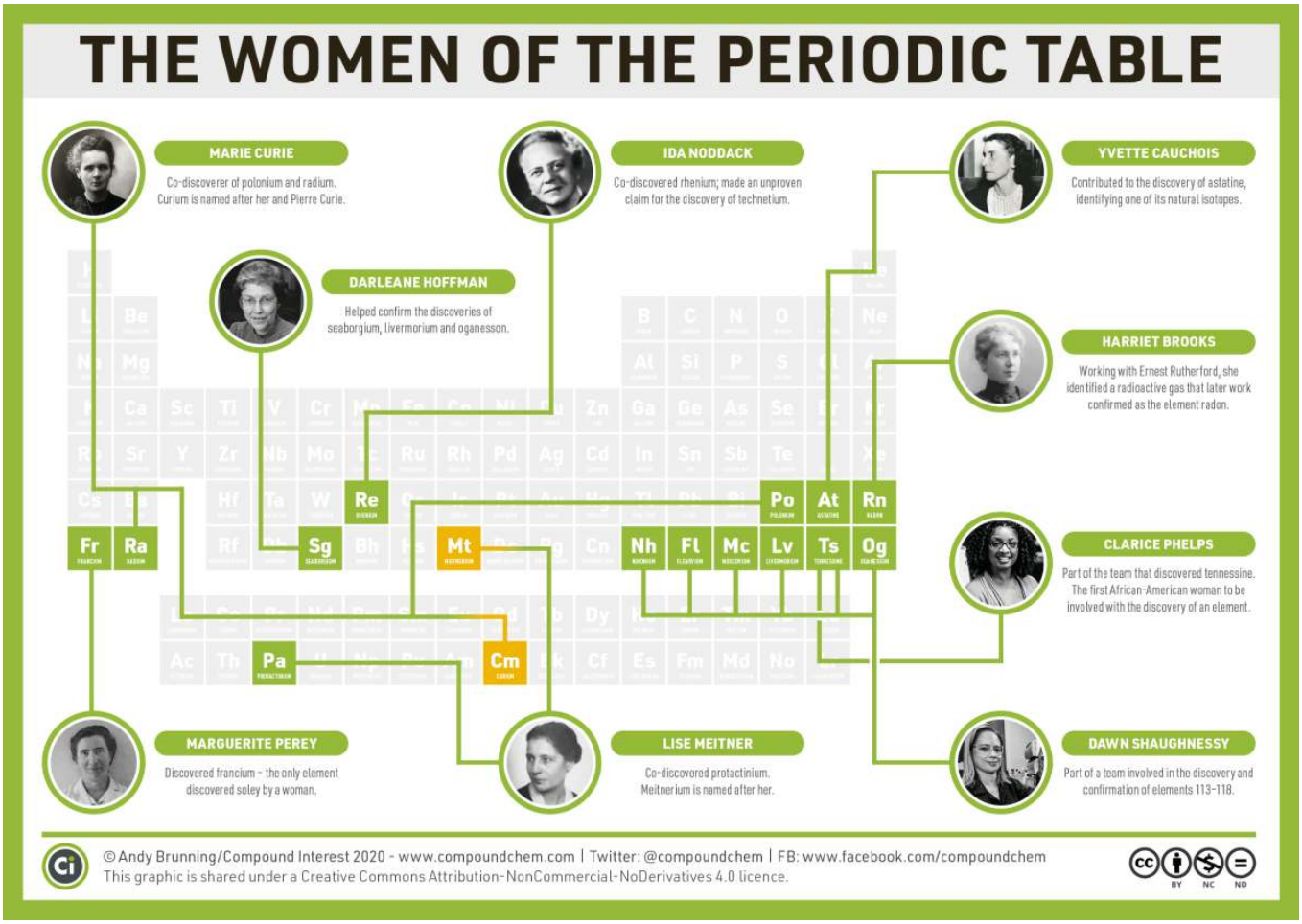


Figure **3.2.7**: The Women of the Periodic Table Graphic by Andy Brunning.

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1. Petrucci, Ralph H., William S. Harwood, F. G. Herring, and Jeffrey D. Madura. General Chemistry: Principles and Modern Applications. 9th ed. Upper Saddle River: Pearson Education, Inc., 2007.
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3. Petrucci, Ralph H., Carey Bissonnette, F. G. Herring, and Jeffrey D. Madura. General Chemistry: Principles and Modern Applications. Custom Edition for CHEM 2. Pearson Learning Solutions, 2010.

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3.3: Subatomic Particles - Electrons, Protons, and Neutrons

Learning Objectives

- Know the basics of the experiments involving the discoveries of the three subatomic particles
- Memorize relative charge values and amu masses of the three subatomic particles.
- Describe the location of the proton, electron, and neutron inside the atomic model.

Identifying and Locating the Subatomic Particles

In 1897, the British physicist J. J. Thomson (1856–1940) proved that atoms were not the most basic form of matter. His experiments involved the use of cathode ray tubes (CRT). Under a vacuumed environment, these devices produce invisible rays that originate from a negative electrode (cathode) and continue to a positive electrode (anode). In these experiments, Thomson demonstrated that cathode rays could be deflected, or bent, by magnetic or electric fields, which indicated that cathode rays consist of charged particles . More importantly, by measuring the extent of the deflection of the cathode rays in magnetic or electric fields of various strengths, Thomson was able to calculate the mass-to-charge ratio of the particles. Because like charges repel each other and opposite charges attract, Thomson concluded that the particles had a net **negative charge**; these particles are now called **electrons**. Most relevant to the field of chemistry, Thomson found that the mass-to-charge ratio of cathode rays is independent of the nature of the metal electrodes or the gas, which suggested that electrons were fundamental components of all atoms.



Video **3.3.1**: A chemistry instructor explains the nature of a cathode ray tube and the discovery of the electron.

During the 1910s, experiments with x-rays led to the useful conclusion: the magnitude of the **positive charge** in the nucleus of every atom of a particular element is the same. In other words, all atoms of the same element have the same number of **protons**. Furthermore, different elements have a different number of protons in their nuclei, so the number of protons in the nucleus of an atom is characteristic of a particular element. This discovery was so important to our understanding of atoms that the number of protons in the nucleus of an atom is now called the atomic number. These experiments were performed by Ernest Rutherford. He is credited with defining the central location of the atom, which has now been named the nucleus.

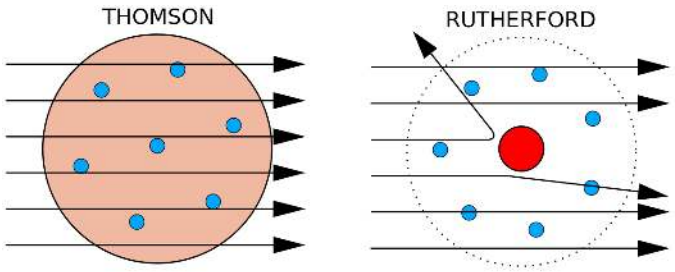


Figure **3.3.1**: Expected results: alpha particles passing through the plum pudding model of the atom with negligible deflection. Bottom: Observed results: a small portion of the particles were deflected by the concentrated positive charge of the nucleus. (Public Domain).

Rutherford was aware that the protons were inside this region. One of Ernest Rutherford's colleagues, James Chadwick, performed and studied radioactive reactions of beryllium. Upon hitting a beryllium nucleus with alpha particles, a **neutron** particle was emitted. In 1932, James Chadwick announced the existence of a third subatomic particle, the neutron. This particle has a mass of 1 atomic mass unit, but **does not have any charge**. After this discovery, nuclear science and technology started immediately.

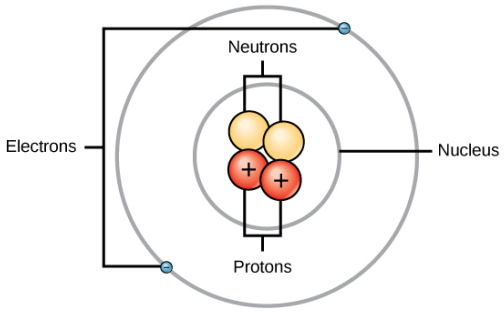


Figure **3.3.2**: Elements, such as helium, depicted here, are made up of atoms. Atoms are made up of protons and neutrons located within the nucleus, with electrons in orbitals surrounding the nucleus.

Masses for the three subatomic particles can be expressed in amu (**atomic mass units**) or grams. For simplicity, we will use the amu unit for the three subatomics. Both neutrons and protons are assigned as having masses of 1 amu each. In contrast, the electron has a negligible mass of .0005 amu. This subatomic's mass is not represented in the decimal mass that is displayed on the periodic table. Only protons and neutrons contribute to an atom's mass value.

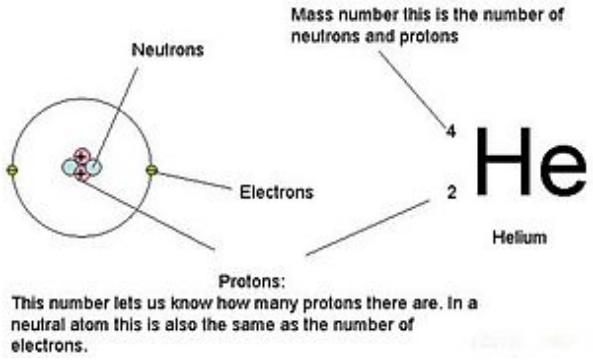


Figure **3.3.3**: An explanation of the superscripts and subscripts seen in atomic number notation. (Copyright; en:User:Materialscientist)

For atoms (neutral species), the number of electrons is equivalent to the number of protons. As a result, all atoms have an overall charge of zero. For discussion of ions (atoms that gain or lose electrons), look to the latter part of this chapter. Atoms that differ in neutron and mass values from the table are called isotopes. These particular species can be seen in the following section of the text.

Table **3.3.1**: Properties of Subatomic Particles

Subatomic particle	Symbol	Relative charge	Location	Amu mass
Proton	p	+1	inside the nucleus	1
Neutron	n	0	inside the nucleus	1
Electron	e^-	-1	outside the nucleus	0.0005 (~0)

Example 3.3.1

Which is true?

a. The nucleus contains protons and electrons.
b. The mass of an electron is included in the mass of the atom

c. For an atom, the number of protons = number of electrons.

Solution

a. False, the nucleus contains the protons and the neutrons. Electrons are outside the core.

b. False, electrons do not contribute to the mass number of an atom.

c. True, all atoms are neutral and must have the same number of protons as electrons.

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3.4: Atomic Mass and Atomic Number

Learning Outcomes

- Define atomic and mass numbers.
- Determine the number of protons, neutrons, and electrons in an atom.
- Identify the charge and relative mass of subatomic particles.
- Label the location of subatomic particles in the atom.
- Determine the mass of an atom based on its subatomic particles.
- Write A/Z and symbol-mass format for an atom.

Atoms are the fundamental building blocks of all matter and are composed of protons, neutrons, and electrons. Because atoms are electrically neutral, the number of positively charged protons must be equal to the number of negatively charged electrons. Since neutrons do not affect the charge, the number of neutrons is not dependent on the number of protons and will vary even among atoms of the same element.

Atomic Number

The **atomic number (represented by the letter Z)** *of an element is the number of protons in the nucleus of each atom of that element*. An atom can be classified as a particular element based solely on its atomic number. For example, any atom with an atomic number of 8 (its nucleus contains 8 protons) is an oxygen atom, and any atom with a different number of protons would be a different element. The periodic table (see figure below) displays all of the known elements and is arranged in order of increasing atomic number. In this table, an element's atomic number is indicated above the elemental symbol. Hydrogen, at the upper left of the table, has an atomic number of 1. Every hydrogen atom has one proton in its nucleus. Next on the table is helium, whose atoms have two protons in the nucleus. Lithium atoms have three protons, beryllium atoms have four, and so on.

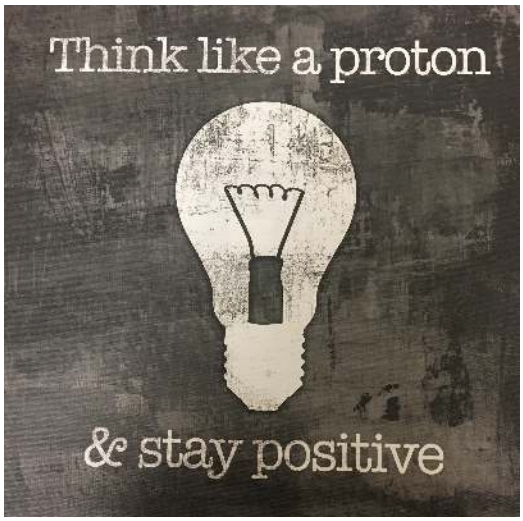


Figure 3.4.1: The social security number subatomic-the proton.

Since atoms are neutral, the number of electrons in an atom is equal to the number of protons. Hydrogen atoms all have one electron occupying the space outside of the nucleus. Helium, with two protons, will have two electrons. In the chemical classroom, the proton count will always be equivalent to an atom's atomic number. This value will not change unless the nucleus decays or is bombarded (nuclear physics).

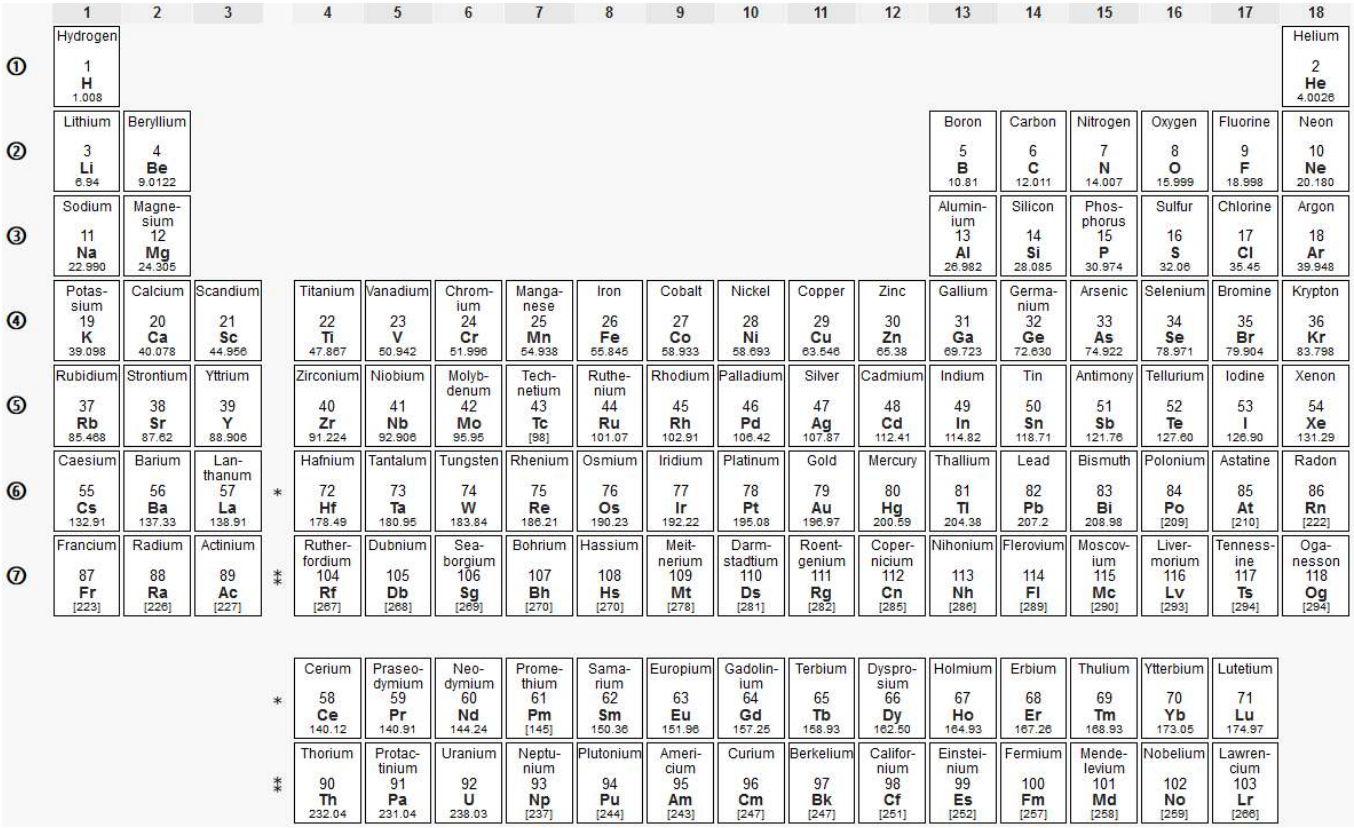


Figure **3.4.3**: The periodic table of the elements. (CC BY-SA 4.0 International; DePiep via Wikipedia).

Mass Number

Experimental data showed that the vast majority of the mass of an atom is concentrated in its nucleus, which is composed of protons and neutrons. The **mass number (represented by the letter A)** *is defined as the total number of protons and neutrons in an atom.* Consider the table below, which shows data from the first six elements of the periodic table.

Table **3.4.1**: Atoms of the First Six Elements

Name	Symbol	Atomic Number (Z)	Protons	Neutrons	Electrons	Mass Number (A) (rounded to two decimals)
hydrogen	**H**	1	1	0	1	1.01
helium	**He**	2	2	2	2	4.00
lithium	**Li**	3	3	4	3	6.94
beryllium	**Be**	4	4	5	4	9.01
boron	**B**	5	5	6	5	10.18
carbon	**C**	6	6	6	6	12.01

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

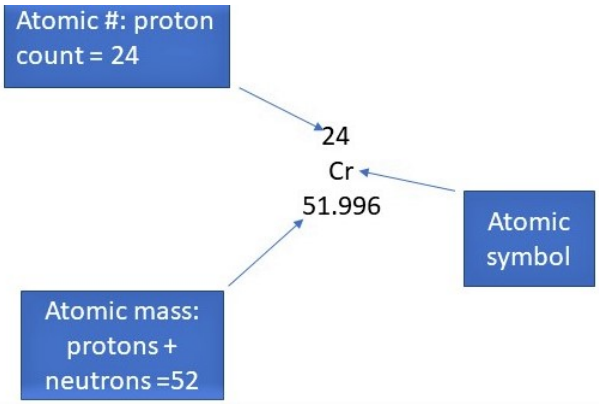


Figure 3.4.4: A/Z format and finding subatomics for elementChromium (Copyright; Elizabeth R. Gordon)

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

$$\textbf{Number of neutrons} = \textbf{ rounded mass number} - \textbf{atomic number}$$

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

$$52 - 24 = 28 \textbf{ neutrons in a chromium atom}$$

The composition of any atom can be illustrated with a shorthand notation called A/Z format. Both the atomic number and mass are written to the left of the chemical symbol. The "A" value is written as a superscript while the "Z" value is written as a subscript. For an example of this notation, look to the chromium atom shown below:

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

Another way to refer to a specific atom is to write the mass number of the atom after the name, separated by a hyphen. The symbol-mass format for the above atom would be written as Cr-52. In this notation, the atomic number is not included. You will need to refer to a periodic table for proton values.

Example 3.4.1

Calculate each of the three subatomic particles and give specific group or period names for each of the following:

a. mercury
b. platinum
c. bromine

Solutions

a. Hg (transition metal)- has 80 electrons, 80 protons, and 121 neutrons
b. Pt (transition metal)- has 78 electrons, 78 protons, and 117 neutrons
c. Br (halogen)- has 35 electrons, 35 protons, and 45 neutrons

Example 3.4.2

Write both A/Z and symbol-mass formats for the atoms in Example 3.4.1.

Solutions

a. $^{201}_{80}\mathbf{Hg}$ and Hg-201
b. $^{195}_{78}\mathbf{Pt}$ and Pt-195
c. $^{80}_{35}\mathbf{Br}$ and Br-80

Example 3.4.3

Identify the elements based on the statements below.

a. Which element has 25 protons?
b. Which element has 0 neutrons?
c. Which element has 83 electrons?

Solutions

a. manganese

b. hydrogen

c. bismuth

Need More Practice?

- Turn to section 3.E of this OER and answer questions #1-#2, #4, and #8.

Contributors and Attributions

-
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3.5: Isotopes

Learning Objectives

- Calculate subatomic particles (protons, neutrons, and electrons) for any element by looking at the periodic table.
- Calculate subatomic particles (protons, neutrons, and electrons) for any element by looking at symbol-mass and A/Z format.
- Understand how isotopes differ in particles and mass.
- Identify the most abundant isotope when given specific values.
- Calculate the atomic mass of an element from the masses and relative percentages of the isotopes of the element.
- Define LEU/HEU with percentages and applications.

Isotopes are atoms of the same element that contain different numbers of neutrons. For these species, the number of electrons and protons remains constant. This difference in neutron amount affects the atomic mass (**A**) but not the atomic number (**Z**). In a chemical laboratory, isotopes of an element appear and react the same. For this reason, it is difficult to distinguish between an atom's isotopes. In contrast, nuclear scientists can identify and separate different types of atomic nuclei (Figure **3.5.1**). The technology required for this process is more sophisticated than what could be found in a typical chemical laboratory.

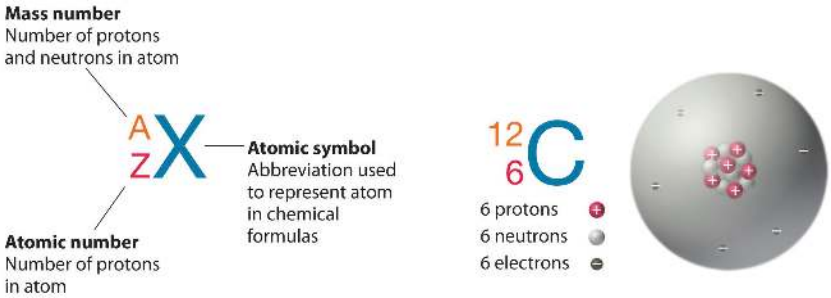


Figure **3.5.1**: Unlike protons, the number of neutrons is not absolutely fixed for most elements. Atoms that have the same number of protons, and hence the same atomic number, but different numbers of neutrons are called isotopes. All isotopes of an element have the same number of protons and electrons, which means they exhibit the same chemistry. The isotopes of an element differ only in their atomic mass, which is given by the mass number (A), the sum of the numbers of protons and neutrons. (CC BY-NS-SA; anonymous by request)

The element carbon (**C**) has an atomic number of 6, which means that all neutral carbon atoms contain 6 protons and 6 electrons. In a typical sample of carbon-containing material, 98.89% of the carbon atoms also contain 6 neutrons, so each has a mass number of 12. An isotope of any element can be uniquely represented as $^{A}_{Z}X$where X is the atomic symbol of the element. The isotope of carbon that has 6 neutrons is therefore $^{12}_{6}C$ The subscript indicating the atomic number is actually redundant because the atomic symbol already uniquely specifies *Z*. Consequently, it is more often written as ^{12}C, which is read as “carbon-12.” Nevertheless, the value of Z is commonly included in the notation for *nuclear* reactions because these reactions involve changes in Z.

Most elements on the periodic table have at least two stable isotopes. For example, in addition to ^{12}C, a typical sample of carbon contains 1.11% $^{13}_{6}C$, with 7 neutrons and 6 protons, and a trace of $^{14}_{6}C$, with 8 neutrons and 6 protons. The nucleus of $^{14}_{6}C$ is not stable, however, but undergoes a slow radioactive decay that is the basis of the carbon-14 dating technique used in archaeology. Many elements other than carbon have more than one stable isotope; tin, for example, has 10 isotopes. There are about twenty elements that exist in only one isotopic form (sodium and fluorine are examples of these). Most scientists cannot tell you how many isotopic forms exist unless they consult an isotopic table.

An important series of isotopes is found with hydrogen atoms. Most hydrogen atoms have a nucleus with only a single proton. About 1 in 10,000 hydrogen nuclei, however, also has a neutron; this particular isotope is called *deuterium*. An extremely rare hydrogen isotope, *tritium*, has 1 proton and 2 neutrons in its nucleus. Figure **3.5.2** compares the three isotopes of hydrogen.

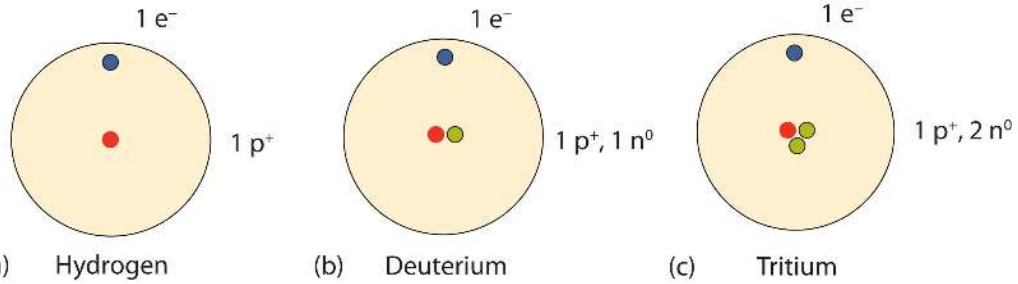


Figure **3.5.2**: a). A small amount of hydrogen exists as the isotope deuterium, which has one proton and one neutron in its nucleus (b). A tiny amount of the hydrogen isotope tritium, with one proton and two neutrons in its nucleus, also exists on Earth (c). The nuclei and electrons are proportionately much smaller than depicted here.

There are currently over 3,500 isotopes known for all the elements. When scientists discuss individual isotopes, they need an efficient way to specify the number of neutrons in any particular nucleus. A/Z and symbol-mass formats (refer to Section 3.4) can be used to display periodic table information. When viewing either of these two notations, isotopic differences can be obtained.

> *The discovery of isotopes required a minor change in Dalton's atomic theory. Dalton thought that all atoms of the same element were exactly the same.*

Look at the **A/Z formats** for the three isotopes of hydrogen in Table **3.5.1**. Note how the atomic number (bottom value) remains the same while the atomic masses (top number) are varied. All isotopes of a particular element will vary in neutrons and mass. This variance in mass will be visible in the **symbol-mass format** of same isotopes as well.

Table **3.5.1**

Common Name	A/Z formats	symbol-mass format	Expanded Name
Hydrogen	$^{1}_{1}\mathbf{H}$	**H-1**	hydrogen-1
Deuterium	$^{2}_{1}\mathbf{H}$	**H-2**	hydrogen-2
Tritium	$^{3}_{1}\mathbf{H}$	**H-3**	hydrogen 3

Using a periodic table, A/Z or symbol-mass formats can be utilized to determine the number of subatomic particles (protons, neutrons, and electrons) contained inside an isotope. When given either format, these mass values should be used to calculate the number of neutrons in the nucleus.

✔ Exercise 3.5.1

How many neutrons are in each atom?

a. $^{36}_{17}\mathrm{Cl}$
b. $^{58}_{26}\mathrm{Fe}$
c. C-14

Solution

a. In $^{36}_{17}\mathrm{Cl}$ there are 19 neutrons in this nucleus. To find this value, subtract A-Z or 36 − 17.
b. In $^{58}_{26}\mathrm{Fe}$ there are 32 neutrons in this nucleus. Again, subtract A-Z or 58-26.
c. In this example, the C-14 represents symbol-mass format. Once the atomic number is located (look at periodic table), subtract 14-6. The final answer will be 8 neutrons.

? Exercise 3.5.2

For the species below, translate the A/Z format to symbol-mass. Then, calculate the number of subatomics for each atom.

a. $^{197}_{79}\mathrm{Au}$
b. $^{23}_{11}\mathrm{Na}$

c. $^{239}_{94}\text{Pu}$

Answer a

Au-197 contains 79 protons, 79 electrons, and 118 neutrons.

Answer b

Na-23 contains 11 protons, 11 electrons, and 12 neutrons.

Answer c

Pu-239 contains 94 protons, 94 electrons, and 145 neutrons.

Calculating Atomic Mass

The **atomic mass** of an element is the weighted mass of all the naturally presented isotopes. On the periodic table, it is assumed that this mass has units of amu (atomic mass unit) which can be abbreviated by using the letter u. To determine the most abundant isotopic form of an element, compare given isotopes to the weighted average on the periodic table. For example, the three hydrogen isotopes (shown above) are H-1, H-2, and H-3. The atomic mass or weighted average of hydrogen is around 1.008 amu (look again at the periodic table). Of the three hydrogen isotopes, H-1 is closest in mass to the weighted average; therefore, it is the most abundant. The other two isotopes of hydrogen are rare but are very exciting in the world of nuclear science.

Example 3.5.2

Identify the true statements:

a. Al-27 is more abundant than Al-25.
b. An appropriate isotope of bromine could be Br-35.
c. A chemist could easily distinguish between Cs-132 and Cs-133 by noting chemical and physical properties.
d. Most scientists know that calcium has 24 isotopes.

Answer a

This statement is true. Aluminum with a mass of 27 is closest to the mass on the periodic table. It would be more abundant than Al-25.

Answer b

This statement is false. An appropriate mass number of an isotope of bromine would be in around 80 amu (atomic mass units), not 35 (which is the atomic number).

Answer c

Chemists cannot distinguish between isotopes by looking at various properties. Most isotopes have similar solubilities, densities, and colors.

Answer d

Unless a scientist works heavily with a particular atom, he or she is not aware of the many forms that cannot exist. They would need a reference guide to know how many natural and artificial isotopes exist for a particular element.

You can calculate the atomic mass (or average mass) of an element provided you know the **relative abundances** (the fraction of an element that is a given isotope), the element's naturally occurring isotopes, and the masses of those different isotopes. We can calculate this by the following equation:

$$\text{Atomic mass} = (\%_1)\,(\text{mass}_1) + (\%_2)\,(\text{mass}_2) + \cdots \tag{3.5.1}$$

To confirm your answer, compare the calculated value to the weighted mass displayed on the periodic table.

> *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. If all*

> *the abundances are not provided, it is safe to assume that all numbers should add up to 100%.*

Example 3.5.3: Atomic mass of Boron

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 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

Boron has two isotopes. We will use the Equation 3.5.1:

$$\text{Atomic mass} = (\%_1)\,(\text{mass}_1) + (\%_2)\,(\text{mass}_2) + \cdots$$

Substitute these into the equation, and we get:

$$\begin{aligned}\text{Atomic mass} &= (0.20)\,(10) + (0.80)\,(11)\\ &= 10.8\ \text{amu}\end{aligned}$$

The mass of an average boron atom, and thus boron's atomic mass, is 10.8 amu.

Example 3.5.4: Atomic mass of Neon

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 amu. Another 0.3% of the atoms are Ne-21, which is an isotope of neon with 11 neutrons and a mass of 20.99 amu. 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 amu. What is the atomic mass of neon?

Solution

Neon has three isotopes. We will use the equation:

$$\text{Atomic mass} = (\%_1)\,(\text{mass}_1) + (\%_2)\,(\text{mass}_2) + \cdots$$

Substitute these into the equation, and we get:

$$\begin{aligned}\text{Atomic mass} &= (0.9092)\,(19.99) + (0.003)\,(20.99) + (0.0885)\,(21.99)\\ &= 20.18\ \text{amu}\end{aligned}$$

The mass of an average neon atom is 20.18 amu

Applications of Isotopes

During the Manhattan project, the majority of federal funding dedicated the separation of uranium isotopes. The two most common isotopes of uranium are U-238 and U-235. About 99.3% of uranium is of the U-238 variety, this form is not fissionable and will not work in a nuclear weapon or reaction. The remaining .7% is U-235 which is fissionable but first had to be separated from U-238. This separation process is called *enrichment*. During World War II, a nuclear facility was built in Oak Ridge, Tennessee to accomplish this project. At the time, the enrichment process only produced enough U-235 for one nuclear weapon. This fuel was placed inside the smaller of the two atomic bombs (Little Boy) dropped over Japan.



Figure **3.5.3**: A billet of highly enriched uranium recovered from scrap processed at the Y-12 National Security Complex Plant. Original and unrotated.

Uranium is a natural element that can be found in several different countries. Countries that do not have natural uranium supplies would need to obtain it from one of the countries below. Most nuclear reactors that provide energy rely on U-235 as a source of fuel. Fortunately, reactors only need 2-5% U-235 for the production of megawatts or even gigawatts of power. If the purification process exceeds this level, then it is likely a country is focusing on making nuclear weapons. For example, Manhattan Project scientists enriched U-235 up to 90% in order to produce the Little Boy weapon.

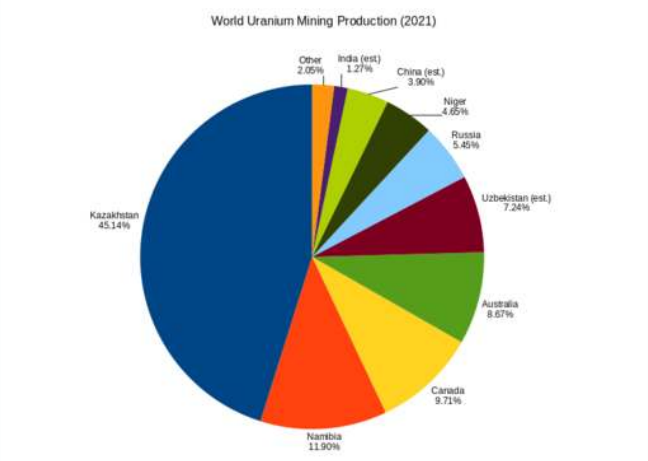


Figure **3.5.4**: World Uranium Mining Production 2021. (CC BY-SA-4.0; by Liberum scientia).

Abbreviations like HEU (highly enriched uranium) and LEU (low-enriched uranium) are used frequently by nuclear scientists and groups. HEU is defined as being over 20% pure U-235 and would not be used in most commercial nuclear reactors. This type of material is used to fuel larger submarines and aircraft carriers. If the purification of U-235 reaches 90%, then the HEU is further classified as being weapons-grade material. This type of U-235 could be used to make a nuclear weapon (fission or even fusion-based). As for LEU, its U-235 level would be below this 20% mark. LEU would be used for commercial nuclear reactors and smaller, nuclear-powered submarines. LEU is not pure enough to be used in a conventional nuclear weapon but could be used in a dirty bomb. This type of weapon uses conventional explosives like dynamite to spread nuclear material. Unlike a nuclear weapon, dirty bombs are not powerful enough to affect large groups of buildings or people. Unfortunately, the spread of nuclear material would cause massive chaos for a community and would result in casualties.

Need More Practice?

- Turn to Section 3.E of this OER and work problems #3, #6, #7, and #10.

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3.6: The Importance of Ions to a Chemist

Learning Objectives

- Identify how a charge affects the electron count of an element.
- Apply a provided charge when calculating the number of subatomic particles.
- Realize that cations are atoms that lose electrons resulting in an overall positive charge.
- Realize that anions are atoms that gain electrons resulting in an overall negative charge.
- Locate regions of the periodic table where cations and anions tend to form.
- Know that chemical energy corresponds to electrons, while nuclear energy results from changing the nucleus.
- Compare and contrast chemical and nuclear energy.
- Relate ion solubility to the Flint River Crisis (see infographic at bottom).

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Chemists appreciate isotopes and use them in basic and applied research. However, they are more concerned with the movement of electrons. When an atom gains or loses electrons, it becomes a charged species or an ion. When this occurs, the nucleus is not altered. For atoms that lose electrons, an overall positive charge will result (**#protons > #electrons**). Atoms that form these types of ions are called cations. Metal atoms (located on the left side of the periodic table) always lose electrons to become cations.

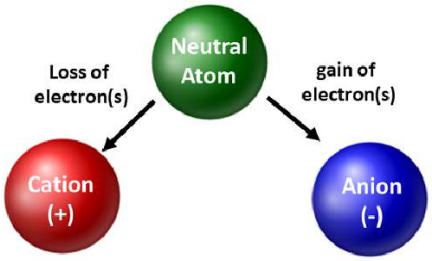
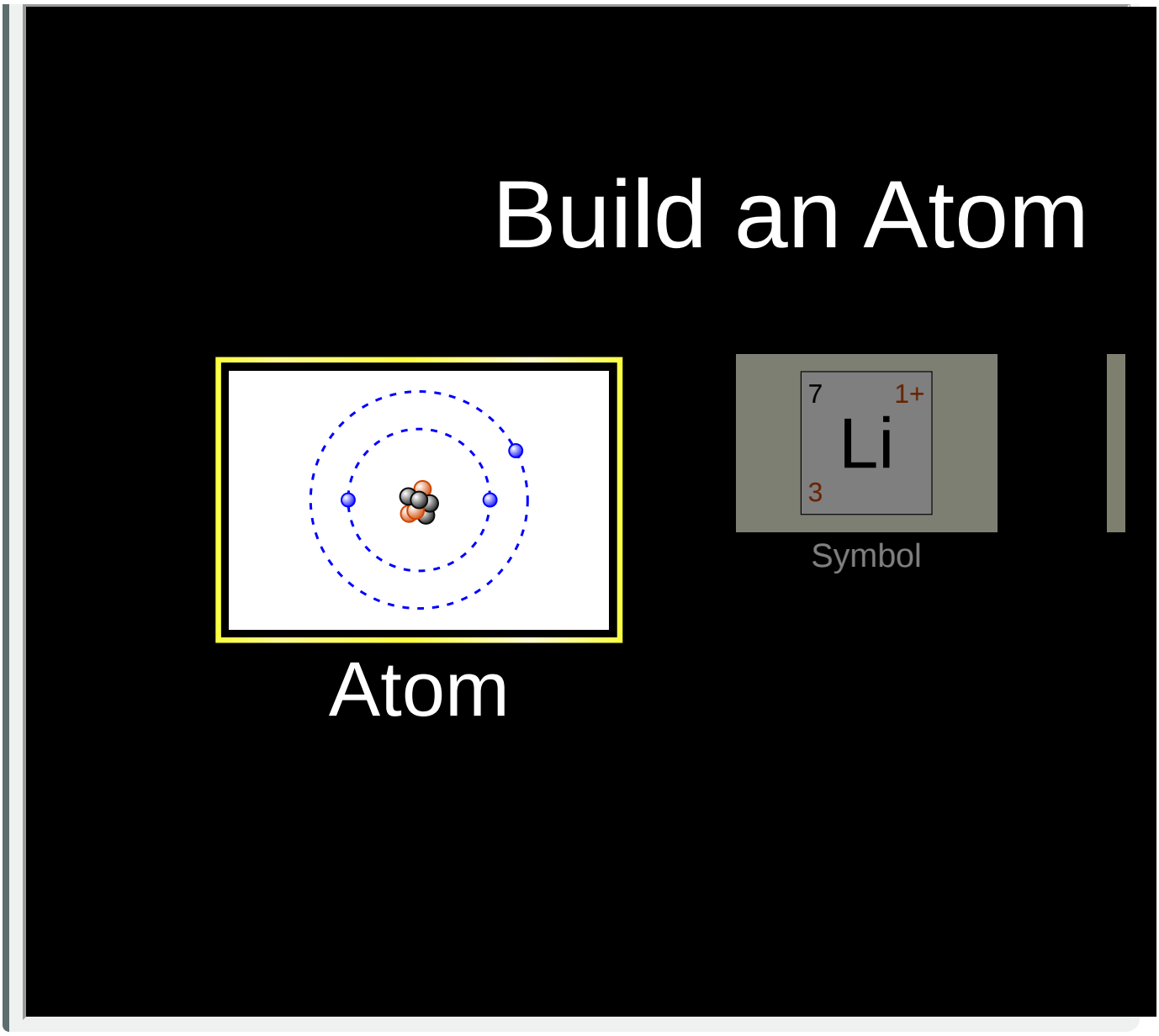


Figure **3.6.1**: Neutral atoms become ions by either losing an electron (to form positively charged cations) or gaining electrons (to form negatively charged anions). (Public Domain; Delmar Larsen)

Unlike metal atoms, nonmetals will gain electrons to become anions. These types of ions have an overall negative charge (**#electrons > #protons**). With the exception of the noble gases, all atoms on the periodic table will lose or gain electrons to achieve electronic stability. Different types of bonding occur when atoms lose, gain, or share electrons. These types of atomic connections will be further discussed in chapter 4 of your textbook.

Interactive: Building an Atom

Build an atom out of protons, neutrons, and electrons, and see how the element, charge, and mass change. Then play a game to test your ideas!



At this point, you should be able to calculate all subatomic particles when given a specific ion charge. In addition, you should master classifications of ions (recognizing cations are positive and anions are negative). Memorizing charges of specific ions will be required when working on chapter 4 in the textbook. **For now, ion charges will be provided and should not be memorized**. Note and appreciate the ion charges for main group elements in the periodic table below. Lastly, chemists do not write a number for charges involving the number one (1). For these species, you will only see a + or - sign. Charges of higher magnitude will always have a number associated with the elemental symbol.

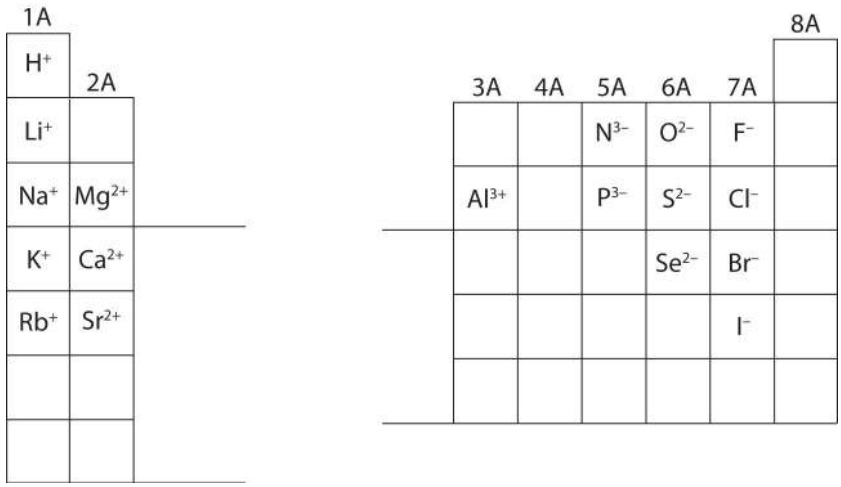


Figure **3.6.2**: Periodic Table with ion charges of common main group elements. The charge that an atom acquires when it becomes an ion is related to the structure of the periodic table. Within a group (family) of elements, atoms form ions of a certain charge. Please note that hydrogen can adopt a + or - charge. When the word hydride is used, this means that hydrogen has a - charge.

Example 3.6.1: IOnic Classification

Calculate the subatomic particles for the species below using the information in Figure **3.6.2**. Label each as being an atom, cation, or anion. Refer to the periodic table for masses, atomic numbers, and specific ion charges.

a. Aluminum ion
b. Zirconium atom
c. Sulfur ion

Solutions

a. There are 13 protons, 14 neutrons, and 10 electrons in the aluminum ion. This ion is positively charged which means it has lost electrons and forms a cation.
b. There are 40 protons, 51 neutrons, and 40 electrons in the zirconium atom. This is an atom which has no overall charge.
c. There are 16 protons, 16 neutrons, and 18 electrons in the sulfur ion. This ion is negatively charged which means it has gained electrons and forms and anion.

Example 3.6.2: A/Z and symbol mass notations

Write A/Z and symbol mass notations for the ions/atom in the previous question.

Solutions

a. $^{27}_{13}Al^{3+}$ and Al-27
b. $^{91}_{40}Zr$ and Zr-91
c. $^{32}_{16}S^{2-}$ and S-32

If an atom gains or loses electrons, this should be represented on the A/Z format. The symbol-mass format does not display ion charge. Remember, neutrons and protons are not affected by changes of electrons.

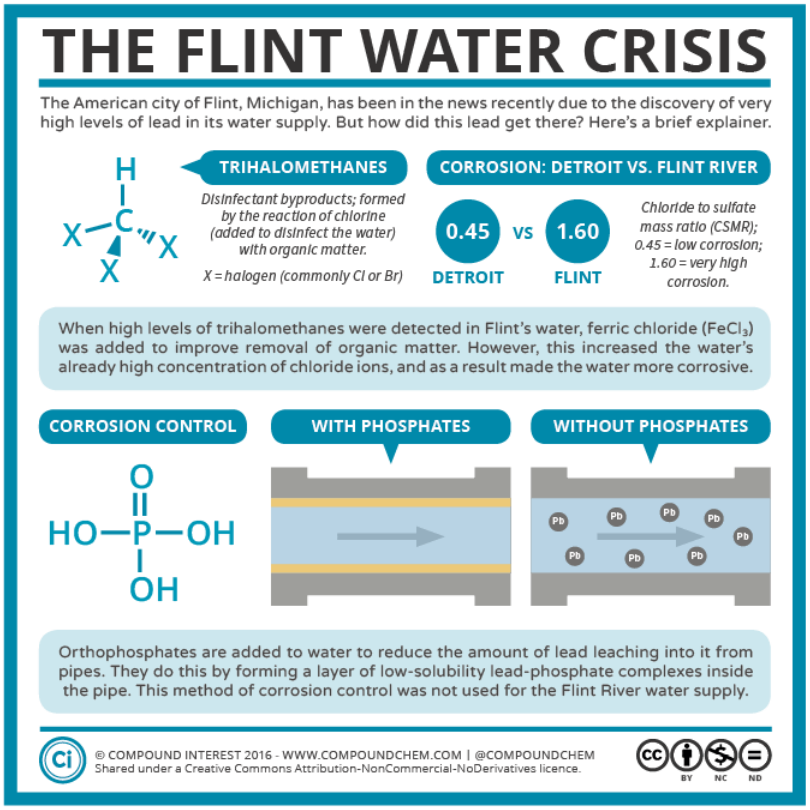


Figure **3.6.3**: The Flint Water Crisis. (Andy Brunning, CC-By-NC-ND)

When compounds are soluble in water, they form homogeneous mixtures or solutions. Disinfectants are compounds (usually chlorine or bromine based) added to water to kill pathogens. These types of chemicals are typically bromine, iodine, or chlorine based. When these species are added, they react with water to produce disinfectant byproducts. Before disinfection, the Flint River was corrosive. After disinfection, the chlorine/bromine ions increased the corrosivity of the water. As a result, the insoluble pipe became soluble releasing iron, copper, and lead atoms in the water. The water turned brownish in color due to the presence of iron cations. Copper and lead ions did not affect the color of the water.



Need More Practice?

- Turn to Section 3.E of this OER and work problems #5 and #9.

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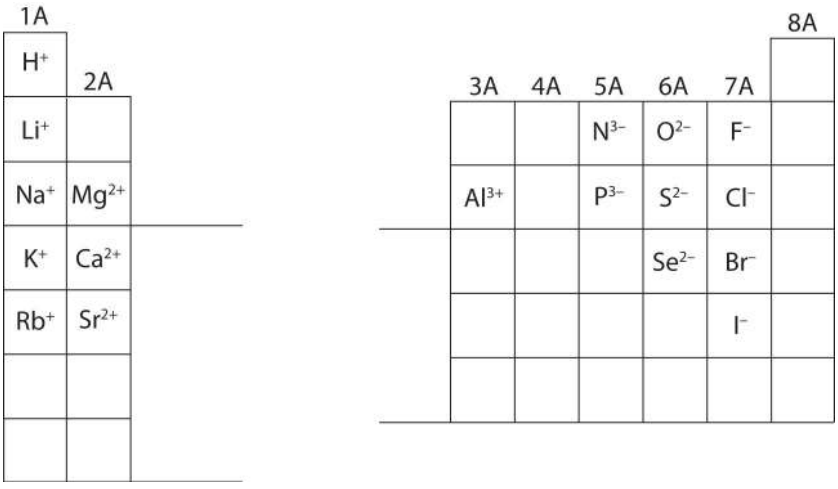
3.E: Atoms and the Periodic Table (Exercises)

Concept Review Exercises

1. Why is the atomic number so important to the identity of an atom?
2. What is the relationship between the number of protons and the number of electrons in an atom?
3. How do isotopes of an element differ from each other?
4. What is the mass number of an element?
5. Calculate the subatomic particles for
    a. Zn-67,
    b. radium,
    c. the aluminum cation,
    d. Mg-23, and
    e. the phosphorus anion.
6. Which element(s) has/have 32 neutrons: germanium, cobalt, or Mn-57?
7. Which natural isotope of platinum is most abundant?
8. Which element has 19 electrons?
9. Write A/Z format for the species in question #5.
10. Calculate the weighted average of nitrogen. N-14 has an exact mass of 14.003074u and is 99.63% abundant. N-15 has a mass of 15.000108u.

Solutions

1. The atomic number defines the identity of an element.
2. In an electrically neutral atom, the number of protons equals the number of electrons.
3. Isotopes have different numbers of neutrons in their nuclei.
4. The mass number is the sum of the numbers of protons and neutrons in the nucleus of an atom.
5. For ion charges, refer to the table for assistance:



Species	Protons	Electrons	Neutrons
Zn-67	30	30	37 (is isotope)
Radium	88	88	138
Aluminum cation	13	10 (look up charge, 3+)	14
Mg-23	12	12	11 (is isotope)
Phosphorus anion	15	18 (look up charge, 3-)	16

6. Both cobalt and Mn-57 have 32 neutrons. Germanium has 41 neutrons.
7. Pt-195 is closest to the weighted average (found on periodic table) and would be the most abundant.
8. If an ion charge is not given, locate the electrons of the element by looking to the atomic number. Potassium is the only atom of these three that would have 19 electrons.
9. $^{67}_{30}\mathrm{Zn}$, $^{226}_{88}\mathrm{Ra}$, $^{27}_{13}\mathrm{Al}^{3+}$, $^{23}_{12}\mathrm{Mg}$ and $^{31}_{15}\mathrm{P}^{3-}$
10. For this problem, you need to assume that all percentages add up to 100%. Since the problem provided 99.63%, you will need to subtract this given percentage from 100.00%.

$$\text{Atomic mass} = (0..9963)\,(14.003074) + (0.0037)\,(15.000108) = 14.01\ \text{amu} \tag{3.E.1}$$

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CHAPTER OVERVIEW

4: Chemical Bonds

- 4.1: The Art of Deduction- Stable Electron Configurations
- 4.2: Lewis (Electron-Dot) Symbols
- 4.3: The Reaction of Sodium with Chlorine
- 4.4: Using Lewis Symbols for Ionic Compounds
- 4.5: Formulas and Names of Binary Ionic Compounds
- 4.6: Free Radicals and the Environment
- 4.7: Free Radicals and Health
- 4.8: Covalent Bonds- Shared Electron Pairs
- 4.9: Unequal Sharing- Polar Covalent Bonds
- 4.10: Polyatomic Molecules- Water, Ammonia, and Methane
- 4.11: Polyatomic Ions
- 4.12: Rules for Writing Lewis Formulas
- 4.13: Molecular Shapes- The VSEPR Theory
- 4.14: Shapes and Properties- Polar and Nonpolar Molecules
- 4.15: Metallic Bonding
  - 4.15.1: Crystal Structure of Metals
- 4.16: Network Covalent Atomic Solids

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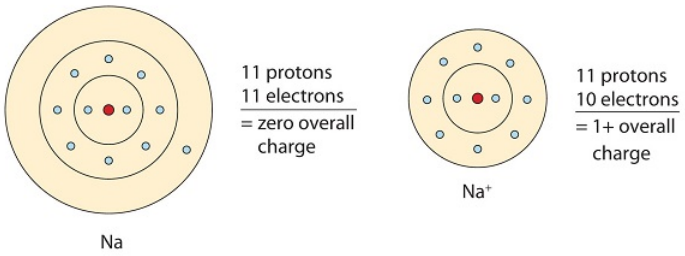
4.1: The Art of Deduction- Stable Electron Configurations

Learning Objective

- Define the octet rule.

The **octet rule** is a chemical rule of thumb that reflects observation that elements tend to bond in such a way that each atom has eight electrons in its valence shell, giving it the same electronic configuration as a noble gas.

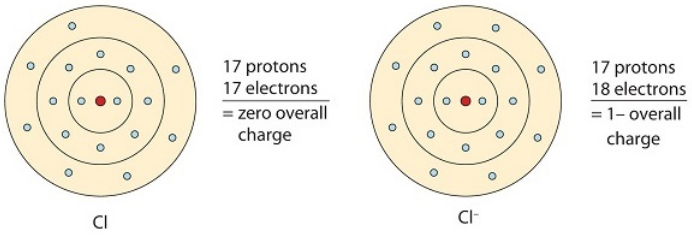
Referring to the octet rule, atoms attempt to get a noble gas electron configuration, which is eight valence electrons. Metals have few electrons in their outer-most orbitals. By losing those electrons, these metals can achieve noble gas configuration and satisfy the octet rule. Sodium has one valence electron, so giving it up would result in the same electron configuration as **neon**. Due to the loss of electron, a positively charged cation (Na^+) called sodium ion is formed.



Sodium (Na) neutral (left): 11 protons and 11 electrons equal zero overall charge; Sodium (Na) positive (right): 11 protons and 10 electrons equals one plus overall charge

Similarly, nonmetals that have close to 8 electrons in their valence shells tend to readily accept electrons to achieve noble gas configuration. Chlorine has seven valence electrons, so if it takes one it will have eight (an octet). Chlorine has the electron configuration of **argon** when it gains an electron. The resulting ion (Cl^-) is called chloride ion.

The octet rule could have been satisfied if chlorine gave up all seven of its valence electrons and sodium took them. In that case, both would have the electron configurations of noble gasses, with a full valence shell. However, their charges would be much higher. It would be Na^{7-} and Cl^{7+}, which is much less stable than Na^+ and Cl^-. Atoms are more stable when they have no charge, or a small charge.



Chlorine (Cl) neutral (left): 17 protons and 17 electrons equal zero overall charge; chlorine (Cl) negative (right): 11 protons and 10 electrons equals one minus overall charge

Summary

The octet rule refers to the tendency of atoms to prefer to have eight electrons in the valence shell.

Contributor

Organic Chemistry Supplemental_Modules_(Organic_Chemistry)/Fundamentals/Ionic_and_Covalent_Bonds

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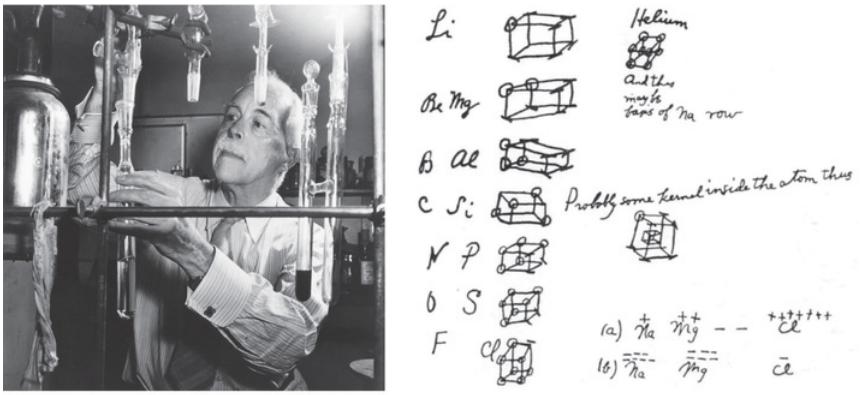
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4.2: Lewis (Electron-Dot) Symbols

Learning Objective

- Draw a Lewis electron dot diagram for an atom.
- Know the importance of Lewis dot in bonding.

At the beginning of the 20th century, an American physical chemist G. N. Lewis (1875–1946) devised a system of symbols—now called *Lewis electron dot symbols* (often shortened to *Lewis dot symbols*) that can be used for predicting the number of bonds formed by most elements in their compounds.



(a) (b)

Figure 4.2.1 G. N. Lewis and the Octet Rule. (a) Lewis is working in the laboratory. (b) In Lewis's original sketch for the octet rule, he initially placed the electrons at the corners of a cube rather than placing them as we do now.

Lewis Dot symbols

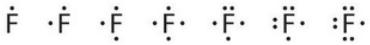
- convenient representation of valence electrons
- allows scientists to keep track of valence electrons during bond formation
- consists of the atomic symbol for the element plus a dot for each **valence** electron

To write an element's Lewis dot symbol, we place dots representing its valence electrons, one at a time, around the element's chemical symbol. Up to four dots are placed above, below, to the left, and to the right of the symbol (in any order, as long as elements with four or fewer valence electrons have no more than one dot in each position). The next dots, for elements with more than four valence electrons, are again distributed one at a time, each paired with one of the first four. For example, the element sulfur has six valence electrons (note roman numeral above group on the periodic table) and its Lewis symbol would be:



S two dots above two dots below and 1 dot left and right

Fluorine, for example, has seven valence electrons, so its Lewis dot symbol is constructed as follows:



Dot symbols for fluorine

Lewis eventually published his theory of chemical bonding in 1916. Formation of chemical bonds to complete the requirement of eight electrons for the atom becomes a natural tendency. Lewis dot symbols of the first two periods are given here to illustrate this point. In fact, the entire group (column) of elements have the same Lewis dot symbols, because they have the same number of valence electrons.

By going through the periodic table, we see that the Lewis electron dot symbols of atoms will never have more than eight dots around the atomic symbo see Table 4.2.1.

Table **4.2.1** Lewis Dot Symbols of the Main Group Elements

H·							He:
Li·	·Be·	\(\ce{ \cdot \underset{\:}{\overset{\Large{\cdot}}{B}} \cdot}\)	·C·	:N·	:O·	:F·	:Ne:
Na	Mg	Al	Si	P	S	Cl	Ar
K	Ca	Ga	Ge	As	Se	Br	Kr
Rb	Sr	In	Sn	Sb	Te	I	At
Cs	Ba	Tl	Pb	Bi	Po	At	Rn

What is the Lewis electron dot diagram for each element?

a. aluminum
b. selenium

Solution

a. The valence electron configuration for aluminum is $3s^2 3p^1$. So it would have three dots around the symbol for aluminum, two of them paired to represent the 3*s* electrons:

$$\dot{Al}:$$

2. The valence electron configuration for selenium is $4s^2 4p^4$. In the highest-numbered shell, the $n = 4$ shell, there are six electrons. Its electron dot diagram is as follows:

$$\cdot\ddot{Se}:$$

? Exercise 4.2.1

What is the Lewis electron dot diagram for each element?

a. phosphorus
b. argon

Answer a

$$\cdot\ddot{P}:$$

Answer b

$$:\ddot{Ar}:$$

Summary

- Lewis electron dot diagrams use dots to represent valence electrons around an atomic symbol.
- Lewis dot symbols can be used to predict the number of bonds formed by elements in a compound.

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4.3: The Reaction of Sodium with Chlorine

Learning Objectives

- Explain the bonding nature of ionic compounds.
- Relate microscopic bonding properties to macroscopic solid properties.

Neutral atoms and their associated ions have very different physical and chemical properties. Sodium *atoms* form sodium metal, a soft, silvery-white metal that burns vigorously in air and reacts explosively with water. Chlorine *atoms* form chlorine gas, Cl_2, a yellow-green gas that is extremely corrosive to most metals and very poisonous to animals and plants. The vigorous reaction between the elements sodium and chlorine forms the white, crystalline compound sodium chloride, common table salt, which contains sodium *cations* and chloride *anions* (Figure **4.3.1**). The compound composed of these ions exhibits properties entirely different from the properties of the elements sodium and chlorine. Chlorine is poisonous, but sodium chloride is essential to life; sodium atoms react vigorously with water, but sodium chloride simply dissolves in water.



Figure **4.3.1** (a) Sodium is a soft metal that must be stored in mineral oil to prevent reaction with air or water. (b) Chlorine is a pale yellow-green gas. (c) When combined, they form white crystals of sodium chloride (table salt). (credit a: modification of work by "Jurii"/Wikimedia Commons) Commons)

Ionic Bonds

When two atoms approach each other, they have the potential to bond (or connect). If a metal and a nonmetal interact, then an ionic bond will result. These types of bonds involve the metal donating it(s) valence electron(s) to a nonmetal. As the electronic transfer occurs, both atoms will achieve more stable confirmations. The end result will be a less reactive compound. These type of species are composed of both cations and anions. In addition, they are crystalline and solid in nature (Figure 4.3.2). A few examples of real-world ionic compounds would be NaCl (table salt) and NaF (active ingredient in toothpaste).

The formula for table salt is NaCl. It is the result of Na^+ ions and Cl^- ions bonding together (Figure **4.3.3**). If sodium metal and chlorine gas mix under the right conditions, they will form salt. The sodium loses an electron, and the chlorine gains that electron. This reaction is highly favorable because of the electrostatic attraction between the particles. In the process, a great amount of light and heat is released. The resulting salt is mostly unreactive — it is stable. It will not undergo any explosive reactions, unlike the sodium and chlorine that it is made of.



***Figure* 4.3.2** *NaCl crystals. (Public Domain; NASA).*

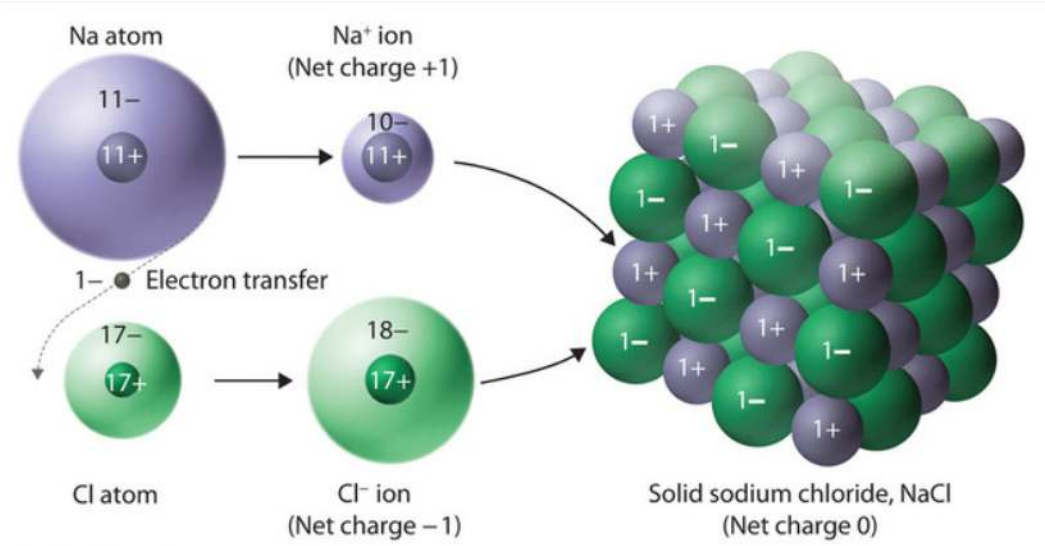
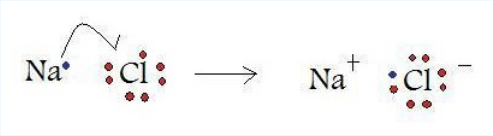


Figure **4.3.3** The formation of sodium chloride from the attraction of sodium and chloride ions.

The reaction is represented with Lewis dot symbols below.

Chloride Salts



The sodium atom is donating its 1 valence electron to the chlorine atom. This creates a sodium cation and a chlorine anion. Notice that the net charge of the resulting compound is 0.

Summary

- An ionic bond is formed when a metal donates it(s) valence electron(s) to a nonmetal.
- The resulting ionic compound is more stable and less reactive.

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4.4: Using Lewis Symbols for Ionic Compounds

Learning Objectives

- State the octet rule.
- Define cations and anions.
- Define *ionic bond*.
- Draw Lewis structures for ionic compounds.

The Octet Rule: The Drive for Eight

The **octet rule** refers to the tendency of atoms to prefer to have eight electrons in the *valence shell*. When atoms have fewer than eight electrons, they tend to react and form more stable compounds. When discussing the octet rule, we do not consider d or f electrons. Only the s and p electrons are involved in the octet rule, making it useful for the *main group elements* (elements not in the transition metal or inner-transition metal blocks); an octet in these atoms corresponds to an electron configurations ending with s^2p^6.

Note

The noble gases rarely form compounds. They have the most stable configuration (full octet, no charge), so they have no reason to react and change their configuration. All other elements attempt to gain, lose, or share electrons to achieve a noble gas configuration.

Most atoms do not have eight electrons in their valence electron shell. Some atoms have only a few electrons in their outer shell, while some atoms lack only one or two electrons to have an octet. In cases where an atom has three or fewer valence electrons, the atom may lose those valence electrons quite easily until what remains is a lower shell that contains an octet. Atoms that lose electrons acquire a positive charge as a result because they are left with fewer negatively charged electrons to balance the positive charges of the protons in the nucleus. Positively charged ions are called cations. Most metals become cations when they make ionic compounds.

Cations

A neutral sodium atom is likely to achieve an octet in its outermost shell by losing its one valence electron.

$$\mathrm{Na} \rightarrow \mathrm{Na^+} + \mathrm{e^-}$$

The **cation** produced in this way, Na^+, is called the sodium ion to distinguish it from the element. The outermost shell of the sodium ion is the second electron shell, which has eight electrons in it. The octet rule has been satisfied. F

Anions

Some atoms have nearly eight electrons in their valence shell and can gain additional valence electrons until they have an octet. When these atoms gain electrons, they acquire a negative charge because they now possess more electrons than protons. Negatively charged ions are called **anions**. Most nonmetals become anions when they make ionic compounds.

A neutral chlorine atom has seven electrons in its outermost shell. Only one more electron is needed to achieve an octet in chlorine's valence shell. (In table salt, this electron comes from the sodium atom.)

$$\mathrm{e^-} + \mathrm{Cl} \longrightarrow \mathrm{Cl^-}$$

In this case, the ion has the same outermost shell as the original atom, but now that shell has eight electrons in it. Once again, the octet rule has been satisfied. The resulting anion, Cl^-, is called the chloride ion; note the slight change in the suffix (*-ide* instead of *-ine*) to create the name of this anion.

> *The names for positive and negative ions are pronounced CAT-eye-ons and ANN-eye-ons, respectively.*

Note the usefulness of the periodic table in predicting likely ion formation and charge (Figure **4.4.1**). Moving from the far left to the right on the periodic table, main-group elements tend to form cations with a charge equal to the group number. That is, group 1 elements form 1+ ions; group 2 elements form 2+ ions, and so on. Moving from the far right to the left on the periodic table, elements often form anions with a negative charge equal to the number of groups moved left from the noble gases. For example, group 17 elements (one group left of the noble gases) form 1− ions; group 16 elements (two groups left) form 2− ions, and so on. This trend can be used as a guide in many cases, but its predictive value decreases when moving toward the center of the periodic table. In fact, transition metals and some other metals often exhibit variable charges that are not predictable by their location in the table. For example, copper can form ions with a 1+ or 2+ charge, and iron can form ions with a 2+ or 3+ charge.

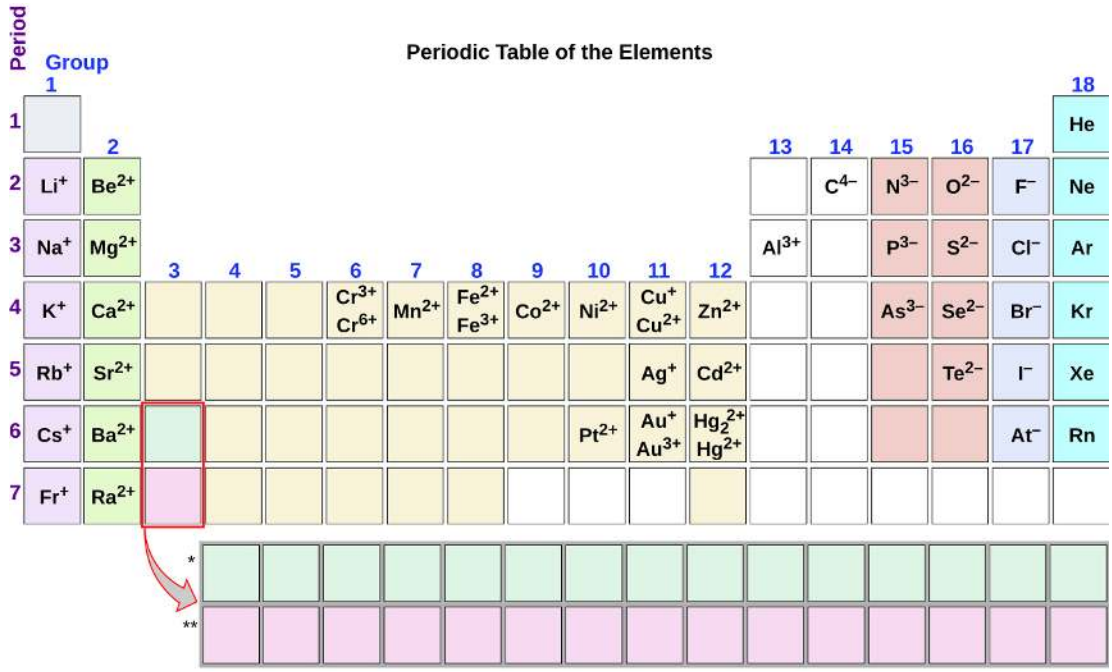


Figure **4.4.1**: Some elements exhibit a regular pattern of ionic charge when they form ions.

Group one of the periodic table contains L i superscript plus sign in period 2, N a superscript plus sign in period 3, K superscript plus sign in period 4, R b superscript plus sign in period 5, C s superscript plus sign in period 6, and F r superscript plus sign in period 7. Group two contains B e superscript 2 plus sign in period 2, M g superscript 2 plus sign in period 3, C a superscript 2 plus sign in period 4, S r superscript 2 plus sign in period 5, B a superscript 2 plus sign in period 6, and R a superscript 2 plus sign in period 7. Group six contains C r superscript 3 plus sign and C r superscript 6 plus sign in period 4. Group seven contains M n superscript 2 plus sign in period 4. Group eight contains F e superscript 2 plus sign and F e superscript 3 plus sign in period 4. Group nine contains C o superscript 2 plus sign in period 4. Group ten contains N i superscript 2 plus sign in period 4, and P t superscript 2 plus sign in period 6. Group 11 contains C U superscript plus sign and C U superscript 2 plus sign in period 4, A g superscript plus sign in period 5, and A u superscript plus sign and A u superscript 3 plus sign in period 6. Group 12 contains Z n superscript 2 plus sign in period 4, C d superscript 2 plus sign in period 5, and H g subscript 2 superscript 2 plus sign and H g superscript 2 plus sign in period 6. Group 13 contains A l superscript 3 plus sign in period 3. Group 14 contains C superscript 4 negative sign in period 2. Group 15 contains N superscript 3 negative sign in period 2, P superscript 3 negative sign in period 3, and A s superscript 3 negative sign in period 4. Group 16 contains O superscript 2 negative sign in period 2, S superscript 2 negative sign in period 3, S e superscript 2 negative sign in period 4 and T e superscript 2 negative sign in period 5. Group 17 contains F superscript negative sign in period 2, C l superscript negative sign in period 3, B r superscript negative sign in period 4, I superscript negative sign in period 5, and A t superscript negative sign in period 6. Group 18 contains H e in period 1, N e in period 2, A r in period 3, K r in period 4, X e in period 5 and R n in period 6.

Lewis Symbols for Ionic Compounds

In the section above, we saw how ions are formed by losing electrons to make cations or by gaining electrons to form anions. The astute reader may have noticed something: Many of the ions that form have eight electrons in their valence shell. Either atoms gain enough electrons to have eight electrons in the valence shell and become the appropriately charged anion, or they lose the electrons in their original valence shell; the *lower* shell, now the valence shell, has eight electrons in it, so the atom becomes positively charged. For whatever reason, having eight electrons in a valence shell is a particularly energetically stable arrangement of

electrons. When atoms form compounds, the octet rule is not always satisfied for all atoms at all times, but it is a very good rule of thumb for understanding the kinds of bonding arrangements that atoms can make.

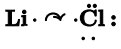
It is not impossible to violate the octet rule. Consider lithium: in its elemental form, it has one valence electron and is stable. It is rather reactive, however, and does not require a lot of energy to remove that electron to make the Li^+ ion. We *could* remove another electron by adding even more energy to the ion, to make the Li^{2+} ion. However, that requires much more energy than is normally available in chemical reactions, so sodium stops at a 1+ charge after losing a single electron. It turns out that the Li^+ ion has a complete octet in its new valence shell, the $n = 2$ shell, which satisfies the octet rule. The octet rule is a result of trends in energies and is useful in explaining why atoms form the ions that they do.

Now consider an Li atom in the presence of a Cl atom. The two atoms have these Lewis electron dot diagrams and electron configurations:

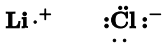


$$[Ne]\,3s^1 \qquad [Ne]\,3s^2 3p^5$$

For the Li atom to obtain an octet, it must lose an electron; for the Cl atom to gain an octet, it must gain an electron. An electron transfers from the Na atom to the Cl atom:

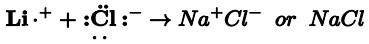


resulting in two ions—the Na^+ ion and the Cl^- ion:



$$[Ne] \qquad [Ne]\,3s^2 3p^6$$

Both species now have complete octets, and the electron shells are energetically stable. From basic physics, we know that opposite charges attract. This is what happens to the Na^+ and Cl^- ions:

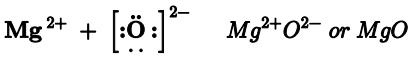


where we have written the final formula (the formula for sodium chloride) as per the convention for ionic compounds, without listing the charges explicitly. The attraction between oppositely charged ions is called an **ionic bond,** and it is one of the main types of chemical bonds in chemistry. Ionic bonds are caused by electrons *transferring* from one atom to another.

In electron transfer, the number of electrons lost must equal the number of electrons gained. We saw this in the formation of NaCl. A similar process occurs between Mg atoms and O atoms, except in this case two electrons are transferred:

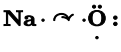


The two ions each have octets as their valence shell, and the two oppositely charged particles attract, making an ionic bond:



Remember, in the final formula for the ionic compound, we do not write the charges on the ions.

What about when an Na atom interacts with an O atom? The O atom needs two electrons to complete its valence octet, but the Na atom supplies only one electron:



The O atom still does not have an octet of electrons. What we need is a second Na atom to donate a second electron to the O atom:



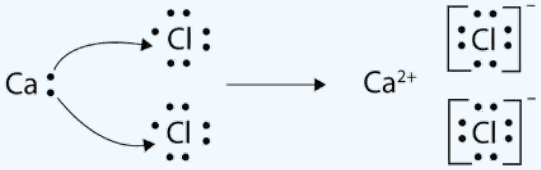
These three ions attract each other to give an overall neutral-charged ionic compound, which we write as Na_2O. The need for the number of electrons lost being equal to the number of electrons gained explains why ionic compounds have the ratio of cations to anions that they do. This is required by the law of conservation of matter as well.

Example 4.4.1: Synthesis of calcium chloride from Elements

With arrows, illustrate the transfer of electrons to form calcium chloride from ***Ca*** atoms and ***Cl*** atoms.

Solution

A ***Ca*** atom has two valence electrons, while a ***Cl*** atom has seven electrons. A ***Cl*** atom needs only one more to complete its octet, while ***Ca*** atoms have two electrons to lose. Thus we need two Cl atoms to accept the two electrons from one ***Ca*** atom. The transfer process looks as follows:

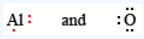


The oppositely charged ions attract each other to make $CaCl_2$.

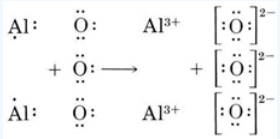
Example 4.4.2: Ionic Formula

Find the formula of the ionic compound formed from O and Al.

Solution: We first write down Lewis diagrams for each atom involved:



We now see that each O atom needs 2 electrons to make up an octet, while each Al atom has 3 electrons to donate. In order that the same number of electrons would be donated as accepted, we need 2 Al atoms ($2 \times 3e^-$ donated) and 3 O atoms ($3 \times 2e^-$ accepted). The whole process is then

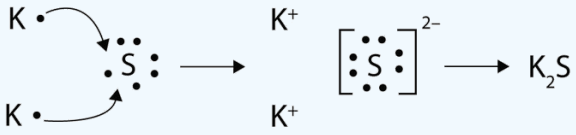


The resultant oxide consists of aluminum ions, Al^{3+}, and oxide ions, O^{2-}, in the ratio of 2:3. The formula is Al_2O_3.

Exercise 4.4.1

With arrows, illustrate the transfer of electrons to form potassium sulfide from ***K*** atoms and ***S*** atoms.

Answer:



Summary

- The tendency to form species that have eight electrons in the valence shell is called the octet rule.
- The attraction of oppositely charged ions caused by electron transfer is called an ionic bond.
- The strength of ionic bonding depends on the magnitude of the charges and the sizes of the ions.

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- Henry Agnew (UC Davis)
- OpenSTAX

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4.5: Formulas and Names of Binary Ionic Compounds

Learning Objectives

- Use the rules for naming ionic compounds.
- Write the correct formula for an ionic compound.

Names of Binary ionic Compounds

After learning a few more details about the names of individual ions, you will be a step away from knowing how to name ionic compounds. This section begins the formal study of nomenclature, the systematic naming of chemical compounds.

Naming Ions

The name of a monatomic cation is simply the name of the element followed by the word *ion*. Thus, Na^+ is the sodium ion, Al^{3+} is the aluminum ion, Ca^{2+} is the calcium ion, and so forth.

We have seen that some elements lose different numbers of electrons, producing ions of different charges (Figure 4.4.1) . Iron, for example, can form two cations, each of which, when combined with the same anion, makes a different compound with unique physical and chemical properties. Thus, we need a different name for each iron ion to distinguish Fe^{2+} from Fe^{3+}. The same issue arises for other ions with more than one possible charge.

There are two ways to make this distinction. In the simpler, more modern approach, called the **Stock system** (Table 4.5.1), an ion's positive charge is indicated by a roman numeral in parentheses after the element name, followed by the word ion. Thus, Fe^{2+} is called the iron(II) ion, while Fe^{3+} is called the iron(III) ion. This system is used only for elements that form more than one common positive ion. We do not call the Na^+ ion the sodium(I) ion because (I) is unnecessary. Sodium forms only a 1+ ion, so there is no ambiguity about the name *sodium ion*.

Table 4.5.1: The Modern and Common System of Cation Names

Element	Stem	Charge	Modern Name (Stock System)	Common Name
iron	ferr-	2+	iron(II) ion	ferrous ion
		3+	iron(III) ion	ferric ion
copper	cupr-	1+	copper(I) ion	cuprous ion
		2+	copper(II) ion	cupric ion
tin	stann-	2+	tin(II) ion	stannous ion
		4+	tin(IV) ion	stannic ion
lead	plumb-	2+	lead(II) ion	plumbous ion
		4+	lead(IV) ion	plumbic ion
chromium	chrom-	2+	chromium(II) ion	chromous ion
		3+	chromium(III) ion	chromic ion
gold	aur-	1+	gold(I) ion	aurous ion
		3+	gold(III) ion	auric ion

The second system, called the **common system**, is not conventional but is still prevalent and used in the health sciences. This system recognizes that many metals have two common cations. The common system uses two suffixes (*-ic* and *-ous*) that are appended to the stem of the element name. The *-ic* suffix represents the greater of the two cation charges, and the *-ous* suffix

represents the lower one. In many cases, the stem of the element name comes from the Latin name of the element. Table **4.5.1** lists the elements that use the common system, along with their respective cation names.

Table **4.5.2**: Some Monatomic Anions

Ion	Name
F^-	fluoride ion
Cl^-	chloride ion
Br^-	bromide ion
I^-	iodide ion
O^{2-}	oxide ion
S^{2-}	sulfide ion
P^{3-}	phosphide ion
N^{3-}	nitride ion

The name of a monatomic anion consists of the stem of the element name, the suffix *-ide*, and then the word *ion*. Thus, as we have already seen, Cl^- is "chlor-" + "-ide ion," or the chloride ion. Similarly, O^{2-} is the oxide ion, Se^{2-} is the selenide ion, and so forth. Table **4.5.2** lists the names of some common monatomic ions.

Example 4.5.1

Name each ion.

a. Ca^{2+}
b. S^{2-}
c. Cu^+

Solution

a. the calcium ion
b. the sulfide ion
c. the copper(I) ion or the cuprous ion

Exercise 4.5.1

Name each ion.

a. Fe^{2+}
b. Fe^{3+}
c. Ba^{2+}

Answer a:
iron(II) ion

Answer b:
iron(III) ion

Answer c:
barium ion

Example 4.5.2

Write the formula for each ion.

a. the bromide ion
b. the cupric ion
c. the magnesium ion

Solution

a. Br^-
b. Cu^{2+}
c. Mg^{2+}

Exercise 4.5.2

Write the formula for each ion.

a. the fluoride ion
b. the stannous ion
c. the potassium ion

Answer a:

F^-

Answer b:

Sn^{2+}

Answer c:

K^+

Naming Binary Ionic Compounds with a Metal that Forms Only One Type of Cation

Now that we know how to name ions, we are ready to name ionic compounds. A **binary** ionic compound is a compound composed of a **monatomic** metal **cation** and a monatomic nonmetal **anion**. The metal cation is named first, followed by the nonmetal anion as illustrated in Figure 4.5.1 for the compound $BaCl_2$. The word *ion* is dropped from both parts.

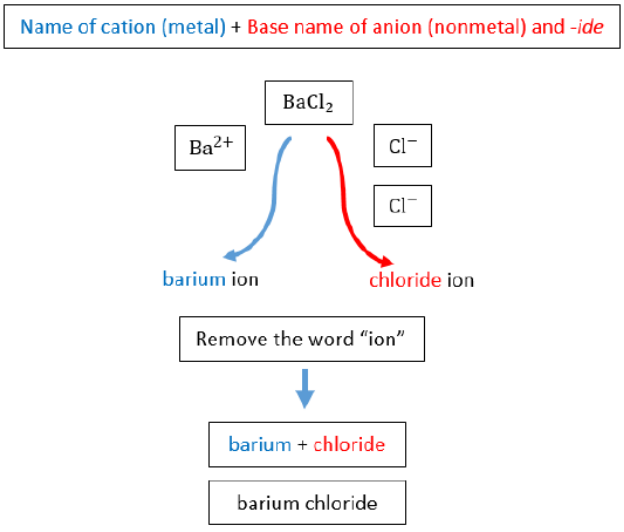


Figure 4.5.1 *Naming* $BaCl_2$

Naming formula: Name of metal cation + base name of nonmetal anion + suffix -ide. BaCl2 is named as barium chloride.

Subscripts in the formula do not affect the name.

Example 4.5.3: Naming Ionic Compounds

Name each ionic compound.

a. $CaCl_2$
b. AlF_3
c. KCl

Solution

a. Using the names of the ions, this ionic compound is named calcium chloride.
b. The name of this ionic compound is aluminum fluoride.
c. The name of this ionic compound is potassium chloride

Exercise 4.5.3

Name each ionic compound.

a. AgI
b. MgO
c. Ca_3P_2

Answer a:

silver iodide

Answer b:

magnesium oxide

Answer c:

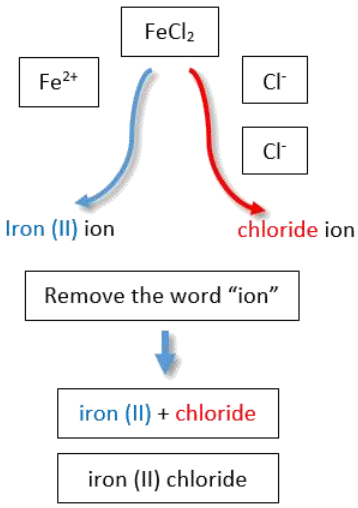
calcium phosphide

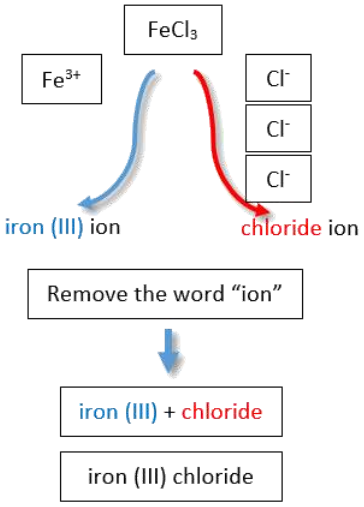
Naming Binary Ionic Compounds with a Metal That Forms More Than One Type of Cation

If you are given a formula for an ionic compound whose cation can have more than one possible charge, you must first determine the charge on the cation before identifying its correct name. For example, consider $FeCl_2$ and $FeCl_3$. In the first compound, the iron ion has a 2+ charge because there are two Cl^- ions in the formula (1− charge on each chloride ion). In the second compound, the iron ion has a 3+ charge, as indicated by the three Cl^- ions in the formula. These are two different compounds that need two different names. By the Stock system, the names are iron(II) chloride and iron(III) chloride (Figure 4.5.2).

Figure 4.5.2 Naming the $FeCl_2$ and $FeCl_3$ compounds in the modern/stock system.

Name of cation (metal) + (Roman Numeral in parenthesis) + Base name of anion (nonmetal) and *-ide*



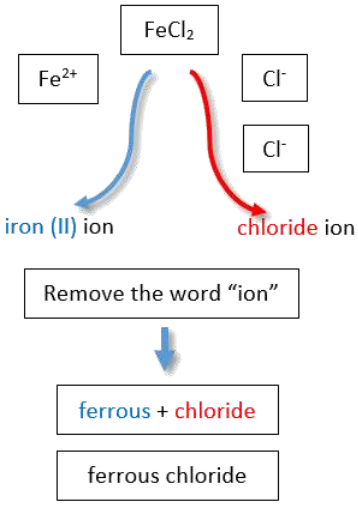


If we were to use the stems and suffixes of the common system, the names would be ferrous chloride and ferric chloride, respectively (Figure 4.5.3) .

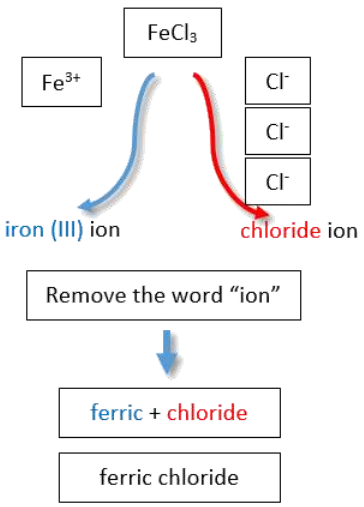
Figure 4.5.3 Naming the $FeCl_2$ and $FeCl_3$ compounds in the old/common System.

"Old" base name of cation (metal) and *-ic or -ous* + Base name of anion (nonmetal) and *-ide*

-ous (for ions with lower charge)



-ic (for ions with higher charge)



Example 4.5.4:

Name each ionic compound.

a. Co_2O_3

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b. FeCl2

Solution

Example **4.5.4**: Explanation of the names of ionic compounds

	Ionic Compound	Explanation	Answer
d	Co_2O_3	We know that cobalt can have more than one possible charge; we just need to determine what it is. • Oxide always has a 2− charge, so with three oxide ions, we have a total negative charge of 6−. • This means that the two cobalt ions have to contribute 6+, which for two cobalt ions means that each one is 3+. • Therefore, the proper name for this ionic compound is cobalt(III) oxide.	cobalt(III) oxide
d	FeCl2	Iron can also have more than one possible charge. • Chloride always has a 1− charge, so with two chloride ions, we have a total negative charge of 2−. • This means that the one iron ion must have a 2+charge. • Therefore, the proper name for this ionic compound is iron(II) chloride.	iron(II) chloride

? Exercise 4.5.4

Name each ionic compound.

a. $AuCl_3$
b. PbO_2
c. CuO

Answer a:
gold(III) chloride

Answer b:
lead(IV) oxide

Answer c:
copper(II) oxide

Figure **4.5.4** is a synopsis of how to name simple ionic compounds.

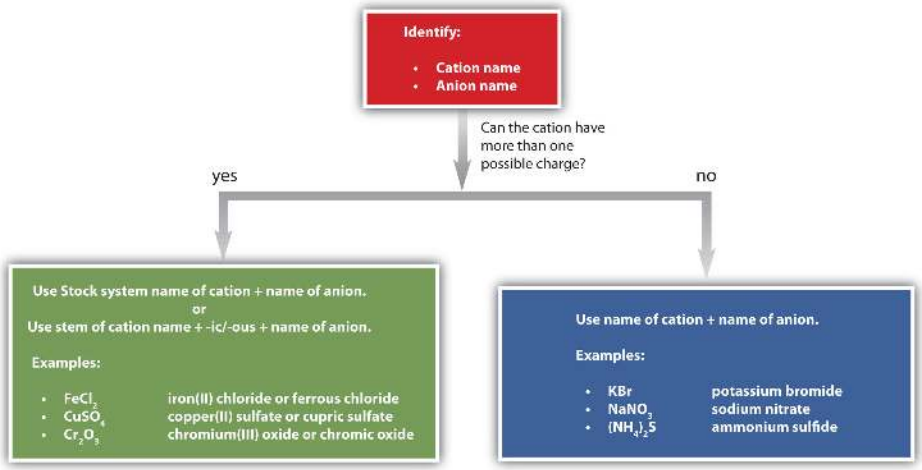


Figure 4.5.4: A Guide to Naming Simple Ionic Compounds.

? Exercise 4.5.5

Name each ionic compound.

a. $ZnBr_2$
b. Al_2O_3
c. AuF_3
d. AgF

Answer a:

zinc bromide

Answer b:

aluminum oxide

Answer c:

gold(III) fluoride or auric fluoride

Answer d:

silver fluoride

Writing Formulas of Ionic Compounds

Ionic compounds do not exist as molecules. In the solid state, ionic compounds are in crystal lattice 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. 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. This section will teach you how to find the correct ratio of ions, so that you can write a correct formula.

If you know the name of a binary ionic compound, you can write its **chemical formula**. Start by writing the metal ion with its charge, followed by the nonmetal ion with its charge. Because the overall compound must be electrically neutral, decide how many of each ion is needed in order for the positive and negative charge to cancel each other out.

✔ Example 4.5.5: Aluminum Nitride and Lithium Oxide

Write the formula for aluminum nitride and lithium oxide.

Solution

Example 4.5.5: Steps for Problem Solving Writing Formulas

Steps for Problem Solving	Write the formula for aluminum nitride	Write the formula for lithium oxide
1. Write the symbol and charge of the cation (metal) first and the anion (nonmetal) second.	Al^{3+} N^{3-}	Li^{+} O^{2-}
2. Use a multiplier to make the total charge of the cations and anions equal to each other.	total charge of cations = total charge of anions 1(3+) = 1(3-) +3 = -3	total charge of cations = total charge of anions 2(1+) = 1(2-) +2 = -2
3. Use the multipliers as subscript for each ion.	Al_1N_1	Li_2O_1
4. Write the final formula. Leave out all charges and all subscripts that are 1.	AlN	Li_2O

An alternative way to writing a correct formula for an ionic compound is to use the **crisscross method**. In this method, the numerical value of each of the ion charges is crossed over to become the subscript of the other ion. Signs of the charges are dropped.

Example 4.5.6: The Crisscross Method for lead (IV) oxide

Write the formula for lead (IV) oxide.

Solution

Example **4.5.6**: Steps For Problem Solving the Crisscross Method for writing formulas.

Crisscross Method	Example: Write the formula for lead (IV) oxide
1. Write the symbol and charge of the cation (metal) first and the anion (nonmetal) second.	Pb^{4+} O^{2-}
2. Transpose only the number of the positive charge to become the subscript of the anion and the number only of the negative charge to become the subscript of the cation.	
3. Reduce to the lowest ratio.	Pb_2O_4
4. Write the final formula. Leave out all subscripts that are 1.	PbO_2

Exercise 4.5.6

Write the chemical formula for an ionic compound composed of each pair of ions.

a. the calcium ion and the oxygen ion
b. the 2+ copper ion and the sulfur ion
c. the 1+ copper ion and the sulfur ion

Answer a:

CaO

Answer b:

CuS

Answer c:

Cu_2S

> *Be aware that ionic compounds are empirical formulas and so must be written as the lowest ratio of the ions.*

Example 4.5.7: Sulfur Compound

Write the formula for sodium combined with sulfur.

Solution

Example **4.5.7**: Steps For Problem Solving the Crisscross Method for writing formulas.

Crisscross Method	Write the formula for sodium combined with sulfur
1. Write the symbol and charge of the cation (metal) first and the anion (nonmetal) second.	Na^{+} S^{2-}
2. Transpose only the number of the positive charge to become the subscript of the anion and the number only of the negative charge to become the subscript of the cation.	
3. Reduce to the lowest ratio.	This step is not necessary.
4. Write the final formula. Leave out all all subscripts that are 1.	Na_2S

Exercise 4.5.7

Write the formula for each ionic compound.

a. sodium bromide
b. lithium chloride
c. magnesium oxide

Answer a:

NaBr

Answer b:

LiCl

Answer c:

MgO

Recognizing Ionic Compounds

There are two ways to recognize ionic compounds. First, compounds between metal and nonmetal elements are usually ionic. For example, $CaBr_2$ contains a metallic element (calcium, a group 2 (or 2A) metal) and a nonmetallic element (bromine, a group 17 (or 7A) nonmetal). Therefore, it is most likely an ionic compound. (In fact, it *is* ionic.) In contrast, the compound NO_2 contains two elements that are both nonmetals (nitrogen, from group 15 (or 5A), and oxygen, from group 16 (or 6A). It is not an ionic compound; it belongs to the category of covalent compounds discussed elsewhere. Also note that this combination of nitrogen and oxygen has no electric charge specified, so it is *not* the nitrite ion.

Second, if you recognize the formula of a polyatomic ion in a compound, the compound is ionic. For example, if you see the formula $Ba(NO_3)_2$, you may recognize the "NO_3" part as the nitrate ion, NO_3^-. (Remember that the convention for writing formulas for ionic compounds is not to include the ionic charge.) This is a clue that the other part of the formula, Ba, is actually the Ba^{2+} ion, with the 2+ charge balancing the overall 2− charge from the two nitrate ions. Thus, this compound is also ionic.

Example 4.5.8

Identify each compound as ionic or not ionic.

a. Na_2O
b. PCl_3
c. OF_2

Solution

Example 4.5.8: Steps For Problem Solving Identifying Ionic Compounds

Explanation	Answer
a. Sodium is a metal, and oxygen is a nonmetal. Therefore, Na_2O is expected to be ionic.	Na_2O, ionic
b. Both phosphorus and chlorine are nonmetals. Therefore, PCl_3 is not ionic.	PCl_3, not ionic
c. Both oxygen and fluorine are nonmetals. Therefore, OF_2 is not ionic.	OF_2, ionic

Exercise 4.5.8

Identify each compound as ionic or not ionic.

a. N_2O
b. $FeCl_3$

Answer a:

not ionic

Answer b:

ionic

Summary

- Ionic compounds are named by stating the cation first, followed by the anion.
- Positive and negative charges must balance.
- Some anions have multiple forms and are named accordingly with the use of roman numerals in parenthesis.
- Formulas for ionic compounds contain the symbols and number of each atom present in a compound in the lowest whole number ratio.

Contributors and Attributions

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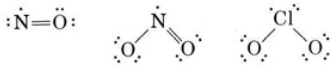
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4.6: Free Radicals and the Environment

Learning Objectives

- Recognize the structures of free radicals.
- Understand how free radicals affect the environment and biological systems.
- Know specific compounds that form photochemical smog.
- Understand how photochemical smog affects the environment and people.
- Realize that ozone in the stratosphere protects the earth from UV rays.
- Explain the basics of the Chapman Cycle.
- Provide sources of chemicals that deplete the ozone layer at an accelerated rate.
- Know where areas of depleted ozone are on the planet.
- Differentiate between CFCs, HCFC, HFC, and halons.
- Know the meaning and environmental impact of ODS and GWP.
- Appreciate the Montreal Protocol.

The majority of molecules or complex ions discussed in general chemistry courses are demonstrated to have *pairs* of electrons. However, there are a few stable molecules which contain an odd number of electrons. These molecules, called ***"free radicals"***, contain at least one unpaired electron, a clear violation of the octet rule. Free radicals play many important roles a wide range of applied chemistry fields, including biology, medicine, and environmental chemistry. Three well-known examples of such molecules are nitrogen monoxide, nitrogen dioxide, and chlorine dioxide. The most plausible Lewis structures for these molecules are



In this course, you need to be concerned with identifying free radical species. It is not necessary for you to know where to place the spare electron. In addition, please focus on the problems with free radicals that are discussed in the sections below.

Photochemical Smog

The two nitrogen-containing compounds above are classified as being NO_{xs}. These free radicals are produced from high-temperature combustion of fuel by vehicles and industry. NO_{xs} can also be produced by natural processes. For example, lightning and volcanic eruptions produce these species. These gases do differ from one another. Nitrogen monoxide (also known as nitric oxide) is a colorless and non-flammable gas. In contrast, nitrogen dioxide is a reddish-orange gas that is extremely flammable. Nitrogen monoxide has a slight odor, while nitrogen dioxide has a very sharp, acrid smell.

Once NO_{xs} are produced, they can react with ultraviolet light to produce more free radicals. After a series of reactions, these species produce ground-level ozone (O_3) which is referred to as smog. In regards to the environment, smog reduces visibility and smog precursors NO_{xs} and SO_{xs} react with water to produce acid rain. As for humans, NO_{xs} can affect lung, heart, and immunity functioning. Photochemical smog is more of an issue in highly populated cities that rely heavily on transportation sources and electrical power plants. Fortunately, the United States Environmental Protection Agency (EPA) regulates NO_{xs} amounts for vehicles and power plants.



Figure **4.6.2**: Arial photograph of photochemical smog in Manhattan, New York. Documerica was a program sponsored by the Environmental Protection Agency to photographically document subjects of environmental concern in America during the 1970s.

Consumers of American cars can review smog ratings before purchasing a vehicle. Cars and trucks produce other chemicals besides NOxs that contribute to smog formation. For a basic rating on smog-producing ability, click here and input your vehicle's information. On this website, smog ratings are assigned to mobile sources (cars, trucks, sports utility vehicles) from one to ten. A low score indicates that the vehicle produces a large number of smog precursors.

Protective Ozone (O_3)

Ozone or O_3 can be harmful or helpful depending on where it is located. In the troposphere (see image below), ozone is referred to as smog. This particular species can be formed from free radicals. Previously, you have learned the harmful effects of being exposed to ground level ozone. However, ozone acts as a protective shield in the stratosphere. Of the three forms of ultraviolet radiation, ozone completely screens the Earth's surface from UV-C radiation. Portions of UV-B (causes more burning of skin) and UV-A (causes more tanning of skin) still reaches the terrestrial environment.

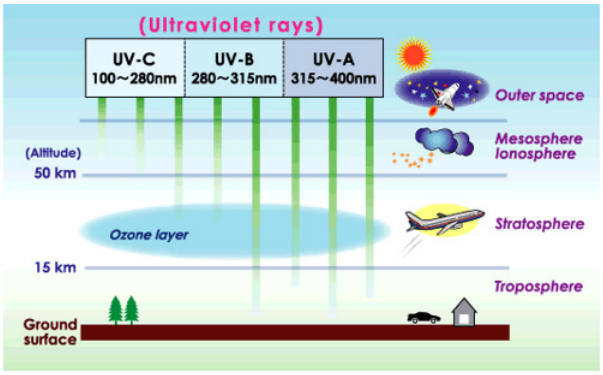


Figure **4.6.3**: Levels of the atmosphere and location of the O_3 layer. Image is taken from commons.wikimedia.org/wiki/F...5%E0%B8%81.jpg

If all the ozone in the atmosphere were combined, it would have a thickness of less than 0.5 cm (.20 inches). Ozone is most concentrated in the lowest 15 km portion of the stratosphere. NASA and other atmospheric scientists utilize the Dobson scale to represent the concentration of ozone molecules. One Dobson Unit (DU) is the number of ozone molecules that could create a 0.01 mm layer of thickness (conditions of 0ºC and 1.0 atm). NASA reports the average thickness of the ozone layer to be **300 DU** which translates to **3 mm**. A depleted ozone layer would register as being equal to or less than **100 DU** or a thickness of **1 mm.** The NASA image below depicts a purplish-blue region that corresponds to the largest area of ozone depletion. First detected in 1985, the ozone hole has grown to a maximum of 7.6 million square miles (or 2.5 times the size of the United States. NASA reported this peak value on September 11, 2017.

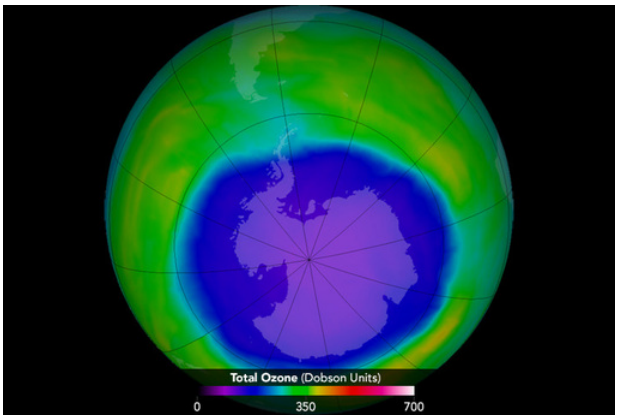


Figure **4.6.4**: NASA image of Dobson units that correlates to O_3 concentration. (Public Domain; NASA)

Ozone is made and decomposed naturally via the Chapman cycle. In the stratosphere, ultraviolet light breaks the double bond of the diatomic oxygen molecule. From this reaction, spare oxygen (O) atoms encounter more diatomic oxygen (O_2) molecules to produce ozone. Ultraviolet light can attack ozone molecules BY CLEAVING ONE oxygen bond in the structure. This natural cycle of ozone production and decomposition repeats in the Chapman Cycle.

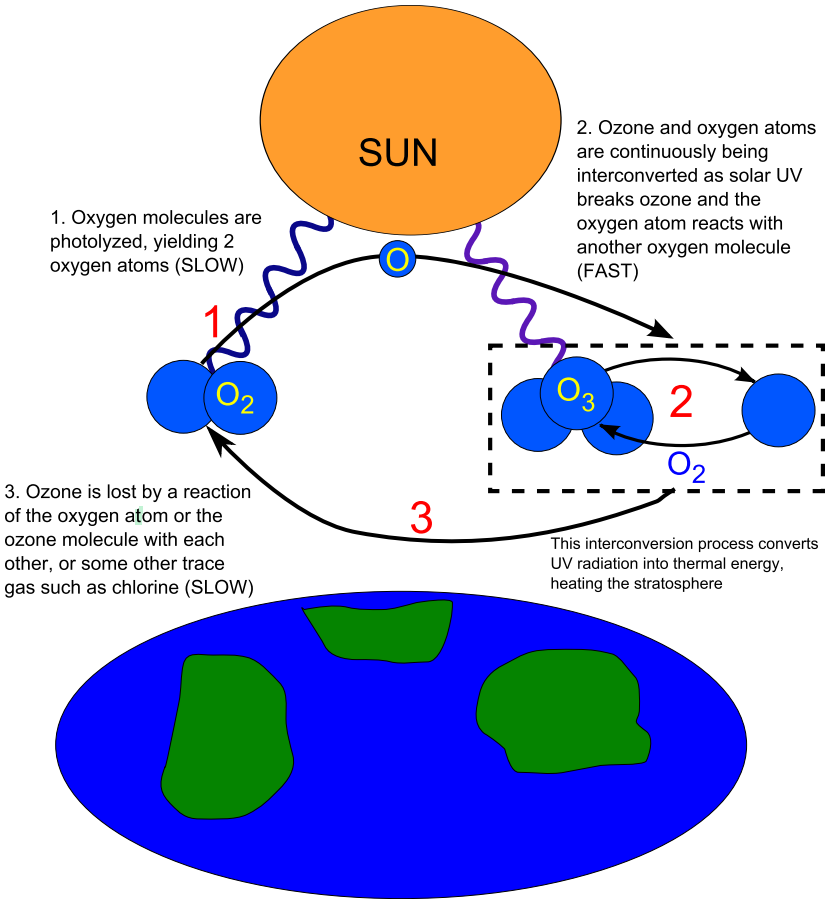


Figure **4.6.5**: Production and decomposition of ozone via the Chapman Cycle. (Public Domain via Wikipedia)

Understanding Stratospheric Ozone

Watch The following video and then answer the questions below:



a. What is the formula for ozone? what types of bonds does this molecule have (you will need to draw)?
b. How many ozone molecules are present per 10 million molecules of air?
c. What percentage of UV rays does ozone layer absorb?
d. What chemicals are responsible for depleting ozone?
e. What are the uses of the chemicals in question #4?
f. When UV light hits ozone-depleting chemicals, what atom is liberated? How many valence electrons does this atom have?
g. Where are the areas on the earth that have ozone holes or patches?
h. Why is the largest area of depletion over Antartica?
i. At this time, is the ozone hole growing or shrinking?
j. What protocol banned the production of ozone-depleting chemicals?

Answer a

Ozone (O_3), which this molecule has a single and a double bond. The single bond is much weaker and longer. It would be easier to break this bond.

Answer b

3

Answer c

98%

Answer d

CFCs are organic compounds that contain different combinations of carbon, chlorine, fluorine, and sometimes hydrogen. The chlorine portion is particularly toxic to the ozone layer.

Answer e

Chlorine gas or chlorine that is used to disinfect drinking water is not a CFC.

Answer f

When ultraviolet light hits a CFC, chlorine is freed and becomes a free radical. This reactive species attacks the ozone molecule at the single bond location. Chlorine atom has seven valence electrons.

Answer g

Both poles contain areas that are lacking in O_3.

Answer h

The CFCS used in northern hemisphere eventually migrated to the cold areas of Antarctica. The temperatures in this area catalyze (speed up) the free radical reactions. This produces more chlorine atoms that will attack ozone molecules.

Answer i

The hole is shrinking!

Answer j

Montreal Protocol

Causes of Depletion

Before the 1920's, the mechanism of chemical refrigeration required such toxic chemicals as ammonia or sulfur dioxide. Frigidaire scientists focused on synthesizing safer compounds to be used in this industry. This research lead to the production of CFCs or compounds that contained a combination of chlorine, carbon, and fluorine. Chemists found these colorless liquids to be very volatile and inert. By the 1970's, the chemical industry was producing one million tons a year of these chemicals to be used as refrigerants, propellants, and foaming agents.



Figure **4.6.6**: Asthma inhaler with CFC propellant. (Public Domain; US Govnerment).

Perhaps the most common CFC made was dichlorodifluoromethane. This CFC is also known as Freon-12 and was used as a refrigerant for cars, commercial, and industrial air conditioning systems. Today, the United States is no longer able to make this compound and distributors must have a Freon license to distribute existing supplies. Even though you might use the term "freon" to describe air conditioning coolant, you are not using this particular chemical due to environmental restrictions.

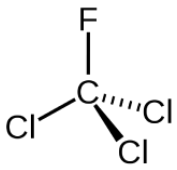


Figure **4.6.7**: Chemical structure of Freon-12.

In the early to late 1970's, many international studies determined CFCs and other halons (once used as fire retardants), particularly those containing bromine, contributed to the destruction of the ozone layer. It was not until the mid-1980's that an international treaty was formulated to reduce the production of certain ODS (ozone depleting substance). In 1987, over 190 countries signed the Montreal Protocol. Upon signature, countries would agree to reduce and then eliminate ODS chemicals that contained chlorine or bromine. Countries that could not afford to find suitable replacements for ODS would be given time extensions and funding.



Figure **4.6.8**: Label indicating ozone friendly packaging. Picture courtesy of Elizabeth R. Gordon

Operation Cool breeze

Even though freon production in the United States has halted, this chemical is still used in refrigeration systems that cannot switch to ozone-friendly replacements. This has opened an illegal smuggling of freon into countries that have signed the Montreal Protocol. In the United States, freon smuggling is an environmental crime. Violators that have been prosecuted have paid fines and/or served time in prison. Read the article in this link and record main ideas regarding EPA/s Operation Cool Breeze.

The United States and several other countries replaced many CFCs with HCFC compounds. By adding hydrogen, this allowed a CFC compound to retain its chlorine atoms. In other words, ultraviolet light would not be able to break the C-Cl bond releasing a chlorine free radical. Unfortunately, HCFCs were found to have higher global warming potentials (GWP) and would need to be phased out as well. For most countries, this HCFC reduction would occur in 2010. During this time, countries substituted HFCs for both HCFC and CFC compounds. HFCs have the lowest OD potential but still, have high GWP. Today, countries are focusing on finding more environmentally friendly replacements for these chemicals as well. Keep in mind, each chemical substitution that has been mentioned is costly and still affects the environment.

Table **4.6.1**: Comparing CFCs, HCFCs, HFCs, and halons.

Chemicals Formula	Classification	Atmospheric lifetime (years)	ODP	GWP
CF_2Cl_3	CFC	69	1.0	4660
CF_2Cl_2	CFC	195	1.0	10,200
CF_3Br	Halon	65	13	6300
CF_2ClBr	Halon	20	5.0	1750
$CHClF_2$	HCFC	13	.055	1760
$CHCl_2CF_3$	HCFC	1.4	.02	80
CH_2F_2	HFC	5	0	677
CHF_2CF_3	HFC	29	0	3170

Free radical formation from the cleavage (breaking) of the C-Cl bond by ultraviolet light can be seen in the reactions below. It is **not** important for you to memorize these series of reactions. However, it should be noted that chlorine and bromine cause ozone depletion when they are freed from ozone-depleting substances.

Ultraviolet radiation, denoted by $h\nu$, breaks the carbon chlorine bond to form two free radicals

$$CF_2Cl_2 + h\,\nu \rightarrow CF_2Cl^{\cdot} + Cl^{\cdot} \tag{4.6.1}$$

Chlorine atom being highly reactive reacts with ozone (O_3).

$$Cl^{\cdot} + O_3 \rightarrow ClO^{\cdot} + O_2 \tag{4.6.2}$$

The monoxide of chlorine further reacts with another molecule of O_3

$$ClO^{\cdot} + O_3 \rightarrow Cl^{\cdot} + 2\,O_2 \tag{4.6.3}$$

The chlorine atom so obtained reacts with another ozone molecule. Hence, steps 4.6.2 and 4.6.3 are repeated again and again and, leads to the depletion of concentration of ozone.

The Montreal Protocol

International policy efforts to restrict production of ozone depleting CFCs culminated in the 1987 treaty known as the **Montreal Protocol** in which signing nations agreed to cut CFC production in half by 1998. At least five follow-up agreements since then helped to deepen the cuts, advanced timetables for compliance, and addressed additional ozone-depleting substances such as halons, methyl chloroform, carbon tetrachloride, and hydrochlorofluorocarbons (HCFCs). Most countries around the world have phased out production of the substances covered by the agreements and industry has been able to shift to safer alternative chemicals. As a result, there's evidence that the Antarctic ozone hole has stopped growing worse, although recovery is not expected anytime soon. Phasing out CFCs and HCFCs is also beneficial in protecting the earth's climate, as these substances are also very damaging greenhouse gases.

As part of the United States' commitment to implementing the Montreal Protocol, the U.S. Congress amended the Clean Air Act (section 6.7), adding provisions for protection of the ozone layer. Most importantly, the amended Act required the gradual end to the production of chemicals that deplete the ozone layer. The Clean Air Act amendments passed by Congress requires the Environmental Protection Agency (EPA) to develop and implement regulations for the responsible management of ozone-depleting substances in the United States. Under the Clean Air Act, EPA has created several regulatory programs to address numerous issues, including:

- ending the production of ozone-depleting substances,
- ensuring that refrigerants and halon fire extinguishing agents are recycled properly,
- identifying safe and effective alternatives to ozone-depleting substances,
- banning the release of ozone-depleting refrigerants during the service, maintenance, and disposal of air conditioners and other refrigeration equipment,
- requiring that manufacturers label products either containing or made with the most harmful ozone depleting substances.

References

1. https://www.nap.edu/read/5744/chapter/5#23
2. https://www.epa.gov/ozone-layer-prot...ing-substances

Contributors and Attributions

- Elizabeth R. Gordon (Furman University)
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- The Montreal Protocol contributed by Caralyn Zehnder et al.

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4.7: Free Radicals and Health

Learning Objectives

- Realize how free radicals can affect your health.
- Name some health conditions and diseases that can result from excessive free radical exposure.
- Provide examples of foods and beverages that contain antioxidants.
- Recognize chemicals in skin care products that can slow the effects of aging

Free radicals can be generated from a variety of processes. For example, combustion of any material will produce $OH^{\cdot}$ (not hydroxide), $NO^{\cdot}$ free radicals. Once inhaled, OH can enter the body and affect cells. Watch the video below to see how free radicals affect biological systems.



Video **4.7.1**: How do antioxidants keep you healthy? Our body is under constant attack from oxidative stress. By wrong lifestyle choices, we make billions of free radicals in our body leading to oxidative stress. This can also increase when we are physically and/or emotionally stressed. Oxidative stress occurs when there is an imbalance of free radicals and antioxidants (too many free radicals and too few antioxidants). It is a condition that results when our body does not have enough antioxidants to counter free radicals in our body.

Free Radicals and Disease

Free radical exposure has been linked to cancer and a number of autoimmune diseases. One way of fighting free radicals is to consume or apply antioxidants. By providing sources of electrons, antioxidants can detour free radicals from attacking healthy cells in the body. The word wall below displays a variety of foods that are rich in antioxidants. Foods and beverages that are rich in vitamins A, C, and E provide sources of electrons for free radicals. Minerals like selenium are also antioxidants. For a more comprehensive list of foods are labeled as being antioxidants, click here.



Figure **4.7.1**: Word wall art displaying antioxidants. Image is taken from pixabay.com/en/cloud-concept...dants-18527

Free Radicals and Aging

Some studies have linked biological free radical production to aging. In a cell's mitochondria, reactive oxygen species are naturally made. These substances damage fats, proteins, and mitochondria DNA. During this process, more free radicals are produced in the cell. Two of these destructive free radicals are superoxide (O_2-) and nitrogen monoxide (NO). These radicals have been linked to cancer, skin aging, heart disease, stroke, and other chronic diseases.

By eating more fruits and vegetables, many nutritionists believe the free radical effect can be reduced in regards to chronic disease. As for aging, many scientists believe that not just one theory can explain why aging occurs. For care of skin, dermatologists recommend that you reduce UV exposure. Ionizing radiation is a source of free radicals that can be minimized. Once the skin has been exposed to UV radiation, there is very little that can be done to counteract its effects.



Figure **4.7.2**: Skin comparison of a younger to an older person (Public Domain; via Wikipedia). Hand creams (Public Dominal Elizabeth R. Gordon)

Dermatologists and nutritionists recommend a diet rich in antioxidants (vitamins C, E, selenium, and coenzyme Q) to protect skin from damaging free radicals. Lotions, moisturizers, and sunscreens can contain these ingredients as well.

Skin Care products

Watch the following video to understand how to care for your skin



1. What are the purposes of the Epidermis and dermis in your skin?
2. What do GAGS do:
3. How can UVB help the body?
4. What do the letters ROS represent?
5. How do free radicals affect DNA, proteins, Fats, and the Dermis?
6. What types of chemicals help repair damaged skin?
7. When should the chemicals in question #6 not be used?
8. How does Salicylic acid make skin appear more youthful?
9. What is the purpose of applying hyaluronic (it is a humectant) acid to skin?
10. Why are peptide products useless?
11. According to this video, what is the best anti-aging product you can purchase?

***Figure* 4.7.11** *Retinol*

Manufacturers of anti-aging lotions or creams might use the scientific chemical names for the antioxidant ingredients. When purchasing these products, remember to translate them accordingly. Consumers often spend excessive amounts of money on anti-aging creams and lotions. The best way to reduce advanced aging is to protect your skin from ultraviolet exposure. In addition, selecting a skin-care product that contains a combination of some of the antioxidants below is helpful. Lastly, there is no need to pay a large amount of money for an anti-aging product.

Table **4.7.2**: Antioxidants and their effect on skin

Antioxidant	Effect on skin
Vitamin E (also known as Alpha-lipoic acid, 3-5%)	protects skin from sun damage
Vitamin A (also known as Retinoic acid, 0.01-0.1%)	treats fine wrinkles, age spots, and rough skin
Flavonoids (extracts from green tea or chocolate)	reverses sun damage
Vitamin B_6	treats fine wrinkles and protects skin from sun damage
Lycopene (a carotene that is present in tomatoes, watermelon, asparagus, and grapefruit)	protects skin from sun damage

References

1. https://www.nap.edu/read/5744/chapter/5#23
2. https://www.epa.gov/ozone-layer-prot...ing-substances

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4.8: Covalent Bonds- Shared Electron Pairs

Learning Objectives

- Define covalent bond.
- Illustrate covalent bond formation with Lewis electron dot diagrams.

Ionic bonding typically occurs when it is easy for one atom to lose one or more electrons and another atom to gain one or more electrons. However, some atoms won't give up or gain electrons easily. Yet they still participate in compound formation. How? There is another mechanism for obtaining a complete valence shell: *sharing* electrons. When electrons are shared between two atoms, they make a bond called a **covalent bond**.

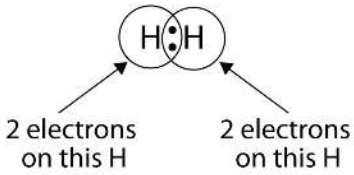
Chemists frequently use Lewis diagrams to represent covalent bonding in molecular substances. For example, the Lewis diagrams of two separate hydrogen atoms are as follows:



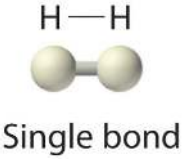
The Lewis diagram of two hydrogen atoms sharing electrons looks like this:



We can use circles to show that each H atom has two electrons around the nucleus, completely filling each atom's valence shell:



Because each H atom has a filled valence shell, this bond is stable, and we have made a diatomic hydrogen molecule. (This explains why hydrogen is one of the diatomic elements.) For simplicity's sake, it is not unusual to represent the covalent bond with a dash, instead of with two dots:



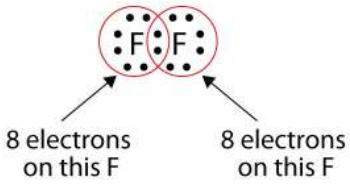
Because two atoms are sharing one pair of electrons, this covalent bond is called a **single bond**. As another example, consider fluorine. F atoms have seven electrons in their valence shell:



These two atoms can do the same thing that the H atoms did; they share their unpaired electrons to make a covalent bond.



Note that each F atom has a complete octet around it now:



We can also write this using a dash to represent the shared electron pair:

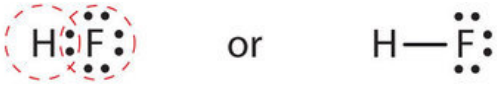


There are two different types of electrons in the fluorine diatomic molecule. The **bonding electron pair** makes the covalent bond. Each F atom has three other pairs of electrons that do not participate in the bonding; they are called **lone pair electrons**. Each F atom has one bonding pair and three lone pairs of electrons.

Covalent bonds can be made between different elements as well. One example is HF. Each atom starts out with an odd number of electrons in its valence shell:



The two atoms can share their unpaired electrons to make a covalent bond:



In this molecule, the hydrogen atom does not have nonbonding electrons, while the fluorine atom has six nonbonding electrons (three lone electron pairs). The circles show how the valence electron shells are filled for both atoms.

Example 4.8.1:

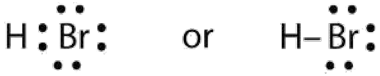
Use Lewis electron dot diagrams to illustrate the covalent bond formation in HBr.

Solution

HBr is very similar to HF, except that it has Br instead of F. The atoms are as follows:



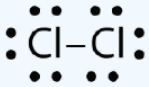
The two atoms can share their unpaired electron:



Exercise 4.8.1

Use Lewis electron dot diagrams to illustrate the covalent bond formation in Cl_2.

Answer:

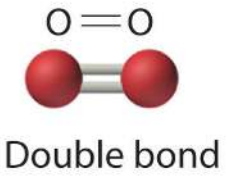


When working with covalent structures, it sometimes looks like you have leftover electrons. You apply the rules you learned so far and there are still some electrons hanging out there unattached. You can't just leave them there. So where do you put them?

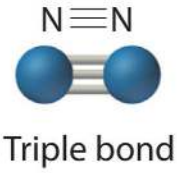
Multiple Covalent Bonds

The sharing of a pair of electrons represents a single covalent bond, usually just referred to as a ***single bond***. However, in many molecules atoms attain complete octets by sharing more than one pair of electrons between them:

- Two electron pairs shared a ***double bond***



- Three electron pairs shared a ***triple bond***



Because each nitrogen contains 5 valence electrons, they need to share 3 pairs to each achieve a valence octet. N_2 is fairly inert, due to the strong triple bond between the two nitrogen atoms.



Summary

- Covalent bonds are formed when atoms share electrons.
- Lewis electron dot diagrams can be drawn to illustrate covalent bond formation.
- Double bonds or triple bonds between atoms may be necessary to properly illustrate the bonding in some molecules.

Contributors and Attributions

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- Anonymous
- Marisa Alviar-Agnew (Sacramento City College)
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4.9: Unequal Sharing- Polar Covalent Bonds

Learning Objectives

- Define electronegativity
- Determine the polarity of a covalent bond.

Electronegativity

The ability of an atom in a molecule to attract shared electrons is called **electronegativity**. 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. This is why metals (low electronegativities) bonded with nonmetals (high electronegativities) typically produce ionic compounds.

A bond may be so polar that an electron actually transfers from one atom to another, forming a true ionic bond. How do we judge the degree of polarity? Scientists have devised a scale called **electronegativity**, a scale for judging how much atoms of any element attract electrons. Electronegativity is a unitless number; the higher the number, the more an atom attracts electrons. A common scale for electronegativity is shown in Figure **4.9.1**.

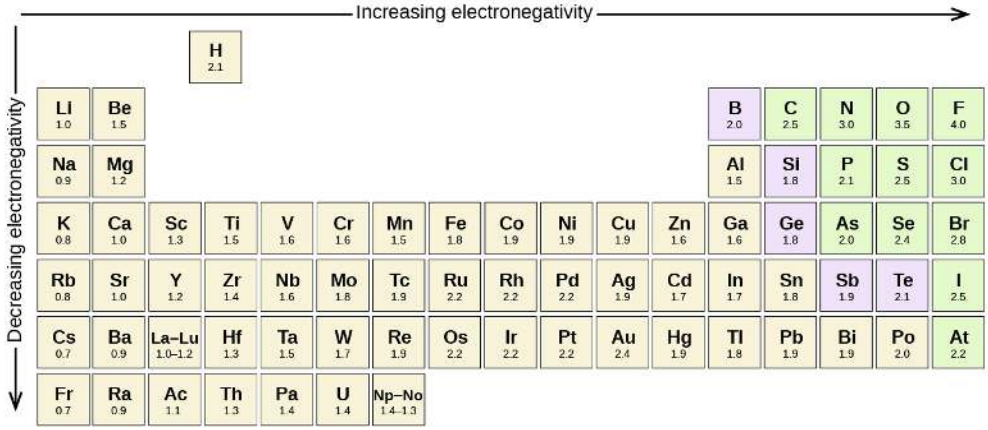


Figure **4.9.1** Electronegativities of the Elements. Electronegativities are used to determine the polarity of covalent bonds.

Bond Polarity

The polarity of a covalent bond can be judged by determining the *difference* of the electronegativities of the two atoms involved in the covalent bond, as summarized in the following table:

Table **4.9.1**:Electronegativity differences and bond type

Electronegativity Difference	Bond Type
0	nonpolar covalent
0–0.4	slightly polar covalent
0.5–2.0	definitely polar covalent
>2.0	likely ionic

Nonpolar Covalent Bonds

A bond in which the electronegativity difference is less than 1.9 is considered to be mostly covalent in character. However, at this point we need to distinguish between two general types of covalent bonds. A **nonpolar covalent bond** is a covalent bond in which

the bonding electrons are shared equally between the two atoms. In a nonpolar covalent bond, the distribution of electrical charge is balanced between the two atoms.

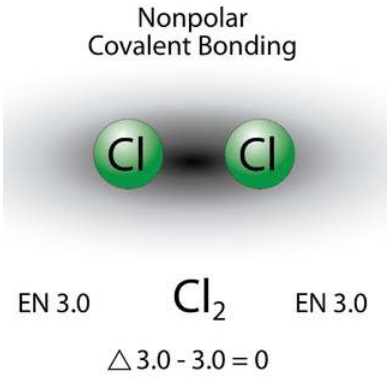


Figure **4.9.2** A nonpolar covalent bond is one in which the distribution of electron density between the two atoms is equal.

The two chlorine atoms share the pair of electrons in the single covalent bond equally, and the electron density surrounding the Cl_2 molecule is symmetrical. Also note that molecules in which the electronegativity difference is very small (<0.5) are also considered nonpolar covalent. An example would be a bond between chlorine and bromine ($\Delta EN = 3.0 - 2.8 = 0.2$).

Polar Covalent Bonds

A bond in which the electronegativity difference between the atoms is between 0.5 and 2.0 is called a polar covalent bond. A **polar covalent bond** is a covalent bond in which the atoms have an unequal attraction for electrons and so the sharing is unequal. In a polar covalent bond, sometimes simply called a polar bond, the distribution of electrons around the molecule is no longer symmetrical.

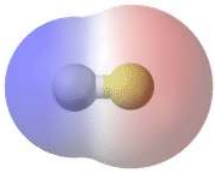


Figure **4.9.3** In the polar covalent bond of **HF**, the electron density is unevenly distributed. There is a higher density (red) near the fluorine atom, and a lower density (blue) near the hydrogen atom.

An easy way to illustrate the uneven electron distribution in a polar covalent bond is to use the Greek letter delta (δ).

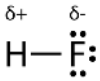


Figure **4.9.4** Use of δ to indicate partial charge.

The atom with the greater electronegativity acquires a partial negative charge, while the atom with the lesser electronegativity acquires a partial positive charge. The delta symbol is used to indicate that the quantity of charge is less than one. A crossed arrow can also be used to indicate the direction of greater electron density.



Figure **4.9.5** Use of crossed arrow to indicate polarity



Electronegativity differences in bonding using Pauling scale. Using differences in electronegativity to classify bonds as covalent, polar covalent, or ionic.

Example 4.9.1: Bond Polarity

What is the polarity of each bond?

a. C–H
b. O–H

Solution

Using Figure 4.9.1, we can calculate the difference of the electronegativities of the atoms involved in the bond.

a. For the C–H bond, the difference in the electronegativities is 2.5 − 2.1 = 0.4. Thus we predict that this bond will be non polar covalent.
b. For the O–H bond, the difference in electronegativities is 3.5 − 2.1 = 1.4, so we predict that this bond will be definitely polar covalent.

Exercise 4.9.1

What is the polarity of each bond?

a. Rb–F
b. P–Cl

Answer a

likely ionic

Answer b

polar covalent

Summary

- The type of bond (polar covalent,non polar covalent or ionic) between two atoms is determined by the differences in electronegativity.
- For atoms sharing a polar covalent bond, the atom with the greater electronegativity acquires a partial negative charge, while the atom with the lesser electronegativity acquires a partial positive charge.

Contributors and Attributions

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4.10: Polyatomic Molecules- Water, Ammonia, and Methane

Learning Objectives

- Determine the number of bonds formed by common nonmetal elements.
- Illustrate covalent bond formation with Lewis electron dot diagrams.

More than two atoms can participate in covalent bonding, although any given covalent bond will be between two atoms only. Water, ammonia, and methane are common examples that will be discussed in detail below. Carbon is unique in the extent to which it forms single, double, and triple bonds to itself and other elements. The number of bonds formed by an atom in its covalent compounds is not arbitrary. Hydrogen, oxygen, nitrogen, and carbon have very strong tendencies to form substances in which they have one, two, three, and four bonds to other atoms, respectively (Table **4.10.1**).

Table **4.10.1** The Number of Bonds That Selected Atoms Commonly Form to Other Atoms

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

Water

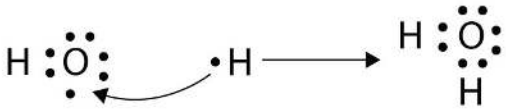
Consider H and O atoms:



The H and O atoms can share an electron to form a covalent bond:



The H atom has a complete valence shell. However, the O atom has only seven electrons around it, which is not a complete octet. We fix this by including a second H atom, whose single electron will make a second covalent bond with the O atom:



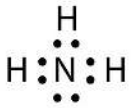
(It does not matter on what side the second H atom is positioned.) Now the O atom has a complete octet around it, and each H atom has two electrons, filling its valence shell. This is how a water molecule, H_2O, is made.

Ammonia

The N atom has the following Lewis electron dot diagram:

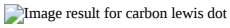


It has three unpaired electrons, each of which can make a covalent bond by sharing electrons with an H atom. The electron dot diagram of NH_3 is as follows:

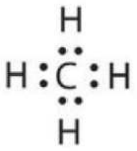


Methane

The C atom has the following Lewis electron dot diagram:



It has four unpaired electrons, each of which can make a covalent bond by sharing electrons with an H atom. The electron dot diagram of CH_4 is as follows:



Summary

In polyatomic molecules, there is a pattern of covalent bonds that different atoms can form.

Contributors and Attributions

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- Marisa Alviar-Agnew (Sacramento City College)

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4.11: Polyatomic Ions

Learning Objectives

- Recognize polyatomic ions in chemical formulas.
- Write the correct formula for ionic compounds with polyatomic ions.
- Use the rules for naming ionic compounds with polyatomic ions.

Polyatomic Ions

Some ions consist of groups of atoms bonded together and have an overall electric charge. Because these ions contain more than one atom, they are called polyatomic ions. Polyatomic ions have characteristic formulas, names, and charges that should be memorized. For example, NO_3^- is the nitrate ion; it has one nitrogen atom and three oxygen atoms and an overall 1− charge. Table **4.11.1** lists the most common polyatomic ions.

Table **4.11.1** Some Polyatomic Ions

Name	Formula
ammonium ion	NH_4^+
acetate ion	$C_2H_3O_2^-$ (also written $CH_3CO_2^-$)
carbonate ion	CO_3^{2-}
chromate ion	CrO_4^{2-}
dichromate ion	$Cr_2O_7^{2-}$
hydrogen carbonate ion (bicarbonate ion)	HCO_3^-
cyanide ion	CN^-
hydroxide ion	OH^-
nitrate ion	NO_3^-
nitrite ion	NO_2^-
permanganate ion	MnO_4^-
phosphate ion	PO_4^{3-}
hydrogen phosphate ion	HPO_4^{2-}
dihydrogen phosphate ion	$H_2PO_4^-$
sulfate ion	SO_4^{2-}
hydrogen sulfate ion (bisulfate ion)	HSO_4^-
sulfite ion	SO_3^{2-}

The rule for constructing formulas for ionic compounds containing polyatomic ions is the same as for formulas containing monatomic (single-atom) ions: the positive and negative charges must balance. If more than one of a particular polyatomic ion is needed to balance the charge, the *entire formula* for the polyatomic ion must be enclosed in parentheses, and the numerical subscript is placed *outside* the parentheses. This is to show that the subscript applies to the entire polyatomic ion. An example is $Ba(NO_3)_2$.

Writing Formulas for Ionic Compounds Containing Polyatomic Ions

Writing a formula for ionic compounds containing polyatomic ions also involves the same steps as for a binary ionic compound. Write the symbol and charge of the cation followed by the symbol and charge of the anion.

Example 4.11.1: Calcium Nitrate

Write the formula for calcium nitrate.

Solution

Example **4.11.1**: Steps For Problem Solving, Write the formula for calcium nitrate

Criss Cross Method	Write the formula for calcium nitrate
1. Write the symbol and charge of the cation (metal) first and the anion (nonmetal) second.	Ca^{2+} NO_3^-
2. Transpose only the number of the positive charge to become the subscript of the anion and the number only of the negative charge to become the subscript of the cation.	 The 2+ charge on Ca becomes the subscript of NO3 and the 1- charge on NO3 becomes the subscript of Ca.
3. Reduce to the lowest ratio.	$Ca_1(NO_3)_2$
4. Write the final formula. Leave out all subscripts that are 1. If there is only 1 of the polyatomic ion, leave off parentheses.	$Ca(NO_3)_2$

Example 4.11.2

Write the chemical formula for an ionic compound composed of the potassium ion and the sulfate ion

Solution

Example **4.11.2**: Explanation for Writing the Chemical Formula for an Ionic Compound Composed of the Potassium Ion and the Sulfate Ion

Explanation	Answer
Potassium ions have a charge of 1+, while sulfate ions have a charge of 2−. We will need two potassium ions to balance the charge on the sulfate ion, so the proper chemical formula is K_2SO_4.	K_2SO_4

Exercise 4.11.1

Write the chemical formula for an ionic compound composed of each pair of ions.

a. the magnesium ion and the carbonate ion
b. the aluminum ion and the acetate ion

Answer a:

$MgCO_3$

Answer b:

$Al(CH_3COO)_3$

Naming Ionic Compounds with Polyatomic Ions

The process of naming ionic compounds with polyatomic ions is the same as naming binary ionic compounds. The cation is named first, followed by the anion. One example is the ammonium Sulfate compound in Figure **4.11.6**.

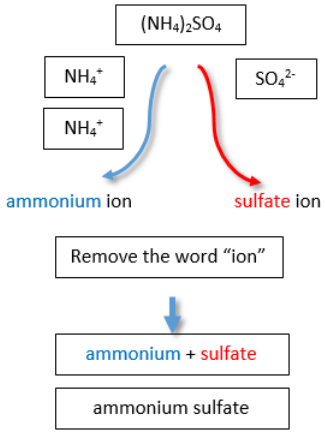


Figure 4.11.2 *Naming Ionic Compounds with Polyatomic Ions*

Example 4.11.3: Naming Ionic Compounds

Write the proper name for each ionic compound.

a. $(NH_4)_2S$
b. $AlPO_4$,
c. $Fe_3(PO_4)_2$

Solution

Example 4.11.3: Explanation for Naming Ionic Compounds

Ionic Compound	Explanation	Answer
a. **$(NH_4)_2S$**	a. The ammonium ion has a 1+ charge and the sulfide ion has a 2− charge. Two ammonium ions need to balance the charge on a single sulfide ion. The compound's name is ammonium sulfide.	ammonium sulfide
b. $AlPO_4$,	b. The ions have the same magnitude of charge, one of each (ion) is needed to balance the charges. The name of the compound is aluminum phosphate.	aluminum phosphate
c. $Fe_3(PO_4)_2$	c. Neither charge is an exact multiple of the other, so we have to go to the least common multiple of 6. To get 6+, three iron(II) ions are needed, and to get 6−, two phosphate ions are needed . The compound's name is iron(II) phosphate.	iron(II) phosphate

Exercise 4.11.2

Write the proper name for each ionic compound.

a. $(NH_4)_3PO_4$

b. $Co(NO_2)_3$

Answer a:

ammonium phosphate

Answer b:

cobalt(III) nitrite

Summary

- Formulas for ionic compounds contain the symbols and number of each atom and/or polyatomic ion present in a compound in the lowest whole number ratio.
- The process of naming ionic compounds with polyatomic ions are the same as binary ionic compounds.

Contributors and Attributions

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4.12: Rules for Writing Lewis Formulas

Learning Objective

- Write Lewis structures for molecules and ions.
- Know the exceptions to the octet rule.

The following procedure can be used to construct Lewis electron structures for more complex molecules and ions:

How-to: Constructing Lewis electron structures

1. Determine the total number of valence electrons in the molecule or ion.

- Add together the valence electrons from each atom. (Recall that the number of valence electrons is indicated by the position of the element in the periodic table.)
- If the species is a polyatomic ion, remember to add or subtract the number of electrons necessary to give the total charge on the ion.

  For CO_3^{2-}, for example, we add two electrons to the total because of the -2 charge.

2. Arrange the atoms to show specific connections.

- When there is a central atom, it is usually the least electronegative element in the compound. Chemists usually list this central atom first in the chemical formula (as in CCl_4 and CO_3^{2-}, which both have C as the central atom), which is another clue to the compound's structure.
- Hydrogen and the halogens are almost always connected to only one other atom, so they are usually *terminal* rather than central.

3. Place a bonding pair of electrons between each pair of adjacent atoms to give a single bond.

- In H_2O, for example, there is a bonding pair of electrons between oxygen and each hydrogen.

4. Beginning with the terminal atoms, add enough electrons to each atom to give each atom an octet (two for hydrogen).

- These electrons will usually be lone pairs.

5. If any electrons are left over, place them on the central atom.

- We will explain later that some atoms are able to accommodate more than eight electrons.

6. If the central atom has fewer electrons than an octet, use lone pairs from terminal atoms to form multiple (double or triple) bonds to the central atom to achieve an octet.

- This will not change the number of electrons on the terminal atoms.

7. Final check

- Always make sure all valence electrons are accounted for and each atom has an octet of electrons except for hydrogen (with two electrons).

The central atom is usually the least electronegative element in the molecule or ion; hydrogen and the halogens are usually terminal.

Now let's apply this procedure to some particular compounds, beginning with one we have already discussed.

Example 4.12.1: Water

Write the Lewis Structure for H_2O.

Solution

Example **4.12.1**: steps for writing the Lewis structure of water

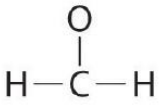
Steps for Writing Lewis Structures	Example 4.12.1:
1. Determine the total number of valence electrons in the molecule or ion.	Each H atom (group 1) has 1 valence electron, and the O atom (group 16) has 6 valence electrons, for a total of 8 valence electrons.
2. Arrange the atoms to show specific connections.	H O H Because H atoms are almost always terminal, the arrangement within the molecule must be HOH.
3. Place a bonding pair of electrons between each pair of adjacent atoms to give a single bond. 4. Beginning with the terminal atoms, add enough electrons to each atom to give each atom an octet (two for hydrogen).	Placing one bonding pair of electrons between the O atom and each H atom gives H -O- H with 4 electrons left over. Each H atom has a full valence shell of 2 electrons.
5. If any electrons are left over, place them on the central atom.	Adding the remaining 4 electrons to the oxygen (as two lone pairs) gives the following structure: 
6. If the central atom has fewer electrons than an octet, use lone pairs from terminal atoms to form multiple (double or triple) bonds to the central atom to achieve an octet.	Not necessary
7. Final check	The Lewis structure gives oxygen an octet and each hydrogen two electrons,

Example 4.12.2

Write the Lewis structure for the CH_2O molecule

Solution

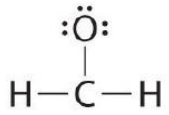
Steps are writing the Lewis structure of the CH_2O molecule

Steps for Writing Lewis Structures	Example 4.12.2
1. Determine the total number of valence electrons in the molecule or ion.	Each hydrogen atom (group 1) has one valence electron, carbon (group 14) has 4 valence electrons, and oxygen (group 16) has 6 valence electrons, for a total of [(2)(1) + 4 + 6] = 12 valence electrons.
2. Arrange the atoms to show specific connections.	 Because carbon is less electronegative than oxygen and hydrogen is normally terminal, C must be the central atom.
3. Place a bonding pair of electrons between each pair of adjacent atoms to give a single bond.	Placing a bonding pair of electrons between each pair of bonded atoms gives the following: 

Six electrons are used, and 6 are left over.

4. Beginning with the terminal atoms, add enough electrons to each atom to give each atom an octet (two for hydrogen).

Adding all 6 remaining electrons to oxygen (as three lone pairs) gives the following:



Although oxygen now has an octet and each hydrogen has 2 electrons, carbon has only 6 electrons.

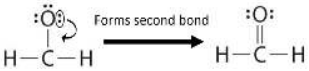
5. If any electrons are left over, place them on the central atom.

Not necessary

There are no electrons left to place on the central atom.

6. If the central atom has fewer electrons than an octet, use lone pairs from terminal atoms to form multiple (double or triple) bonds to the central atom to achieve an octet.

To give carbon an octet of electrons, we use one of the lone pairs of electrons on oxygen to form a carbon–oxygen double bond:

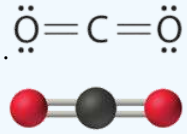


7. Final check Both the oxygen and the carbon now have an octet of electrons, so this is an acceptable Lewis electron structure. The O has two bonding pairs and two lone pairs, and C has four bonding pairs. This is the structure of formaldehyde, which is used in embalming fluid.

? Exercise 4.12.1

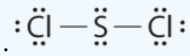
Write Lewis electron structures for CO_2 and SCl_2, a vile-smelling, unstable red liquid that is used in the manufacture of rubber.

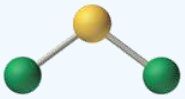
Answer CO_2



Carbon dioxide

Answer SCl_2





Sulfur dichloride

The United States Supreme Court has the unenviable task of deciding what the law is. This responsibility can be a major challenge when there is no clear principle involved or where there is a new situation not encountered before. Chemistry faces the same challenge in extending basic concepts to fit a new situation. Drawing of Lewis structures for polyatomic ions uses the same approach, but tweaks the process a little to fit a somewhat different set of circumstances.

Lewis Structures for Polyatomic Ions

Recall that a polyatomic ion is a group of atoms that are covalently bonded together and which carry an overall electrical charge. The ammonium ion, NH_4^+, is formed when a hydrogen ion (H^+) attaches to the lone pair of an ammonia (NH_3) molecule in a

coordinate covalent bond.

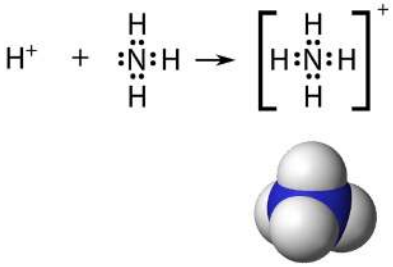


Figure 4.12.3: The ammonium ion.

When drawing the Lewis structure of a polyatomic ion, the charge of the ion is reflected in the number of total valence electrons in the structure. In the case of the ammonium ion:

$$\mathbf{1\,N}\text{ atom} = \mathbf{5}\text{ valence electrons}$$

$$\mathbf{4\,H}\text{ atoms} = 4 \times 1 = 4\text{ valence electrons}$$

subtract 1 electron for the $\mathbf{1+}$charge of the ion

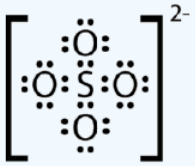
total of 8 valence electrons in the ion

It is customary to put the Lewis structure of a polyatomic ion into a large set of brackets, with the charge of the ion as a superscript outside the brackets.

Exercise 4.12.2

Draw the Lewis electron dot structure for the sulfate ion.

Answer



Exceptions to the Octet Rule

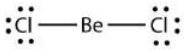
As important and useful as the octet rule is in chemical bonding, there are some well-known violations. This does not mean that the octet rule is useless—quite the contrary. As with many rules, there are exceptions, or violations.

There are three violations to the octet rule. Odd-electron molecules represent the first violation to the octet rule. Although they are few, some stable compounds have an odd number of electrons in their valence shells. With an odd number of electrons, at least one atom in the molecule will have to violate the octet rule. Examples of stable odd-electron molecules are NO, NO_2, and ClO_2. The Lewis electron dot diagram for NO is as follows:

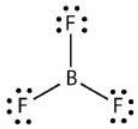


Although the O atom has an octet of electrons, the N atom has only seven electrons in its valence shell. Although NO is a stable compound, it is very chemically reactive, as are most other odd-electron compounds.

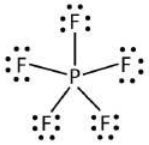
Electron-deficient molecules represent the second violation to the octet rule. These stable compounds have less than eight electrons around an atom in the molecule. The most common examples are the covalent compounds of beryllium and boron. For example, beryllium can form two covalent bonds, resulting in only four electrons in its valence shell:



Boron commonly makes only three covalent bonds, resulting in only six valence electrons around the B atom. A well-known example is BF_3:



The third violation to the octet rule is found in those compounds with more than eight electrons assigned to their valence shell. These are called expanded valence shell molecules. Such compounds are formed only by central atoms in the third row of the periodic table or beyond that have empty *d* orbitals in their valence shells that can participate in covalent bonding. One such compound is PF_5. The only reasonable Lewis electron dot diagram for this compound has the P atom making five covalent bonds:



Formally, the P atom has 10 electrons in its valence shell.

Example 4.12.3: Octet Violations

Identify each violation to the octet rule by drawing a Lewis electron dot diagram.

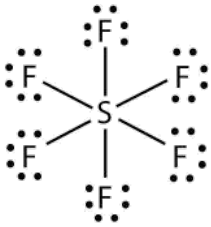
a. ClO
b. SF_6

Solution

a. With one Cl atom and one O atom, this molecule has 6 + 7 = 13 valence electrons, so it is an odd-electron molecule. A Lewis electron dot diagram for this molecule is as follows:



b. In SF_6, the central S atom makes six covalent bonds to the six surrounding F atoms, so it is an expanded valence shell molecule. Its Lewis electron dot diagram is as follows:



Exercise 4.12.3: Xenon Difluoride

Identify the violation to the octet rule in XeF_2 by drawing a Lewis electron dot diagram.

Answer:



The Xe atom has an expanded valence shell with more than eight electrons around it.

Summary

- Lewis dot symbols (Lewis structures) provide a simple rationalization of why elements form compounds with the observed stoichiometries.
- In Lewis electron structures, we encounter **bonding pairs**, which are shared by two atoms, and **lone pairs**, which are not shared between atoms.
- Lewis structures for polyatomic ions follow the same rules as those for other covalent compounds.
- There are three violations to the octet rule: odd-electron molecules, electron-deficient molecules, and expanded valence shell molecules

Contributors and Attributions

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4.13: Molecular Shapes- The VSEPR Theory

Learning Objective

- Determine the shape of simple molecules and polyatomic ions.

Molecules have shapes. There is an abundance of experimental evidence to that effect—from their physical properties to their chemical reactivity. Small molecules—molecules with a single central atom—have shapes that can be easily predicted. The basic idea in molecular shapes is **called valence shell electron pair repulsion (VSEPR).** It basically says that electron pairs, being composed of negatively charged particles, repel each other to get as far away from each other as possible. VSEPR makes a distinction between *electron group geometry*, which expresses how electron groups (bonds and nonbonding electron pairs) are arranged, and *molecular geometry*, which expresses how the atoms in a molecule are arranged. However, the two geometries are related.

There are two types of **electron groups**: any type of bond—single, double, or triple—and lone electron pairs. When applying VSEPR to simple molecules, the first thing to do is to count the number of electron groups around the central atom. Remember that a multiple bond counts as only *one* electron group.

Any molecule with only two atoms is linear. A molecule whose central atom contains only two electron groups orients those two groups as far apart from each other as possible—180° apart. When the two electron groups are 180° apart, the atoms attached to those electron groups are also 180° apart, so the overall molecular shape is linear. Examples include BeH_2 and CO_2:



Figure **4.13.1** *Beryllium hydride and carbon dioxide bonding.*

The two molecules, shown in the figure below in a "ball and stick" model.

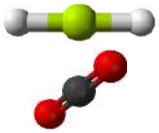


Figure **4.13.2** *Beryllium hydride and carbon dioxide models.*

A molecule with three electron groups orients the three groups as far apart as possible. They adopt the positions of an equilateral triangle—120° apart and in a plane. The shape of such molecules is *trigonal planar*. An example is BF_3:

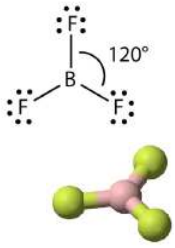


Figure **4.13.3** *Boron trifluoride bonding.*

Some substances have a trigonal planar electron group distribution but have atoms bonded to only two of the three electron groups. An example is GeF_2:

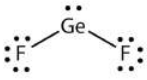


Figure **4.13.4**: Germanium *difluoride bonding.*

From an electron group geometry perspective, GeF_2 has a trigonal planar shape, but its real shape is dictated by the positions of the atoms. This shape is called *bent* or *angular*.

A molecule with four electron groups about the central atom orients the four groups in the direction of a tetrahedron, as shown in Figure **4.13.1** Tetrahedral Geometry. If there are four atoms attached to these electron groups, then the molecular shape is also *tetrahedral*. Methane (CH_4) is an example.

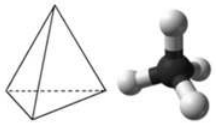


Figure **4.13.5** *Tetrahedral structure of methane.*

This diagram of CH_4 illustrates the standard convention of displaying a three-dimensional molecule on a two-dimensional surface. The straight lines are in the plane of the page, the solid wedged line is coming out of the plane toward the reader, and the dashed wedged line is going out of the plane away from the reader.

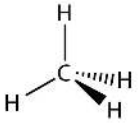


Figure **4.13.6** *Methane bonding.*

NH_3 is an example of a molecule whose central atom has four electron groups but only three of them are bonded to surrounding atoms.

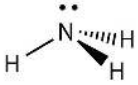


Figure **4.13.7** *Ammonia bonding.*

Although the electron groups are oriented in the shape of a tetrahedron, from a molecular geometry perspective, the shape of NH_3 is *trigonal pyramidal*.

H_2O is an example of a molecule whose central atom has four electron groups but only two of them are bonded to surrounding atoms.



Figure **4.13.8** *Water bonding.*

Although the electron groups are oriented in the shape of a tetrahedron, the shape of the molecule is *bent* or *angular*. A molecule with four electron groups about the central atom but only one electron group bonded to another atom is linear because there are only two atoms in the molecule.

Double or triple bonds count as a single electron group. The Lewis electron dot diagram of formaldehyde (CH_2O) is shown in Figure **4.13.9**.



Figure **4.13.9** *Lewis electron dot diagram of formaldehyde.*

The central C atom has three electron groups around it because the double bond counts as one electron group. The three electron groups repel each other to adopt a trigonal planar shape.

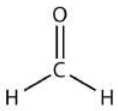


Figure **4.13.10**: Formaldehyde bonding.

(The lone electron pairs on the O atom are omitted for clarity.) The molecule will not be a perfect equilateral triangle because the C–O double bond is different from the two C–H bonds, but both planar and triangular describe the appropriate approximate shape of this molecule. Figure 4.13.11 illustrates several representations of the water, ammonia, and methane molecules.

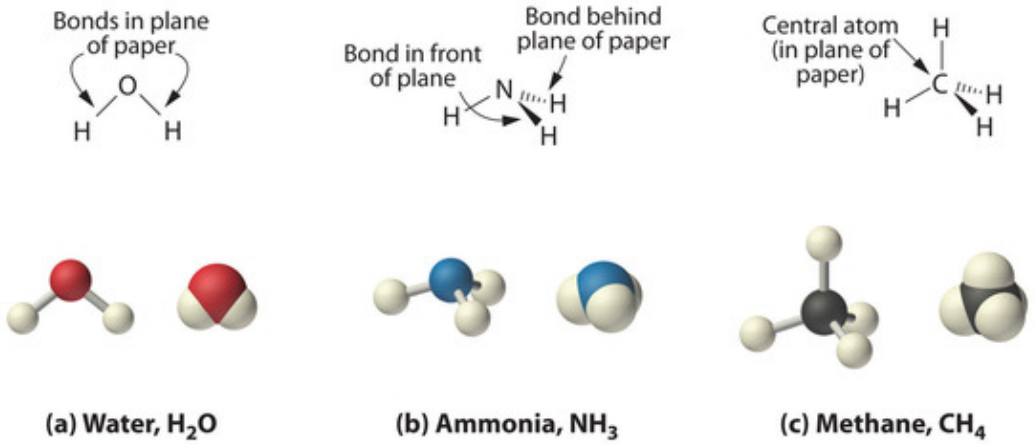


Figure 4.13.11 The three-dimensional structures, ball and stick models,and space filling models of water, ammonia, and methane. *(a) Water is a V-shaped molecule, in which all three atoms lie in a plane. (b) In contrast, ammonia has a pyramidal structure, in which the three hydrogen atoms form the base of the pyramid and the nitrogen atom is at the vertex. (c) The four hydrogen atoms of methane form a tetrahedron; the carbon atom lies in the center.*

Table 4.13.1 summarizes the shapes of molecules based on their number of electron groups and surrounding atoms and the common shapes are shown in figure 4.13.1.

Table 4.13.1: Summary of Molecular Shapes

Number of Electron Groups on Central Atom	Number of Bonding Groups	Number of Lone Pairs	Electron Geometry	Molecular Shape
2	2	0	linear	linear
3	3	0	trigonal planar	trigonal planar
3	2	1	trigonal planar	bent
4	4	0	tetrahedral	tetrahedral
4	3	1	tetrahedral	trigonal pyramidal
4	2	2	tetrahedral	bent

Figure 4.13.12: Common structures for molecules and Ppolyatomic ions that consist of a central atom bonded to two or three other atoms.

Example 4.13.1:

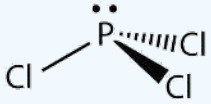
What is the approximate shape of each molecule?

a. PCl_3
b. NOF

Solution

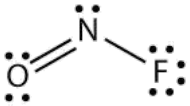
The first step is to draw the Lewis structure of the molecule.

1. For PCl_3, the electron dot diagram is as follows:



The lone electron pairs on the Cl atoms are omitted for clarity. The P atom has four electron groups with three of them bonded to surrounding atoms, so the molecular shape is trigonal pyramidal.

- The electron dot diagram for NOF is as follows:



The N atom has three electron groups on it, two of which are bonded to other atoms. The molecular shape is bent.

? Exercise 4.13.1

What is the approximate molecular shape of CH_2Cl_2?

Answer

Tetrahedral

? Exercise 4.13.2

Ethylene (C_2H_4) has two central atoms. Determine the geometry around each central atom and the shape of the overall molecule. Hint, hydrogen is a terminal atom.

Answer

Trigonal planar about both central C atoms

Summary

The approximate shape of a molecule can be predicted from the number of electron groups and the number of surrounding atoms.

Contributors and Attributions

-
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4.14: Shapes and Properties- Polar and Nonpolar Molecules

Learning Objective

- Determine if a molecule is polar or nonpolar.

Molecular Polarity

To determine if a molecule is polar or nonpolar, it is frequently useful to look at Lewis structures. **Nonpolar compounds** will be symmetric, meaning all of the sides around the central atom are identical - bonded to the same element with no unshared pairs of electrons. Notice that a tetrahedral molecule such as CCl_4 is nonpolar Figure (**4.14.1**. Another non polar molecule shown below is boron trifluoride, BF_3. BF_3 is a trigonal planar molecule and all three peripheral atoms are the same.

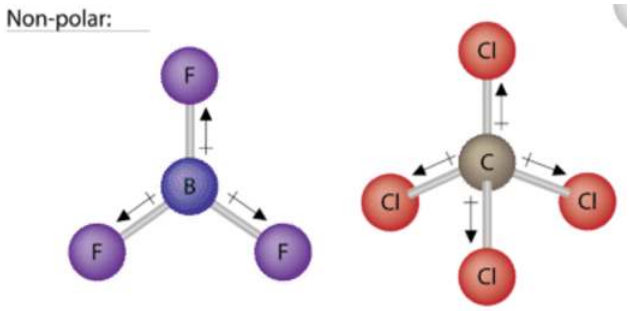
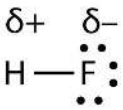


Figure **4.14.1** Some examples of nonpolar molecules based on molecular geometry (BF_3 and CCl_4).

Polar molecules are asymmetric, either containing lone pairs of electrons on a central atom or having atoms with different electronegativities bonded. This works pretty well - as long as you can visualize the molecular geometry. That's the hard part. To know how the bonds are oriented in space, you have to have a strong grasp of Lewis structures and VSEPR theory. Assuming you do, you can look at the structure of each one and decide if it is polar or not - *whether or not you know the individual atom electronegativity*. This is because you know that all bonds between dissimilar elements are polar, and in these particular examples, it doesn't matter which direction the dipole moment vectors are pointing (out or in).

A **polar molecule** is a molecule in which one end of the molecule is slightly positive, while the other end is slightly negative. A diatomic molecule that consists of a polar covalent bond, such as **HF**, is a polar molecule.



As mentioned in section 4.7, because the electrons in the bond are nearer to the F atom, this side of the molecule takes on a partial negative charge, which is represented by δ− (δ is the lowercase Greek letter delta). The other side of the molecule, the H atom, adopts a partial positive charge, which is represented by δ+. The two electrically charged regions on either end of the molecule are called poles, similar to a magnet having a north and a south pole. A molecule with two poles is called a **dipole** (see figure below). Hydrogen fluoride is a dipole.



Figure **4.14.2** A dipole is any molecule with a positive end and a negative end, resulting from unequal distribution of electron density throughout the molecule.

For molecules with more than two atoms, the molecular geometry must also be taken into account when determining if the molecule is polar or nonpolar. The figure below shows a comparison between carbon dioxide and water. Carbon dioxide (CO_2) is a linear molecule. The oxygen atoms are more electronegative than the carbon atom, so there are two individual dipoles pointing

outward from the C atom to each O atom. However, since the dipoles are of equal strength and are oriented this way, they cancel out and the overall molecular polarity of CO_2 is zero.

Water is a bent molecule because of the two lone pairs on the central oxygen atom. The individual dipoles point from the H atoms toward the O atom. Because of the shape, the dipoles do not cancel each other out and the water molecule is polar. In the figure below, the net dipole is shown in blue and points upward.

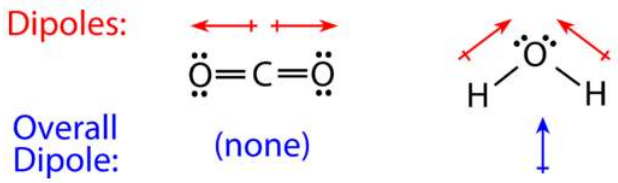


Figure 4.14.3 *The molecular geometry of a molecule affects its polarity. Each CO bond has a dipole moment, but they point in opposite directions so that the net CO2 molecule is nonpolar. In contrast, water is polar because the OH bond moments do not cancel out.*

Three other polar molecules are shown below with the arrows pointing to the more electron dense atoms. Just like the water molecule, none of the bond moments cancel out.

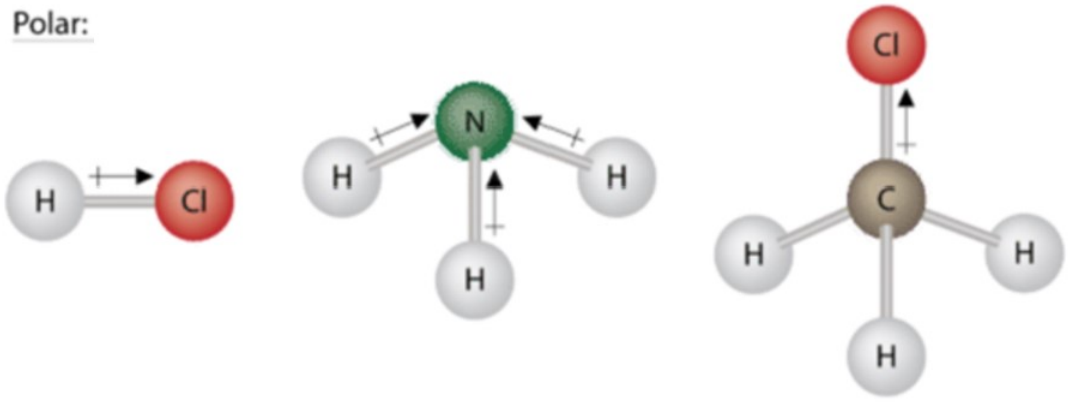


Figure 4.14.4 Some examples of polar molecules based on molecular geometry (HCl, NH3 and CH3Cl).

To summarize, to be polar, a molecule must:

1. Contain at least one polar covalent bond.
2. Have a molecular structure such that the sum of the vectors of each bond dipole moment does not cancel.

Steps to Identify Polar Molecules

1. Draw the Lewis structure
2. Figure out the geometry (using VSEPR theory)
3. Visualize or draw the geometry
4. Find the net dipole moment (you don't have to actually do calculations if you can visualize it)
5. If the net dipole moment is zero, it is non-polar. Otherwise, it is polar.

Example 4.14.1:

Label each of the following as polar or nonpolar.

a. Water, H_2O: 

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b. Methanol, CH_3OH: 

c. Hydrogen Cyanide, HCN: 

d. Oxygen, O_2: 

e. Propane, C_3H_8: 

Solution

a. Water is polar. Any molecule with lone pairs of electrons around the central atom is polar.

b. Methanol is polar. This is not a symmetric molecule. The **−OH** side is different from the other 3 **−H** sides.

c. Hydrogen cyanide is polar. The molecule is not symmetric. The nitrogen and hydrogen have different electronegativities, creating an uneven pull on the electrons.

d. Oxygen is nonpolar. The molecule is symmetric. The two oxygen atoms pull on the electrons by exactly the same amount.

e. Propane is nonpolar, because it is symmetric, with **H** atoms bonded to every side around the central atoms and no unshared pairs of electrons.

? Exercise 4.14.1

Label each of the following as polar or nonpolar.

a. SO_3

b. NH_3

Answer a

non polar

Answer b

polar

Summary

- Non polar molecules are symmetric with no unshared electrons.
- Polar molecules are asymmetric, either containing lone pairs of electrons on a central atom or having atoms with different electronegativities bonded.

Contributors and Attributions

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4.15: Metallic Bonding



Figure 4.15.1: A nineteenth century copper plate. (Public Domain; John Pearson via Wikipedia)

Why do metals behave the way they do?

The image below is of a copper plate that was made in 1893. The utensil has a great deal of elaborate decoration, and the item is very useful. What would have happened if this plate was made of copper (I) chloride instead? Copper (I) chloride does contain copper, after all. However, the CuCl would end up as a powder when a metalworker pounded on it to shape it. Metals behave in unique ways. The bonding that occurs in a metal is responsible for its distinctive properties: luster, malleability, ductility, and excellent conductivity.

The Metallic Bond

Pure metals are crystalline solids, but unlike ionic compounds, every point in the crystal lattice is occupied by an identical atom. The electrons in the outer energy levels of a metal are mobile and capable of drifting from one metal atom to another. This means that the metal is more properly viewed as an array of positive ions surrounded by a sea of mobile valence electrons. Electrons which are capable of moving freely throughout the empty orbitals of the metallic crystal are called **delocalized electrons** (see below). A **metallic bond** is the attraction of the stationary metal cations to the surrounding mobile electrons.

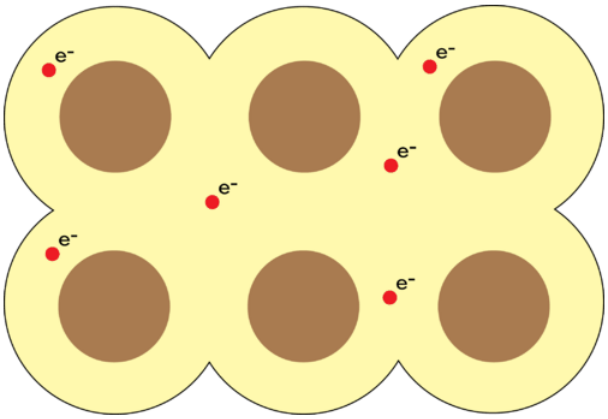


Figure 4.15.2: In a metal, the stationary metal cations are surrounded by a sea of mobile valence electrons that are not associated with any one cation. (CC BY-NC 3.0; Christopher Auyeung via CK-12 Foundation)

Properties of Metals

The metallic bonding model explains the physical properties of metals. Metals conduct electricity and heat very well because of their free-flowing electrons. As electrons enter one end of a piece of metal, an equal number of electrons flow outward from the other end. When light is shone onto the surface of a metal, its electrons absorb small amounts of energy and become excited into one of its many empty orbitals. The electrons immediately fall back down to lower energy levels and emit light. This process is responsible for the high **luster** of metals.



Figure **4.15.3**: The American Platinum Eagle is the official platinum bullion coin of the United States and was first minted in 1997. The luster of a metal is due to its metallic bonds. (Public Domain; the US Mint via Front: http://commons.wikimedia.org/wiki/File:2005_AEPlat_Proof_Obv.png; Back: http://commons.wikimedia.org/wiki/File:American_Platinum_Eagle_2008_Proof_Rev.jpg)

Recall that ionic compounds are very brittle. Application of a force results in like-charged ions in the crystal coming too close to one another, causing the crystal to shatter. When a force is applied to a metal, the free-flowing electrons can slip in between the stationary cations and prevent them from coming in contact. Imagine ball bearings that have been coated with oil sliding past one another. As a result, metals are very **malleable** and **ductile**. They can be hammered into shapes, rolled into thin sheets, or pulled into thin wires.

Summary

- The metallic bond is responsible for the properties of metals.
- Metals conduct electricity and heat well.
- Metals are ductile and malleable.
- Metals have luster.

Review

1. What is a delocalized electron?
2. Why do metals conduct electricity and heat well?
3. Why do metals have luster?

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4.15.1: Crystal Structure of Metals



Figure **4.15.1.1** (Cannon: Public Domain; Cannonballs: CC-BY 2.0; Cannon: User:Sharkface217/Wikipedia; Cannonballs: www.worldislandinfo.com (Flickr: Worldislandinfo.com) via Cannon: Commons Wikimedia, Stevens Institute of Technology cannon [commons.wikimedia.org]; Cannonballs: Flickr, Cannon ball pyramid [www.flickr.com])

How would you stack cannon balls?

Before modern artillery with explosive shells, cannons were used to fire cannon balls at the enemy. The soldiers operating the cannon needed to be able to get to the cannon balls quickly and efficiently. A pyramidal arrangement worked well for this purpose.

Crystal Structures of Metals

When identical spheres are stacked, each successive layer fits into the small spaces where different spheres come together. This orderly and regular arrangement of the metal balls minimizes the empty space between them. **Closest packing** is the most efficient arrangement of spheres. Atoms of a metal crystal are arranged in similar patterns, called close-packed structures. Pure metals adopt one of several related close-packed structures, as shown below.

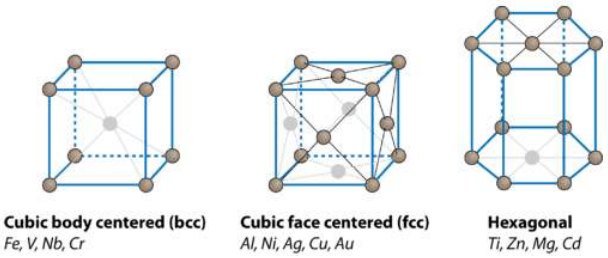


Figure **4.15.1.2**: Most pure metals naturally adopt one of these closest packing arrangements. (CC BY-NC 3.0; CK-12 Foundation - Christopher Auyeung via CK-12 Foundation)

On the far left is the body-centered cubic (bcc) structure. In that crystal, metal atoms occupy the eight corners of a cube along with one atom in the very center. The coordination number of each atom in the body-centered cubic structure is 8. In the face-centered cubic (fcc) structure, there are eight atoms at each corner of the cube and six atoms in the center of each face. The coordination number of each atom in the face-centered cubic structure is 12. The hexagonal close-packed (hcp) structure also has a coordination number of 12, but crystals of this type are hexagonally shaped rather than cubic.





Summary

- Atoms of a metal crystal are arranged in close-packed structures.
- This type of structure minimizes the empty space between the atoms.

Review

1. What is the most efficient arrangement of spheres?
2. What is the coordination number of a face-centered cubic structure?
3. What other structure has a coordination number of 12?

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4.16: Network Covalent Atomic Solids

Covalent Network Solids

Covalent solids are formed by networks or chains of atoms or molecules held together by covalent bonds. A perfect single crystal of a covalent solid is therefore a single giant molecule. For example, the structure of diamond, shown in part (a) in Figure **4.16.2**, consists of carbon atoms, each bonded to four other carbon atoms in a tetrahedral array to create a giant network. The carbon atoms form six-membered rings. In, graphite, the other common allotrope of carbon, has the structure shown in part () in Figure **4.16.1**. It contains planar networks of six-membered rings carbon atoms in which each carbon is bonded to three others. This leaves a single electron in a 2p orbital that can be used to form C=C double bonds, resulting in a ring with alternating double and single bonds.

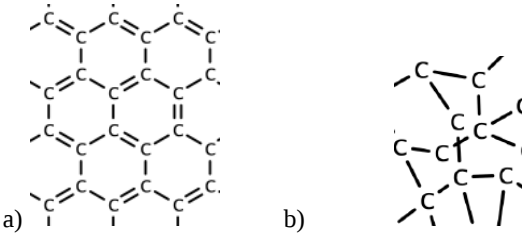


Figure **4.16.1** a) Carbon bonding in graphite; b) Carbon bonding in diamond

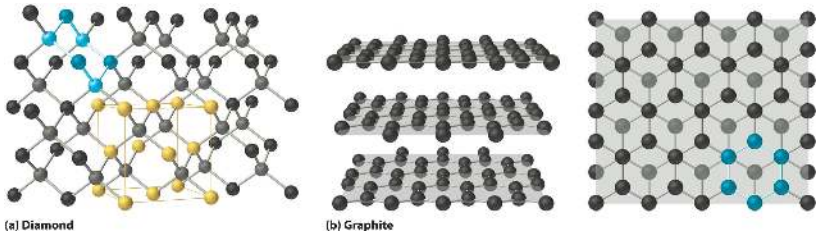


Figure **4.16.2** The Structures of Diamond and Graphite. (a) Diamond consists of sp3 hybridized carbon atoms, each bonded to four other carbon atoms. The tetrahedral array forms a giant network in which carbon atoms form six-membered rings. (b) These side (left) and top (right) views of the graphite structure show the layers of fused six-membered rings and the arrangement of atoms in alternate layers of graphite. The rings in alternate layers are staggered, such that every other carbon atom in one layer lies directly under (and above) the center of a six-membered ring in an adjacent layer.

Elemental silicon has the same structure, as does silicon carbide (SiC), which has alternating C and Si atoms. The structure of crystalline quartz (silicon dioxide, SiO_2), shown in **4.16.3** can be viewed as being derived from the structure of silicon by inserting an oxygen atom between each pair of silicon atoms.



4.16.3 . Network covalent solid structure of SiO_2.Image by Smokefoot, CC BY-SA 4.0, via Wikimedia Commons

All compounds with the diamond and related structures are extremely hard, high-melting-point solids that are not easily deformed. Instead, they tend to shatter when subjected to large stresses, and they usually do not conduct electricity very well. In fact, diamond (melting point = 3500°C at 63.5 atm) is one of the hardest substances known, and silicon carbide (melting point = 2986°C) is used commercially as an abrasive in sandpaper and grinding wheels. It is difficult to deform or melt these and related compounds because strong covalent (C–C or Si–Si) or polar covalent (Si–C or Si–O) bonds must be broken, which requires a large input of energy.

Fullerenes

Until the mid 1980's, pure carbon was thought to exist in two forms: graphite and diamond. The discovery of C_{60} molecules in interstellar dust in 1985 added a third form to this list. The existence of C_{60}, which resembles a soccer ball, had been hypothesized

by theoretians for many years. In the late 1980's synthetic methods were developed for the synthesis of C_{60}, and the ready availability of this form of carbon led to extensive research into its properties.

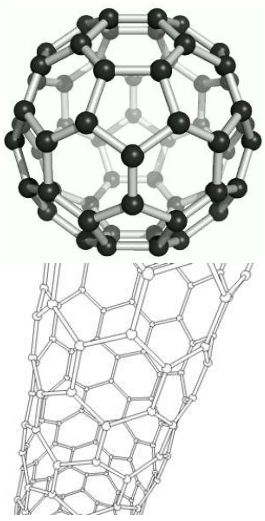


Figure **4.16.4**: Example of fullerenes: a buckyball (*C_{60} on left and an extended bucktube. Images used with permission from Wikipedia.*

The C_{60} molecule (Figure **4.16.4**; left), is called buckminsterfullerene, though the shorter name fullerene is often used. The name is a tribute to the American architect R. Buckminster Fuller, who is famous for designing and constructing geodesic domes which bear a close similarity to the structure of C_{60}. As is evident from the display, C_{60} is a sphere composed of six-member and five-member carbon rings. These balls are sometimes fondly referred to as "Bucky balls". It should be noted that fullerenes are an entire class of pure carbon compounds rather than a single compound. A distorted sphere containing more than 60 carbon atoms have also been found, and it is also possible to create long tubes (Figure **4.16.4**; right). All of these substances are pure carbon.

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CHAPTER OVERVIEW

5: Chemical Reactions

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5.1: Word Equations



Figure **5.1.1** (Public Domain; User:Daderot/Wikimedia Commons via Wikipedia)

What's for Dinner?

Various ways of recording recipes have developed over the centuries. The cookbook shown above was written by a woman who probably collected all her own recipes. Later, printed cookbooks became available (even guys had no excuse for not being able to cook). Today we can find recipes on a number of internet sites and can quickly search for information on how to cook anything we want. Reading a recipe sometimes requires we understand a few codes and symbols (what's the difference between a tsp and a Tsp?), but the information on what we start with and what we end up with is there.

Writing Chemical Equations

Chemical reactions are occurring all around us. Plants use sunlight to drive their photosynthetic process and produce energy. Cars and other vehicles burn gasoline in order to power their engines. Batteries use electrochemical reactions to produce energy and power many everyday devices. Many chemical reactions are going on within the human body as well, particularly during the digestion of food.

In math class, you have written and solved many mathematical equations. Chemists keep track of chemical reactions by writing equations as well. In any chemical reaction, one or more substances—called **reactants**—are converted into one or more new substances—called **products**. The general form of the equation for such a process looks like this:

$$\text{Reactants} \rightarrow \text{Products}$$

Unlike a math equation, a chemical equation does not use an equal sign. Instead, the arrow is called a yield sign and so the equation is described as "reactants yield products".

Word Equations

You can describe a chemical reaction by writing a **word equation**. When silver metal is exposed to sulfur, it reacts to form silver sulfide. Silver sulfide is commonly known as tarnish and turns the surface of silver objects dark and streaky black (see figure below). The sulfur that contributes to tarnish can come from traces of sulfur in the air, or from foods such as eggs. The word equation for the process is:

$$\text{Silver} + \text{sulfur} \rightarrow \text{Silver sulfide}$$

The silver and the sulfur are the reactants in the equation, while the silver sulfide is the product.



Figure **5.1.2:** You can see dark spots of tarnished (silver sulfide) forming on this ring as it reacts with sulfur compounds in the air. (CK-12 Curriculum Materials license; CK-12 Foundation via CK-12 Foundation)

Another common chemical reaction is the burning of methane gas. Methane is the major component of natural gas and is commonly burned on a gas stove or in a Bunsen burner (figure below). Burning is a chemical reaction in which some type of fuel is reacted with oxygen gas. The products of the reaction in the burning of methane, as well as other fuels, are carbon dioxide and water. The word equation for this reaction is:

$$\text{Methane} + \text{oxygen} \rightarrow \text{carbon dioxide} + \text{water}$$

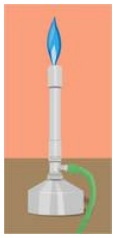


Figure **5.1.3**: A Bunsen burner is commonly used to heat substances in a chemistry lab. Methane is reacted with oxygen to form carbon dioxide and water. (CK-12 Curriculum Materials license; CK-12 Foundation via CK-12 Foundation)

Word equations can be very useful, but do have one major drawback—they cannot be used for any quantitative work. A word equation does not tell how many moles of each material are needed, or how many moles of product are formed.



Summary

- Word equations are used to describe the conversion of reactants to products.

Review

1. Write the generic form of a chemical reaction.
2. What are reactants?
3. What are products?

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5.2: Chemical Equations



Figure **5.2.1** (Public Domain; jons2 at pdphoto.org via Wikipedia)

How do you make shrimp gumbo?

Shrimp gumbo is one of many dishes that are part of the Cajun culture in Louisiana. It's a spicy dish that needs careful control of all the ingredients so that it has a "kick", but is not overwhelming. Recipes convey not only what the preparation entails, but also describe how much of each ingredient is needed, and the details of how to cook the meal. Similarly, we need this type of information in order to carry out chemical reactions successfully and safely.

Chemical Equations

Word equations are time-consuming to write and do not prove to be convenient for many of the things that chemists need to do with equations. A **chemical equation** is a representation of a chemical reaction that displays the reactants and products with chemical formulas. The chemical equation for the reaction of methane with oxygen is shown:

$$\mathrm{CH_4 + O_2 \rightarrow CO_2 + H_2O}$$

The equation above, called a **skeleton equation**, is an equation that shows only the formulas of the reactants and products with nothing to indicate the relative amounts. The first step in writing an accurate chemical equation is to write the skeleton equation, making sure that the formulas of all substances involved are written correctly. All reactants are written to the left of the yield arrow, separated from one another by a plus sign. Likewise, products are written to the right of the yield arrow, also separated with a plus sign.

It is often important to know the physical states of the reactants and products taking part in a reaction. To do this, put the appropriate symbol in parentheses after each formula: (s) for solid, (l) for liquid, (g) for gas, and (aq) for an aqueous (water-based) solution. The previous reaction becomes:

$$\mathrm{CH_4\,(g) + O_2\,(g) \rightarrow CO_2\,(g) + H_2O\,(l)}$$

The table below shows a listing of symbols used in chemical equations. Some, such as the double arrow which represents equilibrium, and the use of a catalyst in a reaction, will be detailed in other concepts.

Table **5.2.1**: Symbols Used in Chemical Equations

Symbols	Description
$+$	Used to separate multiple reactants or products.
$\rightarrow$	Yield sign; separates reactants from products.
$\rightleftharpoons$	Replaces the yield sign for reversible reactions that reach equilibrium.
(s)	Reactant or product in the solid state.
(l)	Reactant or product in the liquid state.
(g)	Reactant or product in the gaseous state.
(aq)	Reactant or product in an aqueous solution (dissolved in water).
$\xrightarrow{\text{Pt}}$	Formula written above the arrow is used as a catalyst in the reaction.
$\xrightarrow{\Delta}$	Triangle indicates that the reaction is being heated.



Summary

- A chemical equation is representation a chemical reaction using chemical formulas reactants and products, as well as symbols.
- Symbols used in chemical equations are described and explained.

Review

1. What does a skeleton equation tell you?
2. Why would you want to know the physical state of materials in a chemical reaction?
3. In a chemical reaction what does symbol → mean?
4. If I see Δ over the arrow, what does this indicate?

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5.3: Balancing Equations



Figure **5.3.1** (Public Domain; Joseph Allen via Wikipedia)

Any leftovers?

When you cook a meal, quite often there are leftovers because you prepared more than people would eat at one sitting. Sometimes when you repair a piece of equipment, you end up with what are called "pocket parts"—small pieces you put in your pocket because you're not sure where they belong. Chemistry tries to avoid leftovers and pocket parts. In normal chemical processes, we cannot create or destroy matter (law of conservation of mass). If we start out with ten carbon atoms, we need to end up with ten carbon atoms. John Dalton's atomic theory said that chemical reactions basically involve the rearrangement of atoms. Chemical equations need to follow these principles in order to be correct.

Balancing Chemical Equations

A **balanced equation** is a chemical equation in which mass is conserved and there are equal numbers of atoms of each element on both sides of the equation. We can write a chemical equation for the reaction of carbon with hydrogen gas to form methane ($\mathbf{CH_4}$):

$$\underset{\text{2 C atoms}}{\mathbf{C}\,(s)} \quad + \quad \underset{\text{2 H atoms}}{\mathbf{H_2}\,(g)} \quad \rightarrow \quad \underset{\text{1 C atom, 4 H atoms}}{\mathbf{CH_4}\,(g)}$$

In order to write a correct equation, you must first write the correct skeleton equation with the correct chemical formulas. Recall that hydrogen is a diatomic molecule and so is written as $\mathbf{H_2}$.

When we count the number of atoms of both elements, shown under the equation, we see that the equation is not balanced. There are only 2 atoms of hydrogen on the reactant side of the equation, while there are 4 atoms of hydrogen on the product side. We can balance the above equation by adding a coefficient of 2 in front of the formula for hydrogen.

$$\mathbf{C}\,(s) + 2\mathbf{H_2}\,(g) \rightarrow \mathbf{CH_4}\,(g)$$

A **coefficient** is a small whole number placed in front of a formula in an equation in order to balance it. The 2 in front of the $\mathbf{H_2}$ means that there are a total of $\mathbf{2 \times 2 = 4}$ atoms of hydrogen as reactants. Visually, the reaction looks like the figure below.

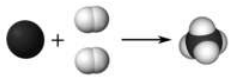


Figure **5.3.2**: Reaction between carbon and hydrogen to form methane. (Public Domain; Ben Mills (Wikimedia: Benjah-bmm27 via Wikipedia and http://commons.wikimedia.org/wiki/File:Methane-3D-space-filling.png)

In the balanced equation, there is one atom of carbon and four atoms of hydrogen on both sides of the arrow. Below are guidelines for writing and balancing chemical equations.

1. Determine the correct chemical formulas for each reactant and product.
2. Write the skeleton equation.
3. Count the number of atoms of each element that appears as a reactant and as a product. If a polyatomic ion is unchanged on both sides of the equation, count it as a unit.
4. Balance each element one at a time by placing coefficients in front of the formulas.
    a. It is best to begin by balancing elements that only appear in one chemical formula on each side of the equation.
    b. No coefficient is written for a 1.

c. NEVER change the subscripts in a chemical formula—you can only balance equations by using coefficients.

5. Check each atom or polyatomic ion to be sure that they are equal on both sides of the equation.
6. Make sure that all coefficients are in the lowest possible ratio. If necessary, reduce to the lowest ratio.

Example 5.3.1: Balancing Chemical Equations

Aqueous solutions of lead (II) nitrate and sodium chloride are mixed. The products of the reaction are an aqueous solution of sodium nitrate and a solid precipitate of lead (II) chloride. Write the balanced chemical equation for this reaction.

Solution

Step 1: Plan the problem.

Follow the steps for writing and balancing a chemical equation listed in the text.

Step 2: Solve.

Write the skeleton equation with the correct formulas.

$$\mathrm{Pb(NO_3)_2}\,(aq) + \mathrm{NaCl}\,(aq) \rightarrow \mathrm{NaNO_3}\,(aq) + \mathrm{PbCl_2}\,(s)$$

Count the number of each atom or polyatomic ion on both sides of the equation.

Reactants	Products
1 Pb atom	1 Pb atom
2 NO_3^- ions	1 NO_3^- ions
1 Na atom	1 Na atom
1 Cl atom	2 Cl atoms

The nitrate ions and the chlorine atoms are unbalanced. Start by placing a 2 in front of the NaCl. This increases the reactant counts to 2 Na atoms and 2 Cl atoms. Then place a 2 in front of the $\mathrm{NaNO_3}$. The result is:

$$\mathrm{Pb(NO_3)_2}\,(aq) + 2\mathrm{NaCl}\,(aq) \rightarrow 2\mathrm{NaNO_3}\,(aq) + \mathrm{PbCl_2}\,(s)$$

The new count for each atom and polyatomic ion becomes:

Reactants	Products
1 Pb atom	1 Pb atom
2 NO_3^- ions	2 NO_3^- ions
2 Na atom	2 Na atom
2 Cl atom	2 Cl atoms

Step 3: Think about your result.

The equation is now balanced since there are equal numbers of atoms of each element on both sides of the equation.



Summary

- The process of balancing chemical equations is described.

Review

1. What is the law of conservation of mass?
2. How did Dalton describe the process of a chemical reaction?
3. Why don’t we change the subscripts in order to balance an equation?

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5.4: The Haber Process

The Haber Process is used in the manufacturing of ammonia from nitrogen and hydrogen, and then goes on to explain the reasons for the conditions used in the process. The process combines nitrogen from the air with hydrogen derived mainly from natural gas (methane) into ammonia. The reaction is reversible and the production of ammonia is exothermic.

$$\mathrm{N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)} \tag{5.4.1}$$

with $\Delta H = -92.4 kJ/mol$.

A flow scheme for the Haber Process looks like this:

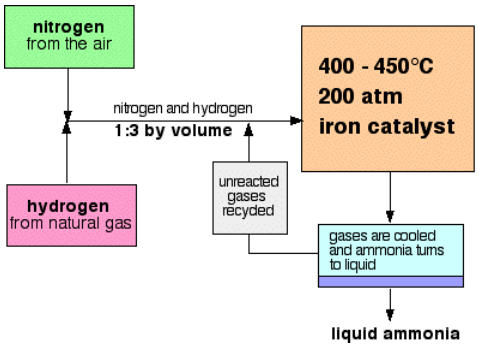


Figure 5.4.1: Scheme of the Haber Process

General Conditions of the Process

- **The catalyst:** The catalyst is actually slightly more complicated than pure iron. It has potassium hydroxide added to it as a promoter - a substance that increases its efficiency.
- **The pressure**: The pressure varies from one manufacturing plant to another, but is always high. You cannot go far wrong in an exam quoting 200 atmospheres.
- **Recycling:** At each pass of the gases through the reactor, only about 15% of the nitrogen and hydrogen converts to ammonia. (This figure also varies from plant to plant.) By continual recycling of the unreacted nitrogen and hydrogen, the overall conversion is about 98%.

Composition

The proportions of nitrogen and hydrogen: The mixture of nitrogen and hydrogen going into the reactor is in the ratio of 1 volume of nitrogen to 3 volumes of hydrogen. Avogadro's Law says that equal volumes of gases at the same temperature and pressure contain equal numbers of molecules. That means that the gases are going into the reactor in the ratio of 1 molecule of nitrogen to 3 of hydrogen. That is the proportion demanded by the equation.

In some reactions you might choose to use an excess of one of the reactants. You would do this if it is particularly important to use up as much as possible of the other reactant - if, for example, it was much more expensive. That does not apply in this case. There is always a down-side to using anything other than the equation proportions. If you have an excess of one reactant there will be molecules passing through the reactor which cannot possibly react because there is not anything for them to react with. This wastes reactor space - particularly space on the surface of the catalyst.

Temperature

- **Equilibrium considerations**: You need to shift the position of the equilibrium (Equation 5.4.1) as far as possible to the right in order to produce the maximum possible amount of ammonia in the equilibrium mixture. The forward reaction is exothermic with $\Delta H = -92.4 kJ/mol$. According to Le Chatelier's Principle, this will be favored if you lower the temperature. The system will respond by moving the position of equilibrium to counteract this - in other words by producing more heat. To get as much ammonia as possible in the equilibrium mixture, you need as low a temperature as possible. However, 400 - 450° C is not a low temperature!

- **Rate considerations**: The lower the temperature you use, the slower the reaction becomes. A manufacturer is trying to produce as much ammonia as possible per day. It makes no sense to try to achieve an equilibrium mixture which contains a very high proportion of ammonia if it takes several years for the reaction to reach that equilibrium. You need the gases to reach equilibrium within the very short time that they will be in contact with the catalyst in the reactor.
- **The compromise:** 400 - 450°C is a compromise temperature producing a reasonably high proportion of ammonia in the equilibrium mixture (even if it is only 15%), but in a very short time.

Pressure

Notice that there are 4 molecules on the left-hand side of Equation 5.4.1, but only 2 on the right. According to Le Chatelier's Principle, if you increase the pressure the system will respond by favoring the reaction which produces fewer molecules. That will cause the pressure to fall again. In order to get as much ammonia as possible in the equilibrium mixture, you need as high a pressure as possible. 200 atmospheres is a high pressure, but not amazingly high.

- **Rate considerations:** Increasing the pressure brings the molecules closer together. In this particular instance, it will increase their chances of hitting and sticking to the surface of the catalyst where they can react. The higher the pressure the better in terms of the rate of a gas reaction.
- **Economic considerations:** Very high pressures are very expensive to produce on two counts. You have to build extremely strong pipes and containment vessels to withstand the very high pressure. That increases your capital costs when the plant is built. High pressures cost a lot to produce and maintain. That means that the running costs of your plant are very high.
- **The compromise**: 200 atmospheres is a compromise pressure chosen on economic grounds. If the pressure used is too high, the cost of generating it exceeds the price you can get for the extra ammonia produced.

Catalyst

- **Equilibrium considerations:** The catalyst has no effect whatsoever on the position of the equilibrium. Adding a catalyst doesn't produce any greater percentage of ammonia in the equilibrium mixture. Its only function is to speed up the reaction.
- **Rate considerations:** In the absence of a catalyst the reaction is so slow that virtually no reaction happens in any sensible time. The catalyst ensures that the reaction is fast enough for a dynamic equilibrium to be set up within the very short time that the gases are actually in the reactor.
- **Separating the ammonia**: When the gases leave the reactor they are hot and at a very high pressure. Ammonia is easily liquefied under pressure as long as it is not too hot, and so the temperature of the mixture is lowered enough for the ammonia to turn to a liquid. The nitrogen and hydrogen remain as gases even under these high pressures, and can be recycled.

By mixing one part ammonia to nine parts air with the use of a catalyst, the ammonia will get oxidized to *nitric acid*.

$$4\,NH_3 + 5\,O_2 \rightarrow 4\,NO + 6\,H_2O$$
$$2\,NO + O_2 \rightarrow 2\,NO_2$$
$$2\,NO_2 + 2\,H_2O \rightarrow 2\,HNO_3 + H_2$$

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5.5: Avogadro's Number and the Mole

Learning Objectives

- Use Avogadro's number to convert to moles and vice versa given the number of particles of an element.
- Know the definition of the mole.
- Determine the formula mass of an ionic or molecular compound.
- Determine the percent composition of each element in a compound from the chemical formula.

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 are 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.

Avogadro's Number:Counting Atoms

Owing to their tiny size, atoms and molecules cannot be counted by direct observation. But much as we do when "counting" beans in a jar, we can estimate the number of particles in a sample of an element or compound if we have some idea of the volume occupied by each particle and the volume of the container. Once this has been done, we know the number of formula units (to use the most general term for any combination of atoms we wish to define) in any arbitrary weight of the substance. The number will of course depend both on the formula of the substance and on the weight of the sample. However, if we consider a weight of substance that is the same as its formula (molecular) weight expressed in grams, we have only one number to know: **Avogadro's number**.

Avogadro's number

Avogadro's number is known to ten significant digits:

$$N_A = 6.022141527 \times 10^{23}.$$

However, you only need to know it to three significant figures:

$$N_A \approx 6.02 \times 10^{23}. \tag{5.5.1}$$

So 6.02×10^{23} of *what*? Well, of anything you like: apples, stars in the sky, burritos. However, the only *practical* use for N_A is to have a more convenient way of expressing the huge numbers of the tiny particles such as atoms or molecules that we deal with in chemistry. Avogadro's number is a *collective number*, just like a dozen. Students can think of 6.02×10^{23} as the "chemist's dozen".

Before getting into the use of Avogadro's number in problems, take a moment to convince yourself of the reasoning embodied in the following examples.

Things to understand about Avogadro's number

- It is a *number*, just as is "dozen", and thus is *dimensionless*.
- It is a *huge* number, far greater in magnitude than we can visualize
- Its practical use is limited to counting tiny things like atoms, molecules, "formula units", electrons, or photons.
- The value of N_A can be known only to the precision that the number of atoms in a measurable weight of a substance can be estimated. Because large numbers of atoms cannot be counted directly, a variety of ingenious indirect measurements have been made involving such things as Brownian motion and X-ray scattering.

The Mole: "A Dozen Eggs and a Mole of Sugar, Please"

The **mole** (symbol: **mol**) is the base unit of amount of substance ("number of substance") in the International System of Units or System International (SI), defined as exactly 6.02214076×10^{23} particles, e.g., atoms, molecules, ions or electrons. The current definition was adopted in November 2018, revising its old definition based on the number of atoms in 12 grams of carbon-12 (^{12}C) (the isotope of carbon with relative atomic mass 12 Daltons by definition).

It is not obvious why eggs come in dozens rather than 10s or 14s, or why a ream of paper contains 500 sheets rather than 400 or 600. The definition of a mole—that is, the decision to base it on 12 g of carbon-12—is also arbitrary. The important point is that 1 mole of carbon—or of anything else, whether atoms, compact discs, or houses—always has the same number of objects: 6.02×10^{23}.

The Mole



***Video* 5.5.1** *How big is a mole?*

Converting Between Number of Atoms to Moles and Vice Versa

We can use Avogadro's number as a conversion factor, or ratio, in dimensional analysis problems. If we are given the number of atoms of an element X, we can convert it into moles of by using the relationship

$$\mathbf{1\ mol\ X = 6.022 \times 10^{23}\ X\ atoms.}$$

An example on the use of Avogadro's number as a conversion factor is given below for carbon.

Example 5.5.1: Moles of Carbon

The element carbon exists in two primary forms: graphite and diamond. How many moles of carbon atoms is $\mathbf{4.72 \times 10^{24}}$ atoms of carbon?

Solution

Example **5.5.1**:Steps for Problem Solving how many moles of carbon atoms is $\mathbf{4.72 \times 10^{24}}$ atoms of carbon?

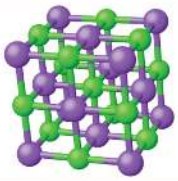
Steps for Problem Solving	Example
Identify the "given"information and what the problem is asking you to "find."	Given: 4.72×10^{24} C atoms Find: mol C
List other known quantities	$1\,mol = 6.022 \times 10^{23}$ C atoms
Prepare a concept map and use the proper conversion factor.	# C atoms → mol C $\frac{1\,mol\,C}{6.022 \times 10^{23} C\,atoms}$
Cancel units and calculate.	$4.72 \times 10^{24}\ \cancel{C\,atoms} \times \frac{1\ mol\ C}{6.02 \times 10^{23}\ \cancel{C\,atoms}} = 7.84\ mol\ C$
Think about your result.	The given number of carbon atoms was greater than Avogadro's number,so the number of moles of C atoms is greater than 1 mole. Since Avogadro's number is a measured quantity with three significant figures, the result of the calculation is rounded to three significant figures

Formula Mass

One skill needed in future chapters is the ability to determine the mass of the formula of various chemical substances. This quantity is called the formula mass. The **formula mass** is obtained by adding the masses of each individual atom in the formula of the substance. Because a proper formula is electrically neutral (with no net electrons gained or lost), the ions can be considered atoms for the purpose of calculating the formula mass.

Let us start by calculating the formula mass of sodium chloride (NaCl). This formula mass is the sum of the atomic masses of one sodium atom and one chlorine atom, which we find from the periodic table; here, we use the masses to two decimal places:

Element	Quantity		Average atomic mass (amu)		Subtotal
Na	1	×	22.99	=	22.99
Cl	1	×	35.45	=	35.45
				Formula mass	58.44

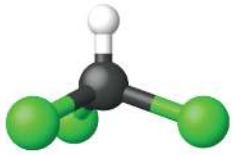


A table and diagram are shown. The table is made up of six columns and four rows. The header row reads: “Element,” “Quantity,” a blank space, “Average atomic mass (a m u),” a blank space and “Subtotal (a m u).” The first column contains the symbols “N a”, “C l,” and a merged cell. The merged cell runs the length of the first five columns. The second column contains the numbers “1” and “1” as well as the merged cell. The third column contains the multiplication symbol in each cell except for the last, merged cell. The fourth column contains the numbers “22.99” and “35.45” as well as the merged cell. The fifth column contains the symbol “=” in each cell except for the last, merged cell. The sixth column contains the values “22.99,” “35.45,” and “58.44.” There is a thick black line below the number “35.45.” The merged cell under the first five columns reads “Formula mass.” To the left of the table is a diagram of a chemical structure. The diagram shows green and purple spheres placed in an alternating pattern, making up the corners of eight stacked cubes to form one larger cube. The green spheres are slightly smaller than the purple spheres.

To two decimal places, the formula mass of NaCl is 58.44 amu.

For covalent substances, the formula represents the numbers and types of atoms composing a single molecule of the substance; therefore, the formula mass may be correctly referred to as a **molecular mass**. Consider chloroform ($CHCl_3$), a covalent compound once used as a surgical anesthetic and now primarily used in the production of tetrafluoroethylene, the building block for the “anti-stick” polymer, Teflon. The molecular formula of chloroform indicates that a single molecule contains one carbon atom, one hydrogen atom, and three chlorine atoms. The average molecular mass of a chloroform molecule is therefore equal to the sum of the average atomic masses of these atoms.

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
C	1	×	12.01	=	12.01
H	1	×	1.008	=	1.008
Cl	3	×	35.45	=	106.35
				Molecular mass	119.37



A table and diagram are shown. The table is made up of six columns and five rows. The header row reads: “Element,” “Quantity,” a blank space, “Average atomic mass (a m u),” a blank space, and “Subtotal (a m u).” The first column contains the symbols “C,” “H,” “C l” and a blank, merged cell that runs the width of the first five columns. The second column contains the numbers “1,” “1,” and “3” as well as the merged cell. The third column contains the multiplication symbol in each cell except for the last, merged cell. The fourth column contains the numbers “12.01,” “1.008,” and “35.45” as well as the merged cell. The fifth column contains the symbol “=” in each cell except for the last, merged cell. The sixth column contains the values “12.01,” “1.008,” “106.35,” and “119.37.” There is a thick black line below the number 106.35. The merged cell under the first five columns reads “Molecular mass.” To the left of the table is a diagram of a molecule. Three green spheres are attached to a slightly smaller black sphere, which is also attached to a smaller white sphere. The green spheres lie beneath and to the sides of the black sphere while the white sphere is located straight up from the black sphere.

To two decimal places, the formula mass of $CHCl_3$ is 119.37 amu.

For ionic compounds with polyatomic ions, the sum must include the number and mass of each atom in the formula for the polyatomic ion. as shown in the example below for aluminum sulfate, $Al_2(SO_4)_3$.

✔ Example 5.5.2 Formula Mass for an Ionic Compound

Aluminum sulfate, $Al_2(SO_4)_3$, is an ionic compound that is used in the manufacture of paper and in various water purification processes. What is the formula mass (amu) of this compound?

Solution

The formula for this compound indicates it contains Al^{3+} and SO_4^{2-} ions combined in a 2:3 ratio. For purposes of computing a formula mass, it is helpful to rewrite the formula in the simpler format, $Al_2S_3O_{12}$. Following the approach outlined above, the formula mass for this compound is calculated as follows:



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The formula mass for $Al_2(SO_4)_3$, is 342.14 amu.

? Exercise 5.5.1

Use the atomic masses (rounded to two decimal places) to determine the formula mass for each ionic compound.

a. TiO_2
b. AgBr
c. $Au(NO_3)_3$
d. $Fe_3(PO_4)_2$

Answer

a. 79.87 amu

b. 187.77 amu

c. 383.0 amu

Percent Composition of a Compound from a Chemical Formula

The percent composition of a compound can also be determined from the formula of the compound. The subscripts in the formula are first used to calculate the mass of each element in one mole of the compound. That is divided by the molar mass of the compound and multiplied by 100%.

$$\%\text{ by mass} = \frac{\text{mass of element in 1 mol}}{\text{molar mass of compound}} \times 100\%$$

The percent composition of a given compound is always the same as long as the compound is pure.

Example 5.5.3

Dichlorine heptoxide (Cl_2O_7) is a highly reactive compound used in some organic synthesis reactions. Calculate the percent composition of dichlorine heptoxide.

Solution

Example 5.5.3: Steps for Problem Solving calculate the percent composition of dichlorine heptoxide (Cl_2O_7).

Steps for Problem Solving	Example
Identify the "given"information and what the problem is asking you to "find."	Given : Cl_2O_7 Find: % Composition (% Cl and %O)
List other known quantities	Mass of Cl in 1 mol Cl_2O_7 , 2 Cl : 2 x 35.45 g = 70.90 g Mass of O in 1 mol Cl_2O_7 , 7 O: 7 x 16.00 g = 112.00 g Molar mass of Cl_2O_7 = 182.90 g/mol
Cancel units and calculate.	$$\%Cl = \frac{70.90\text{ g Cl}}{182.90\text{ g}} \times 100\% = 38.76\%\text{ Cl}$$ $$\%\text{ O} = \frac{112.00\text{ g O}}{182.90\text{ g}} \times 100\% = 61.24\%\text{ O}$$ Calculate the percent by mass of each element by dividing the mass of that element in 1 mole of the compound by the molar mass of the compound and multiplying by 100%.
Think about your result.	The percentages add up to 100%.

Percent composition can also be used to determine the mass of a certain element that is contained in any mass of a compound. In the previous sample problem, it was found that the percent composition of dichlorine heptoxide is 38.76% Cl and 61.24% O. Suppose that you needed to know the masses of chlorine and oxygen present in a 12.50 g sample of dichlorine heptoxide. You can set up a conversion factor based on the percent by mass of each element.

$$12.50\text{ g } Cl_2O_7 \times \frac{38.76\text{ g Cl}}{100\text{ g } Cl_2O_7} = 4.845\text{ g Cl}$$

$$12.50\text{ g } Cl_2O_7 \times \frac{61.24\text{ g O}}{100\text{ g } Cl_2O_7} = 7.655\text{ g O}$$

The sum of the two masses is 12.50 g, the mass of the sample size.

Exercise 5.5.2

Barium fluoride is a transparent crystal that can be found in nature as the mineral frankdicksonite. Determine the percent composition of barium fluoride.

Answer a:

78.32% Ba and 21.67% F

Summary

- The **mole** (symbol: **mol**) is the base unit of amount of substance ("number of substance") in the International System of Units or System International (SI), defined as exactly $6.02214076 \times 10^{23}$ particles, e.g., atoms, molecules, ions or electrons.
- Avogadro's number is related to moles of any substance X as follows:

$$1 \text{ mol X} = 6.022 \times 10^{23} \text{ X atoms.}$$

- Formula masses of ionic and molecular compounds can be determined from the masses of the atoms in their formulas.
- Processes are described for calculating the percent composition of a compound based on the chemical formula.

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5.6: Molar Mass- Mole-to-Mass and Mass-to-Mole Conversions

Learning Objectives

- Perform conversions between mass and moles of a substance.
- Convert from mass or moles of one substance to mass or moles of another substance in a chemical reaction.
- Use a balanced chemical equation to determine molar relationships between substances.

Molar Mass

The **molar mass** of any substance is the mass in grams of one mole of representative particles of that substance. The representative particles can be atoms, molecules, or formula units of ionic compounds. This relationship is frequently used in the laboratory. The simplest type of manipulation using molar mass as a conversion factor is a mole-mass conversion (or its reverse, a mass-mole conversion). In such a conversion, we use the molar mass of a substance as a conversion factor to convert mole units into mass units (or, conversely, mass units into mole units).

We also established that 1 mol of Al has a mass of 26.98 g (Example). Stated mathematically,

$$1 \text{ mol Al} = 26.98 \text{ g Al}$$

We can divide both sides of this expression by either side to get one of two possible conversion factors:

$$\frac{1 \text{ mol Al}}{26.98 \text{ g Al}} \text{ and } \frac{26.98 \text{ g Al}}{1 \text{ mol Al}} \tag{5.6.1}$$

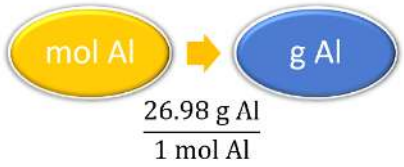
The first conversion factor can be used to convert from mass to moles, and the second converts from moles to mass. Both can be used to solve problems that would be hard to do “by eye.”

Example 5.6.1

What is the mass of 3.987 mol of Al?

Solution

Example **5.6.1**: Steps for Problem Solving the mass of 3.987 moles of aluminum (Al).

Steps for Problem Solving	Example
Identify the "given"information and what the problem is asking you to "find."	Given: 3.987 mol of Al Find: g Al
List other known quantities	1 mol Al = 26.98 g Al
Prepare a concept map and use the proper conversion factor.	
Cancel units and calculate.	$3.987 \cancel{\text{mol Al}} \times \frac{26.98 \text{ g Al}}{1 \cancel{\text{mol Al}}} = 107.6 \text{ g Al}$
Think about your result.	The calculated value makes sense because it is almost four times times the mass for 1 mole of aluminum. Our final answer is expressed to four significant figures.

Exercise 5.6.1

How many moles are present in 100. g of Al? (Hint: you will have to use the other conversion factor we obtained for aluminum.)

Answer

3.71 g Al

Conversions like this are possible for any substance, as long as the proper atomic mass, formula mass, or molar mass is known (or can be determined) and expressed in grams per mole. Figure 5.6.1 is a chart for determining what conversion factor is needed, and Figure 5.6.2 is a flow diagram for the steps needed to perform a conversion.

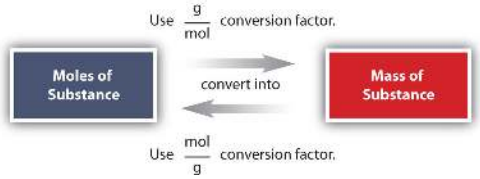


Figure 5.6.1 A Simple Flowchart for Converting between Mass and Moles of a Substance. It takes one mathematical step to convert from moles to mass or from mass to moles.

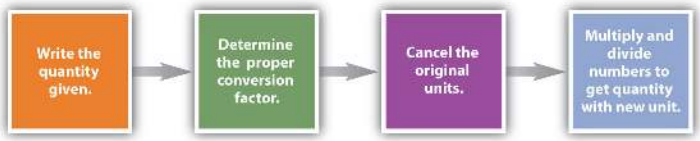


Figure 5.6.2 A Flowchart Illustrating the Steps in Performing a Unit Conversion. When performing many unit conversions, the same logical steps can be taken.

Suppose that for a certain experiment you need 3.00 moles of calcium chloride ($CaCl_2$). Since calcium chloride is a solid, it would be convenient to use a balance to measure the mass that is needed. Dimensional analysis will allow you to calculate the mass of $CaCl_2$ that you should measure as show in Example 5.6.3.

Example 5.6.2: Calcium Chloride

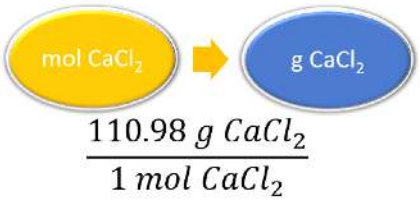
Calculate the mass of 3.00 moles of calcium chloride ($CaCl_2$).



Figure 5.6.1: Calcium chloride is used as a drying agent and as a road deicer.

Solution

Example 5.6.2: Steps for Problem Solving the mass of 3.00 moles of calcium chloride (CaCl2).

Steps for Problem Solving	Example
Identify the "given"information and what the problem is asking you to "find."	Given: 3.00 moles of $CaCl_2$ Find: g $CaCl_2$
List other known quantities	1 ml $CaCl_2$ = 110.98 g $CaCl_2$
Prepare a concept map and use the proper conversion factor.	 $\frac{110.98\ g\ CaCl_2}{1\ mol\ CaCl_2}$
Cancel units and calculate.	$3.00\ \cancel{mol\ CaCl_2} \times \frac{110.98\ g\ CaCl_2}{1\ \cancel{mol\ CaCl_2}} = 333\ g\ CaCl_2$
Think about your result.	

Exercise 5.6.2: Calcium Oxide

What is the mass of $7.50\ mol$ of (calcium oxide) CaO?

Answer:

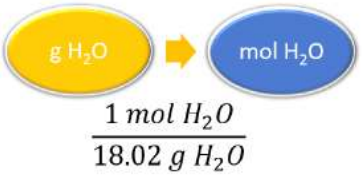
420.60 g

Example 5.6.3: Water

How many moles are present in 108 grams of water?

Solution

Example 5.6.3: Steps for Problem Solving moles in 108 grams of water?

Steps for Problem Solving	Example
Identify the "given"information and what the problem is asking you to "find."	Given: 108 g H_2O Find: mol H_2O
List other known quantities	$1\ mol\ H_2O = 18.02\ g$ H_2O
Prepare a concept map and use the proper conversion factor.	 $\frac{1\ mol\ H_2O}{18.02\ g\ H_2O}$
Cancel units and calculate.	$108\ \cancel{g\ H_2O} \times \frac{1\ mol\ H_2O}{18.02\ \cancel{g\ H_2O}} = 5.99\ mol\ H_2O$
Think about your result.	

Exercise 5.6.3: Nitrogen Gas

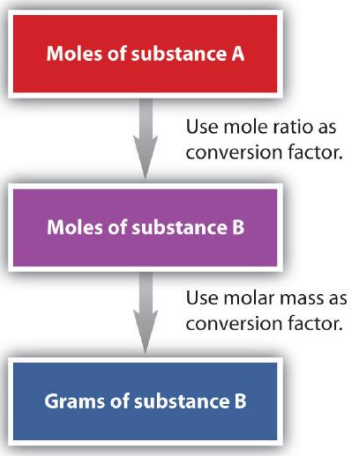
What is the mass of $7.50\ mol$ of Nitrogen gas N_2?

Answer:

210 g

Mole and Mass Relationships in Chemical Equations

We have established that a balanced chemical equation is balanced in terms of moles as well as atoms or molecules. We have used balanced equations to set up ratios, now in terms of moles of materials, that we can use as conversion factors to answer stoichiometric questions, such as how many moles of substance A react with so many moles of reactant B. We can extend this technique even further. Recall that we can relate a molar amount to a mass amount using molar mass. We can use that ability to answer stoichiometry questions in terms of the masses of a particular substance, in addition to moles. We do this using the following sequence:



Collectively, these conversions are called mole-mass calculations.

As an example, consider the balanced chemical equation

$$Fe_2O_3 + 3SO_3 \rightarrow Fe_2(SO_4)_3$$

If we have 3.59 mol of Fe_2O_3, how many grams of SO_3 can react with it? Using the mole-mass calculation sequence, we can determine the required mass of SO_3 in two steps. First, we construct the appropriate molar ratio, determined from the balanced chemical equation, to calculate the number of moles of SO_3 needed. Then using the molar mass of SO_3 as a conversion factor, we determine the mass that this number of moles of SO_3 has.

As usual, we start with the quantity we were given:

$$3.59 \ \cancel{\text{mol Fe}_2\text{O}_3} \times \left(\frac{3 \text{ mol SO}_3}{1 \ \cancel{\text{mol Fe}_2\text{O}_3}} \right) = 10.77 \text{ mol SO}_3 \tag{5.6.2}$$

The mol Fe_2O_3 units cancel, leaving mol SO_3 unit. Now, we take this answer and convert it to grams of SO_3, using the molar mass of SO_3 as the conversion factor:

$$10.77 \ \cancel{\text{mol SO}_3} \times \left(\frac{80.06 \text{ g SO}_3}{1 \ \cancel{\text{mol SO}_3}} \right) = 862 \text{ g SO}_3 \tag{5.6.3}$$

Our final answer is expressed to three significant figures. Thus, in a two-step process, we find that 862 g of SO_3 will react with 3.59 mol of Fe_2O_3. Many problems of this type can be answered in this manner.

The same two-step problem can also be worked out in a single line, rather than as two separate steps, as follows:

$$3.59 \ \cancel{mol\ Fe_2O_3} \times \underbrace{\left(\frac{3 \ \cancel{mol\ SO_3}}{1 \ \cancel{mol\ Fe_2O_3}} \right)}_{\text{converts to moles of SO}_3} \times \underbrace{\left(\frac{80.06\, g\, SO_3}{1 \ \cancel{mol\ SO_3}} \right)}_{\text{converts to grams of SO}_3} = 862\, g\, SO_3$$

We get exactly the same answer when combining all the math steps together as we do when we calculate one step at a time.

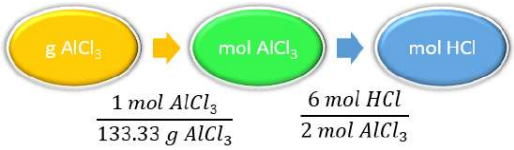
Example 5.6.4: Generation of Aluminum Oxide

How many moles of HCl will be produced when 249 g of $AlCl_3$ are reacted according to this chemical equation?

$$2AlCl_3 + 3H_2O(\ell) \rightarrow Al_2O_3 + 6HCl(g)$$

Solution

Example 5.6.4: Steps for Problem Solving how many moles are in 249 g of $AlCl_3$?

Steps for Problem Solving	Example
Identify the "given"information and what the problem is asking you to "find."	Given: 249 g $AlCl_3$ Find: moles HCl
List other known quantities	1 mol $AlCl_3$ = 133.33 g/mol 6 mol of HCl to 2 mol $AlCl_3$
Prepare a concept map and use the proper conversion factor.	
Cancel units and calculate.	$249\ \cancel{g\ AlCl_3} \times \frac{1\ \cancel{mol\ AlCl_3}}{133.33\ \cancel{g\ AlCl_3}} \times \frac{6\ mol\ HCl}{2\ \cancel{mol\ AlCl_3}} = 5.60\ mol\ HCl$
Think about your result.	Since 249 g of $AlCl_3$ is less than 266.66 g, the mass for 2 moles of $AlCl_3$ and the relationship is 6 mol of HCl to 2 mol $AlCl_3$, the answer should be less than 6 moles of HCl.

Exercise 5.6.4: Generation of Aluminum Oxide

How many moles of Al_2O_3 will be produced when 23.9 g of H_2O are reacted according to this chemical equation?

$$2AlCl_3 + 3H_2O(\ell) \rightarrow Al_2O_3 + 6HCl(g)$$

Answer

0.442 mol Al_2O_3

Molar Relationships in Chemical Equations

Previously, you learned to balance chemical equations by comparing the numbers of each type of atom in the reactants and products. The coefficients in front of the chemical formulas represent the numbers of molecules or formula units (depending on the type of substance). Here, we will extend the meaning of the coefficients in a chemical equation.

Consider the simple chemical equation

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

The convention for writing balanced chemical equations is to use the lowest whole-number ratio for the coefficients. However, the equation is balanced as long as the coefficients are in a 2:1:2 ratio. For example, this equation is also balanced if we write it as

$$4H_2 + 2O_2 \rightarrow 4H_2O$$

The ratio of the coefficients is 4:2:4, which reduces to 2:1:2. The equation is also balanced if we were to write it as

$$22H_2 + 11O_2 \rightarrow 22H_2O$$

because 22:11:22 also reduces to 2:1:2.

Suppose we want to use larger numbers. Consider the following coefficients:

$$12.044 \times 10^{23}\ H_2 + 6.022 \times 10^{23}\ O_2 \rightarrow 12.044 \times 10^{23}\ H_2O$$

These coefficients also have the ratio 2:1:2 (check it and see), so this equation is balanced. But 6.022×10^{23} is 1 mol, while 12.044×10^{23} is 2 mol (and the number is written that way to make this more obvious), so we can simplify this version of the equation by writing it as

$$2\ mol\ H_2 + 1\ mol\ O_2 \rightarrow 2\ mol\ H_2O$$

We can leave out the word *mol* and not write the 1 coefficient (as is our habit), so the final form of the equation, still balanced, is

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

Now we interpret the coefficients as referring to molar amounts, not individual molecules. The lesson? *Balanced chemical equations are balanced not only at the molecular level but also in terms of molar amounts of reactants and products.* Thus, we can read this reaction as "two moles of hydrogen react with one mole of oxygen to produce two moles of water."

By the same token, the ratios we constructed to describe molecules reaction can also be constructed in terms of moles rather than molecules. For the reaction in which hydrogen and oxygen combine to make water, for example, we can construct the following ratios:

$$\frac{2\ \text{mol}\ H_2}{1\ \text{mol}\ O_2} \text{ or } \frac{1\ \text{mol}\ O_2}{2\ \text{mol}\ H_2}$$

$$\frac{2\ \text{mol}\ H_2O}{1\ \text{mol}\ O_2} \text{ or } \frac{1\ \text{mol}\ O_2}{2\ \text{mol}\ H_2O}$$

$$\frac{2\ \text{mol}\ H_2}{2\ \text{mol}\ H_2O} \text{ or } \frac{2\ \text{mol}\ H_2O}{2\ \text{mol}\ H_2}$$

We can use these ratios to determine what amount of a substance, in moles, will react with or produce a given number of moles of a different substance. The study of the numerical relationships between the reactants and the products in balanced chemical reactions is called *stoichiometry*.

Example 5.6.5

How many moles of oxygen react with hydrogen to produce 27.6 mol of H_2O?

Solution

Example **5.6.5**: Steps for Problem Solving how many moles of oxygen react with hydrogen to produce 27.6 mol of H2O?

Steps for Problem Solving	Example
Find a balanced equation that describes the reaction	Unbalanced: $H_2 + O_2 \rightarrow H_2O$ Balanced: $\underline{2}H_2 + O_2 \rightarrow \underline{2}H_2O$
Identify the "given"information and what the problem is asking you to "find."	Given: moles H_2O Find: moles oxygen
List other known quantities	1 mol O_2 = 2 mol H_2O
Prepare a concept map and use the proper conversion factor.	mol H_2O → mol O_2 $\frac{1\ mol\ O_2}{2\ mol\ H_2O}$
Cancel units and calculate.	$\cancel{27.6\ mol\ H_2O} \times \frac{1\ mol\ O_2}{\cancel{2\ mol\ H_2O}} = 13.8\ mol\ O_2$ To produce 27.6 mol of H_2O, 13.8 mol of O_2 react.
Think about your result.	Since each mole of oxygen produces twice as many moles of water, it makes sense that the produced amount is greater than the reactant amount

Example 5.6.6

How many moles of ammonia are produced if 4.20 moles of hydrogen are reacted with an excess of nitrogen?

Solution

Example **5.6.6**: Steps for Problem Solving how many moles of ammonia are produced if 4.20 moles of hydrogen are reacted with an excess of nitrogen

Steps for Problem Solving	Example
Find a balanced equation that describes the reaction	Unbalanced: $N_2 + H_2 \rightarrow NH_3$ Balanced: $N_2 + \underline{3}H_2 \rightarrow \underline{2}NH_3$
Identify the "given"information and what the problem is asking you to "find."	Given: $\mathbf{H_2 = 4.20\ mol}$ Find: **mol** of $\mathbf{NH_3}$
List other known quantities	3 mol H_2 = 2 mol NH_3
Prepare a concept map and use the proper conversion factor.	mol H_2 → mol NH_3 $\frac{2\ mol\ NH_3}{3\ mol\ H_2}$
Cancel units and calculate.	$\cancel{4.20\ mol\ H_2} \times \frac{2\ mol\ NH_3}{\cancel{3\ mol\ H_2}} = 2.80\ mol\ NH_3$ The reaction of **4.20 mol** of hydrogen with excess nitrogen produces **2.80 mol** of ammonia
Think about your result.	The result corresponds to the 3:2 ratio of hydrogen to ammonia from the balanced equation.

Exercise 5.6.5

a. Given the following balanced chemical equation,

$$C_5H_{12} + 8\,O_2 \longrightarrow 5\,CO_2 + 6\,H_2O$$

how many moles of H_2O can be formed if 0.0652 mol of C_5H_{12} were to react?

b. Balance the following unbalanced equation and determine how many moles of H_2O are produced when 1.65 mol of NH_3 react.

$$NH_3 + O_2 \longrightarrow N_2 + H_2O$$

Answer a:

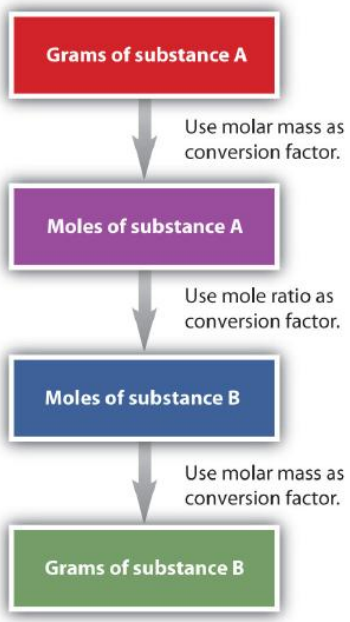
3.14 mol H_2O

Answer b:

$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$; 2.48 mol H_2O

Mass Relationships in Chemical Equations

It is a small step from mole-mass calculations to mass-mass calculations. If we start with a known mass of one substance in a chemical reaction (instead of a known number of moles), we can calculate the corresponding masses of other substances in the reaction. The first step in this case is to convert the known mass into moles, using the substance's molar mass as the conversion factor. Then—and only then—we use the balanced chemical equation to construct a conversion factor to convert that quantity to moles of another substance, which in turn can be converted to a corresponding mass. Sequentially, the process is as follows:



This three-part process can be carried out in three discrete steps or combined into a single calculation that contains three conversion factors. The following example illustrates both techniques.

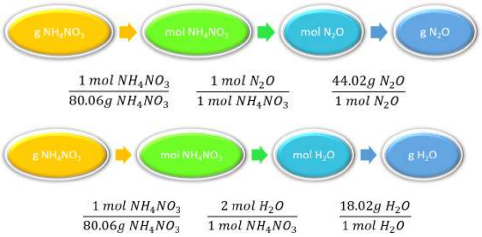
Example 5.6.7: Decomposition of Ammonium Nitrate

Ammonium nitrate decomposes to dinitrogen monoxide and water according to the following equation.

$$NH_4NO_3\,(s) \rightarrow N_2O\,(g) + 2H_2O\,(l)$$

In a certain experiment, **45.7 g** of ammonium nitrate is decomposed. Find the mass of each of the products formed.

Example **5.6.7**: Steps for Problem Solving the Decomposition of Ammonium Nitrate

Steps for Problem Solving	Example 5.6.2
Identify the "given"information and what the problem is asking you to "find."	Given: $45.7\ g\ NH_4NO_3$ Find: Mass $N_2O = ?\ g$ Mass $H_2O = ?\ g$
List other known quantities	1 mol $NH_4NO_3 = 80.06\ g/mol$ 1 mol $N_2O = 44.02\ g/mol$ 1 mol $H_2O = 18.02\ g/mol$ 1 mol NH_4NO_3 to 1 mol N_2O to 2 mol H_2O
Prepare two concept maps and use the proper conversion factor.	
Cancel units and calculate.	$45.7\ g\ NH_4NO_3 \times \frac{1\ mol\ NH_4NO_3}{80.06\ g\ NH_4NO_3} \times \frac{1\ mol\ N_2O}{1\ mol\ NH_4NO_3} \times \frac{44.02\ g\ N_2O}{1\ mol\ N_2O} = 25.1\ g\ N_2O$ $45.7\ g\ NH_4NO_3 \times \frac{1\ mol\ NH_4NO_3}{80.06\ g\ NH_4NO_3} \times \frac{2\ H_2O}{1\ mol\ NH_4NO_3} \times \frac{18.02\ g\ H_2O}{1\ mol\ H_2O} = 20.6\ g\ H_2O$
Think about your result.	The total mass of the two products is equal to the mass of ammonium nitrate which decomposed, demonstrating the law of conservation of mass. Each answer has three significant figures.

? Exercise 5.6.6: Carbon Tetrachloride

Methane can react with elemental chlorine to make carbon tetrachloride (CCl_4). The balanced chemical equation is as follows.

$$CH_4(g) + 4\,Cl_2(g) \longrightarrow CCl_2(l) + 4\,HCl(l)$$

How many grams of HCl are produced by the reaction of 100.0g of CH_4?

Answer

908.7g HCl

Summary

- Calculations involving conversions between moles of a substance and the mass of that substance are described.
- The balanced chemical reaction can be used to determine molar and mass relationships between substances.

Contributors and Attributions

- TextMap: The Basics of GOB Chemistry (Ball et al.)
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5.7: Enthalpy and Chemical Reactions

Learning Objectives

- Define *enthalpy*.
- Properly express the enthalpy change of chemical reactions.
- Explain how enthalpy changes are measured experimentally.

Now that we have shown how energy, work, and heat are related, we are ready to consider energy changes in chemical reactions. A fundamental concept is that *every chemical reaction occurs with a concurrent change in energy*. Now we need to learn how to properly express these energy changes.

Our study of gases in Chapter 6, and our definition of work in Section 7.3, indicate that conditions like pressure, volume, and temperature affect the energy content of a system. What we need is a definition of energy that holds when some of these conditions are specified (somewhat similar to our definition of standard temperature and pressure in our study of gases). We define the **enthalpy change** (ΔH) as the heat of a process when pressure is held constant:

$$\Delta H \equiv q \text{ at constant pressure}$$

The letter H stands for "enthalpy," a kind of energy, while the Δ implies a change in the quantity. We will always be interested in the change in H, rather than the absolute value of H itself.

When a chemical reaction occurs, there is a characteristic change in enthalpy. The enthalpy change for a reaction is typically written after a balanced chemical equation and on the same line. For example, when two moles of hydrogen react with one mole of oxygen to make two moles of water, the characteristic enthalpy change is 570 kJ. We write the equation as

$$2\,H_2\,(g) + O_2\,(g) \longrightarrow 2\,H_2O(\ell)$$

with $\Delta H = -570\,kJ$

A chemical equation that includes an enthalpy change is called a **thermochemical equation**. A thermochemical equation is assumed to refer to the equation in molar quantities, which means it must be interpreted in terms of moles, not individual molecules.

Example 5.7.1

Write the thermochemical equation for the reaction of $PCl_3(g)$ with $Cl_2(g)$ to make $PCl_5(g)$, which has an enthalpy change of −88 kJ.

Solution

The thermochemical equation is

$$PCl_3(g) + Cl_2(g) \rightarrow PCl_5(g)\ \Delta H = -88\text{ kJ}$$

Exercise 5.7.1

Write the thermochemical equation for the reaction of $N_2(g)$ with $O_2(g)$ to make $2NO(g)$, which has an enthalpy change of 181 kJ.

Answer

$$N_2(g) + O_2(g) \rightarrow 2NO(g)\ \Delta H = 181\text{ kJ}$$

You may have noticed that the ΔH for a chemical reaction may be positive or negative. The number is assumed to be positive if it has no sign; a + sign can be added explicitly to avoid confusion. A chemical reaction that has a positive ΔH is said to be **endothermic**, while a chemical reaction that has a negative ΔH is said to be **exothermic**.

What does it mean if the ΔH of a process is positive? It means that the system in which the chemical reaction is occurring is gaining energy. If one considers the energy of a system as being represented as a height on a vertical energy plot, the enthalpy change that accompanies the reaction can be diagrammed as in part (a) of Figure **5.7.1** Reaction Energy: the energy of the reactants has some energy, and the system increases its energy as it goes to products. The products are higher on the vertical scale than the reactants. Endothermic, then, implies that the system *gains*, or absorbs, energy.

An opposite situation exists for an exothermic process, as shown in part (b) of Figure **5.7.1** - Reaction Energy. If the enthalpy change of a reaction is negative, the system is losing energy, so the products have less energy than the reactants, and the products are lower on the vertical energy scale than the reactants are. Exothermic, then, implies that the system *loses*, or gives off, energy.

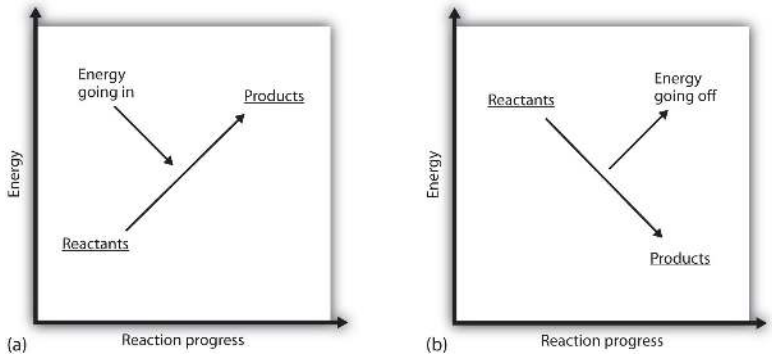


Figure **5.7.1** Reaction Energy (a) In an endothermic reaction, the energy of the system increases (i.e., moves higher on the vertical scale of energy). (b) In an exothermic reaction, the energy of the system decreases (i.e., moves lower on the vertical scale of energy).

Example 5.7.2

Consider this thermochemical equation.

$$2\,CO\,(g) + O_2\,(g) \longrightarrow 2\,CO_2\,(g)$$

with $\Delta H = -565$ kJ

Is it exothermic or endothermic? How much energy is given off or absorbed?

Solution

By definition, a chemical reaction that has a negative ΔH is exothermic, meaning that this much energy—in this case, 565 kJ—is given off by the reaction.

Exercise 5.7.2

Consider this thermochemical equation.

$$CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)\ \Delta H = 42\text{ kJ}$$

Is it exothermic or endothermic? How much energy is given off or absorbed?

Answer

Endothermic; 42 kJ are absorbed.

How are ΔH values measured experimentally? Actually, ΔH is not measured; q is measured. But the measurements are performed under conditions of constant pressure, so ΔH is equal to the q measured.

Experimentally, q is measured by taking advantage of the equation

$$q = mc\Delta T$$

We pre-measure the mass of the chemicals in a system. Then we let the chemical reaction occur and measure the change in temperature (ΔT) of the system. If we know the specific heat of the materials in the system (typically we do), we can calculate q. That value of q is numerically equal to the ΔH of the process, which we can scale up to a molar scale. The container in which the system resides is typically insulated, so any energy change goes into changing the temperature of the system, rather than being leaked from the system. The container is referred to as a **calorimeter**, and the process of measuring changes in enthalpy is called **calorimetry**.

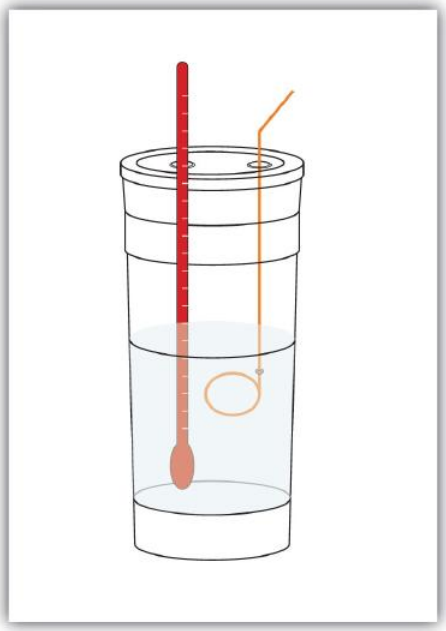


Figure 5.7.2 Calorimeters. A simple calorimeter can be constructed from some nested foam coffee cups, a cover, a thermometer, and a stirrer.

For example, suppose 4.0 g of NaOH, or 0.10 mol of NaOH, are dissolved to make 100.0 mL of aqueous solution; while 3.65 g of HCl, or 0.10 mol of HCl, are dissolved to make another 100.0 mL of aqueous solution. The two solutions are mixed in an insulated calorimeter, a thermometer is inserted, and the calorimeter is covered (See Figure 5.7.2 - Calorimeters for an example setup). The thermometer measures the temperature change as the following chemical reaction occurs:

$$\text{NaOH (aq)} + \text{HCl(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O}(\ell)$$

An observer notes that the temperature increases from 22.4°C to 29.1°C. Assuming that the heat capacities and densities of the solutions are the same as those of pure water, we now have the information we need to determine the enthalpy change of the chemical reaction. The total amount of solution is 200.0 mL, and with a density of 1.00 g/mL, we thus have 200.0 g of solution. Using the equation for q, we substitute for our experimental measurements and the specific heat of water (in Table 5.7.1 of Section 7.3).

$$q = (200.0 \cancel{g})\left(4.184 \frac{J}{\cancel{g} \cdot \cancel{^\circ C}}\right)(6.7 \cancel{^\circ C})$$

Solving for q, we get

$$q = 5600\ J \equiv \Delta H \text{ for the reaction}$$

The heat q is equal to the ΔH for the reaction because the chemical reaction occurs at constant pressure. However, the reaction is giving off this amount of energy, so the actual sign on ΔH is negative:

$$\Delta H = -5{,}600 \text{ J for the reaction}$$

Thus, we have the following thermochemical equation for the chemical reaction that occurred in the calorimeter:

$$\frac{1}{10}NaOH(aq) + \frac{1}{10}HCl(aq) \rightarrow \frac{1}{10}NaCl(aq) + \frac{1}{10}H_2O(l)\ \Delta H = -5600\ J$$

The 1/10 coefficients are present to remind us that we started with one-tenth of a mole of each reactant, so we make one-tenth of a mole of each product. Typically, however, we report thermochemical equations in terms of moles, not one-tenth of a mole. To scale up to molar quantities, we must multiply the coefficients by 10. However, when we do this, we get 10 times as much energy. Thus, we have

$$\text{NaOH (aq)} + \text{HCl(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O}(\ell)\ \Delta H = -56{,}000\ \text{J}$$

The ΔH can be converted into kJ units, so our final thermochemical equation is

$$\text{NaOH (aq)} + \text{HCl(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O}(\ell)\ \Delta H = -56\ \text{kJ}$$

We have just taken our experimental data from calorimetry and determined the enthalpy change of a chemical reaction. Similar measurements on other chemical reactions can determine the ΔH values of any chemical reaction you want to study.

Example 5.7.3

A 100 mL solution of 0.25 mol of $Ca^{2+}(aq)$ was mixed with 0.50 mol of $F^-(aq)$ ions, and CaF_2 was precipitated:

$$Ca^{2+}(aq) + 2F^-(aq) \rightarrow CaF_2(s)$$

The temperature of the solution increased by 10.5°C. What was the enthalpy change for the chemical reaction? What was the enthalpy change for the production of 1 mol of CaF_2? Assume that the solution has the same density and specific heat as water.

Solution

Because we are given ΔT directly, we can determine the heat of the reaction, which is equal to ΔH:

$$q = (100\ \cancel{g})\left(4.184\frac{J}{\cancel{g}\cdot\cancel{^\circ C}}\right)(10.5\ \cancel{^\circ C})$$

Solving for q, we get

$$q = 4{,}400\ \text{J}$$

Therefore, $\Delta H = -4{,}400$ J.

According to the stoichiometry of the reaction, exactly 0.25 mol of CaF_2 will form, so this quantity of heat is for 0.25 mol. For 1 mol of CaF_2, we need to scale up the heat by a factor of four:

$$q = 4{,}400\ \text{J} \times 4 = 17{,}600\ \text{J for 1 mol } CaF_2$$

On a molar basis, the change in enthalpy is

$$\Delta H = -17{,}600\ \text{J} = -17.6\ \text{kJ}$$

Exercise 5.7.3

In a calorimeter at constant pressure, 0.10 mol of $CH_4(g)$ and 0.20 mol of $O_2(g)$ are reacted.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell)$$

The reaction warms 750.0 g of H_2O by 28.4°C. What is ΔH for the reaction on a molar scale?

Answer

−891 kJ

Key Takeaways

- Every chemical reaction occurs with a concurrent change in energy.
- The change in enthalpy equals heat at constant pressure.

- Enthalpy changes can be expressed by using thermochemical equations.
- Enthalpy changes are measured by using calorimetry.

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5.8: Coal - The Carbon Rock of Ages

Learning Objectives

- Describe coal and its processing.
- List the products of coal burning that promotes pollution.

Coal is a complex solid material derived primarily from plants that died and were buried hundreds of millions of years ago and were subsequently subjected to high temperatures and pressures. It is a combustible black or brownish-black sedimentary rock with a high amount of carbon and hydrocarbons. Coal is classified into four main types, or ranks depending on the types and amounts of carbon present and on the amount of heat energy the coal can produce, including anthracite, bituminous, subbituminous, and lignite (highest to lowest ranked, pictured in *Figure* **5.8.1**.

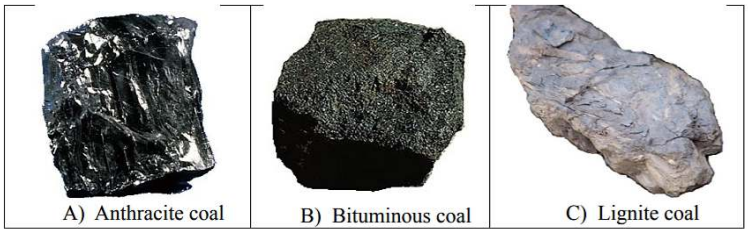


Figure **5.8.1** Different types of coal. Images obtained from Wikimedia Commons.

There are four distinct classes of coal (Table **5.8.1**); their hydrogen and oxygen contents depend on the length of time the coal has been buried and the pressures and temperatures to which it has been subjected. The most abundant form in the United States is bituminous coal, which has a high sulfur content becauseof the presence of small particles of pyrite (FeS_2). The combustion of coal releases the sulfur in FeS_2 as SO_2, which is a major contributor to acid rain.

Table **5.8.1** *Properties of Different Types of Coal.*

Type	% Carbon	Hydrogen:Carbon Mole Ratio	% Oxygen	% Sulfur	US Deposits
anthracite	92	0.5	3	1	Pennsylvania, New York
bituminous	80	0.6	8	5	Appalachia, Midwest, Utah
subbituminous	77	0.9	16	1	Rocky Mountains
lignite	71	1.0	23	1	Montana

Peat, a precursor to coal, is the partially decayed remains of plants that grow in swampy areas. It is removed from the ground in the form of soggy bricks of mud that will not burn until they have been dried. If a peat bog were buried under many layers of sediment for a few million years, the peat could eventually be compressed and heated enough to become lignite, the lowest grade of coal; given enough time and heat, lignite would eventually become anthracite, a much better fuel.

For us to use the potential energy stored in coal, it first must be mined from the ground. This process in itself uses a great deal of resources and has its own environmental impacts. Coal then typically undergoes processing to make it suitable for use in **coal-fire power plants**. Finally, the processed coal is burned in these power plants, and the kinetic energy released from its combustion is harnessed for electricity generation or other purposes. Figure **5.8.2** below is a schematic diagram showing a typical layout of a coal-fire power plant. You can also watch a short video of a virtual tour of a coal power plant at the URL provided below.

Power Plant Virtual Tour

***Video* 5.8.1** *Coal-Fueled Power Plant Virtual Tour Video*

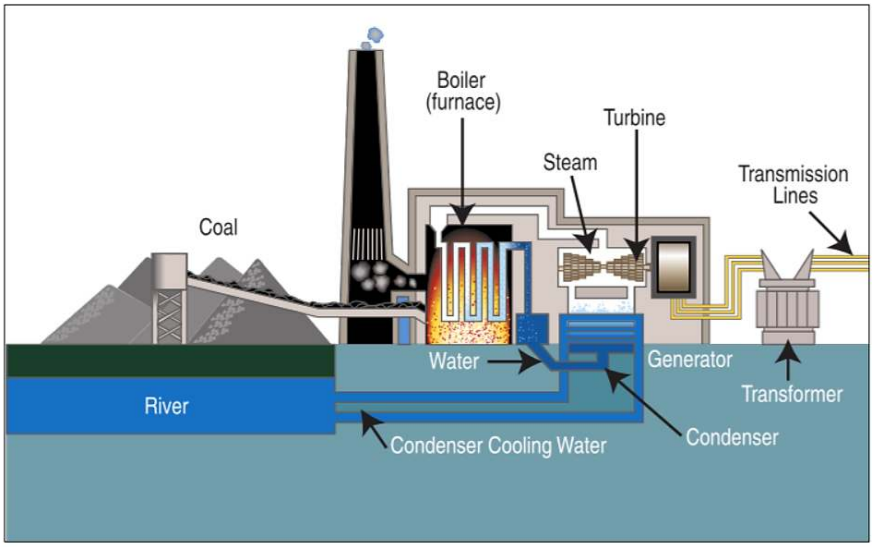


Figure **5.8.2** Diagram of a typical steam-cycle coal power plant (proceeding from left to right). Image by US Tennessee Valley Authority – Public domain. www.tva.com

The Global Carbon Cycle

Figure **5.8.3** illustrates the global carbon cycle, the distribution and flow of carbon on Earth. Normally, the fate of atmospheric CO_2 is to either (1) dissolve in the oceans and eventually precipitate as carbonate rocks or (2) be taken up by plants. The rate of uptake of CO_2 by the ocean is limited by its surface area and the rate at which gases dissolve, which are approximately constant. The rate of uptake of CO_2 by plants, representing about 60 billion metric tons of carbon per year, partly depends on how much of Earth's surface is covered by vegetation. Unfortunately, the rapid deforestation for agriculture is reducing the overall amount of vegetation, and about 60 billion metric tons of carbon are released annually as CO_2 from animal respiration and plant decay. The amount of carbon released as CO_2 every year by fossil fuel combustion is estimated to be about 5.5 billion metric tons. The net result is a system that is slightly out of balance, experiencing a slow but steady increase in atmospheric CO_2 levels. As a result, average CO_2 levels have increased by about 30% since 1850.

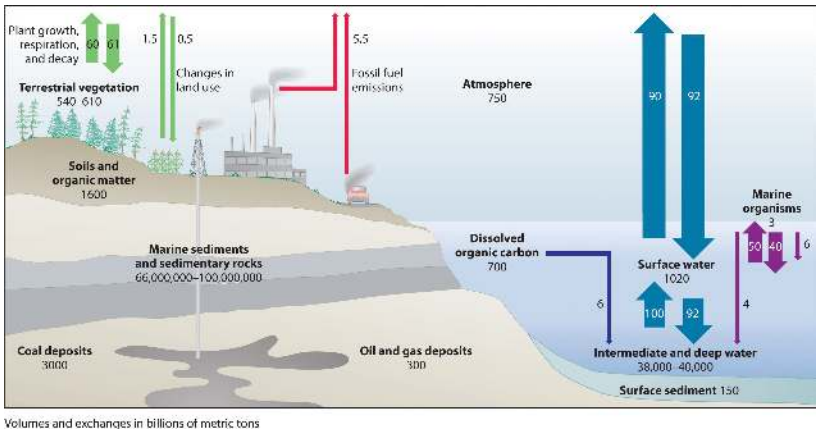


Figure **5.8.3** The global carbon cycle.

Most of Earth's carbon is found in the crust, where it is stored as calcium and magnesium carbonate in sedimentary rocks. The oceans also contain a large reservoir of carbon, primarily as the bicarbonate ion (HCO_3^-). Green plants consume about 60 billion metric tons of carbon per year as CO_2 during photosynthesis, and about the same amount of carbon is released as CO_2 annually from animal and plant respiration and decay. The combustion of fossil fuels releases about 5.5 billion metric tons of carbon per year as CO_2.

Pollution from Coal Burning

In the United States and most of the world, most of the coal consumed is used as a fuel to generate electricity. Burning coal produces emissions such as **sulfur dioxide** (SO_2) and **nitrogen oxides** (NO_x) that are associated with acid rain (more on this in chapter 6). **Carbon dioxide** (CO_2), another emission resulting from burning coal, is a major greenhouse gas that is associated with global warming (see Chapter 13). Burning of coal is classified as incomplete combustion, since the reaction of carbon (in coal) with oxygen produces carbon monoxide and/or carbon (soot) in addition to carbon dioxide.

Burning coal produces emissions that also impact human health. Emissions such as sulfur dioxide (SO_2), nitrogen oxides (NO_x) and particulates contribute to respiratory illnesses. Particulates also contribute to a condition among coal miners and other coal workers known as coal workers' pneumoconiosis (CWP) or black lung disease, which results from long exposure to coal dust. Inhaled coal dust progressively builds up in the lungs and is unable to be removed by the body; this leads to inflammation, fibrosis, and in worse cases, tissue death (necrosis).

Coal is the largest source of **mercury** and also a source of other **heavy metals**, many of which have been linked to both neurological and developmental problems in humans and other animals. Mercury concentrations in the air usually are low and of little direct concern. However, when mercury enters water, either directly or through deposition from the air, biological processes transform it into **methylmercury**, a highly toxic chemical that accumulates in fish and the animals (including humans) that eat fish.

Reducing the Environmental Impacts of Coal Use

Regulations such as the **Clean Air Act** and the **Clean Water Act** require industries to reduce pollutants released into the air and water. Below are some actions that have been taken to reduce the negative impacts of coal on human and environmental health:

• **Clean coal technology**: Industry has found several ways to reduce sulfur, NO_x, and other impurities from coal before burning.

• Coal consumers have shifted toward greater use of low sulfur coal.

• Power plants use **scrubbers**, to clean SO_2, NO_x, particulate matter, and mercury from the smoke before it leaves their smokestacks. In addition, industry and the U.S. government have cooperated to develop technologies that make coal more energy-efficient so less needs to be burned.

• Research is underway to address emissions of carbon dioxide from coal combustion. **Carbon capture & sequestration** separates CO_2 from emissions sources and recovers it in a concentrated stream. The CO_2 can then be sequestered, which puts CO_2 into storage, possibly underground, where it will remain permanently.

• Reuse and recycling can also reduce coal's environmental impact. Land that was previously used for coal mining can be reclaimed and used for airports, landfills, and golf courses. Waste products captured by scrubbers can be used to produce products like cement and synthetic gypsum for wallboard.

Summary

- Coal is a complex solid material derived primarily from plants that died and were buried hundreds of millions of years ago and were subsequently subjected to high temperatures and pressures.
- Coal is classified into four main types, depending on the types and amounts of carbon present and on the amount of heat energy the coal can produce, including anthracite, bituminous, subbituminous, and lignite.
- The processing of coal is described as well as the environmental and health impacts of its use.
- Research is underway and various approaches are implemented (clean coal technology, use of low sulfur coal, use of scrubbers etc.) to reduce the environmental impacts of coal use.

Contributors and Attributions

Libretext: Introduction to Environmental Science (Zendher et al.)

Libretext: General Chemistry (Petrucci et al.)

Anne Marie Helmenstine, Ph.D. "What Is a Combustion Reaction?" *ThoughtCo*, www.thoughtco.com/combustion-reactions-604030.

- Marisa Alviar-Agnew (Sacramento City College)

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5.9: Natural Gas and Petroleum

Learning Objectives

- Describe the nature and processing of natural gas, petroleum, and gasoline.
- List different alternative fuels.

Crude oil is frequently found in reservoirs along with natural gas. In the past, natural gas was either burned or allowed to escape into the atmosphere. Now, technology has been developed to capture the natural gas and either reinject it into the well or compress it into **liquid natural gas** (LNG).

Natural Gas

Natural gas is predominately composed of methane (CH_4). Some of the gases that are produced along with methane, such as butane and propane (by-products), are separated and cleaned at a gas processing plant. The by-products, once removed, are used in a number of ways. For example, propane can be used for cooking on gas grills. Natural gas withdrawn from a well may contain liquid hydrocarbons and non-hydrocarbon gases. This is called "wet" natural gas. The natural gas is separated from these components near the site of the well or at a processing plant. The gas is then considered "dry" and is sent through pipelines to a local distribution company, and, ultimately, to the consumer.

Most of the natural gas consumed in the United States is produced in the United States. Some is imported from Canada and shipped to the United States in pipelines. A small amount of natural gas is shipped to the United States as LNG.

Fracking for Gas

Conventional natural gas is found in permeable reservoirs, typically composed of sandstone or limestone, where extraction is relatively straightforward because the gas generally flows freely. Unconventional gas is found in rocks with extremely low permeability, which makes extracting it much more difficult. Such gas is extracted by employing so-called “unconventional” techniques such as hydraulic fracturing (fracking), which has been in use since the late 1940s. In recent decades, fracking technology has greatly improved, and its use has been expanded. The process of fracking for gas is very similar to that of fracking for oil, and the environmental impacts are similar also.

Petroleum

Petroleum Oil is currently the most widely used fossil fuel and accounts for about one third of global energy consumption. Unlike coal, which is primarily used as a fuel for electricity generation, oil is primarily used as a fuel for **transportation**. Oil is also used to manufacture plastics and other synthetic compounds ubiquitous to our everyday life. **Crude** (unprocessed) oil varies greatly in appearance depending on its composition. It is usually black or dark brown (although it may be yellowish, reddish, or even greenish). In the reservoir it is usually found in association with natural gas, which being lighter forms a gas cap over the oil.

Oil is made up of hydrocarbons which are molecules that contain hydrogen and carbon in various lengths and structures, from straight chains to branching chains to rings. Hydrocarbons contain a lot of energy and many of the things derived from crude oil like gasoline, diesel fuel, paraffin wax and so on take advantage of this energy.

Extraction

Oil is mainly obtained by drilling either on land (**onshore**) or in the ocean (**offshore**). Early offshore drilling was generally limited to areas where the water was less than 300 feet deep. Oil and natural gas drilling rigs now operate in water as deep as two miles. Offshore oil producers are required to take precautions to prevent pollution, spills, and significant changes to the ocean environment. Offshore rigs are designed to withstand hurricanes. Offshore production is much more expensive than land-based production. When offshore oil wells are no longer productive enough to be economical, they are sealed and abandoned according to applicable regulations.

Processing and Refining

When extracted, crude oil consists of many types of hydrocarbons as well as some unwanted substances such as sulfur, nitrogen, oxygen, dissolved metals, and water all mixed together. Unprocessed crude oil is therefore, not generally useful in industrial applications and must first be separated into different useable products at a **refinery** (Figure 5.9.1). All refineries perform three basic steps: separation, conversion, and treatment in the processing and refining of crude oil.



Figure 5.9.1 *Tesoro Corporation Oil Refinery in Anacortes, Washington. Photo by Walter Siegmund.* commons.wikimedia.org/wiki/O...nery_31904.JPG

During **separation**, the various products (hydrocarbons) are separated in to different components (called *fractions*), by taking advantage of the differences in boiling temperature of the components. This process is called *fractional distillation* and involves heating up the crude, letting it vaporize and then condensing the vapor. The lightest components have the lowest boiling temperature and rise to the top while the heaviest which also have the highest boiling temperature remain at the bottom.

Conversion is the chemical processing in which some of the fractions are transformed in to other products, for example, a refinery can turn diesel fuel into gasoline depending on the demand for gasoline. Conversion can involve breaking larger hydrocarbon chains into smaller ones (cracking), combining smaller chains into larger ones (unification) or rearranging the molecules to created desired products (alteration).

Treatment is done to the fractions to remove impurities such as sulfur, nitrogen and water among others. Refineries also combine the various fractions (processed and unprocessed) into mixtures to make desired products. For example, different mixtures of hydrocarbon chains can create gasolines with different octane ratings, with and without additives, lubricating oils of various weights and grades (e.g., WD-40, 10W-40, 5W-30, etc.), heating oil and many others. The products are stored on-site until they can be delivered to various markets such as gas stations, airports and chemical plants.

A 42 U.S. gallon barrel of crude oil yields about 45 gallons of petroleum products because of refinery processing gain. This increase in volume is similar to what happens to popcorn when it is popped. Gasoline makes up the largest fraction of all petroleum products obtained (Figure 5.9.2). Other products include diesel fuel and heating oil, jet fuel, petrochemical feedstocks, waxes, lubricating oils, and asphalt.

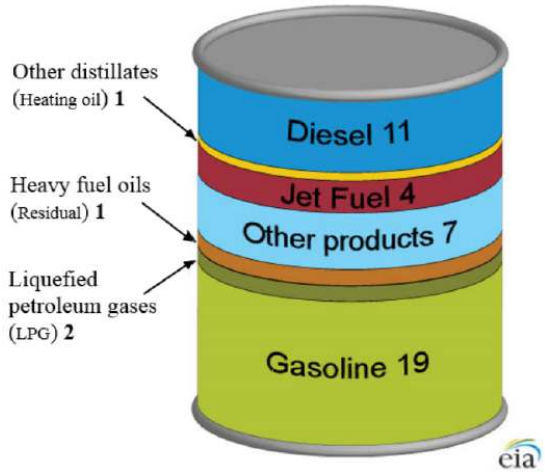


Figure **5.9.2** Main products (measured in gallons) made from a barrel of crude oil, 2013. Source: U.S. Energy information administration http://www.eia.gov/energyexplained/i...?page=oil_home

Fracking for oil

Hydraulic fracturing, informally referred to as "fracking," is an oil well development process that typically involves injecting water, sand, and chemicals under high pressure into a bedrock formation via the well. This process is intended to create new fractures in the rock as well as increase the size, extent, and connectivity of existing fractures. Hydraulic fracturing is a well-stimulation technique used commonly in low-permeability rocks like tight sandstone, shale, and some coal beds to increase oil flow to a well from petroleum-bearing rock formations.

There are concerns regarding the potential contamination of fresh groundwater resources from oil and gas extraction wells that use hydraulic fracturing; either from the petroleum resource being produced or from the chemicals introduced in the fracturing process. Fracking fluid flowback – the fluid pumped out of the well and separated from oil and gas – not only contains the chemical additives used in the drilling process but also contains heavy metals, radioactive materials, **volatile organic compounds** (VOCs) and hazardous air pollutants such as benzene, toluene, ethylbenzene and xylene. In some cases, this contaminated water is sent to water treatment plants that are not equipped to deal with some of these classes of contamination.

Gasoline

Petroleum is converted to useful products such as gasoline in three steps: distillation, cracking, and reforming. Part (a) in Figure \(\PageIndex{3}\) shows a cutaway drawing of a column used in the petroleum industry for separating the components of crude oil. The petroleum is heated to approximately 400°C (750°F), at which temperature it has become a mixture of liquid and vapor. This mixture, called the feedstock, is introduced into the refining tower. The most volatile components (those with the lowest boiling points) condense at the top of the column where it is cooler, while the less volatile components condense nearer the bottom. Some materials are so nonvolatile that they collect at the bottom without evaporating at all. Thus the composition of the liquid condensing at each level is different. These different fractions, each of which usually consists of a mixture of compounds with similar numbers of carbon atoms, are drawn off separately. Part (b) Figure \(\PageIndex{3}\) shows the typical fractions collected at refineries, the number of carbon atoms they contain, their boiling points, and their ultimate uses. These products range from gases used in natural and bottled gas to liquids used in fuels and lubricants to gummy solids used as tar on roads and roofs.

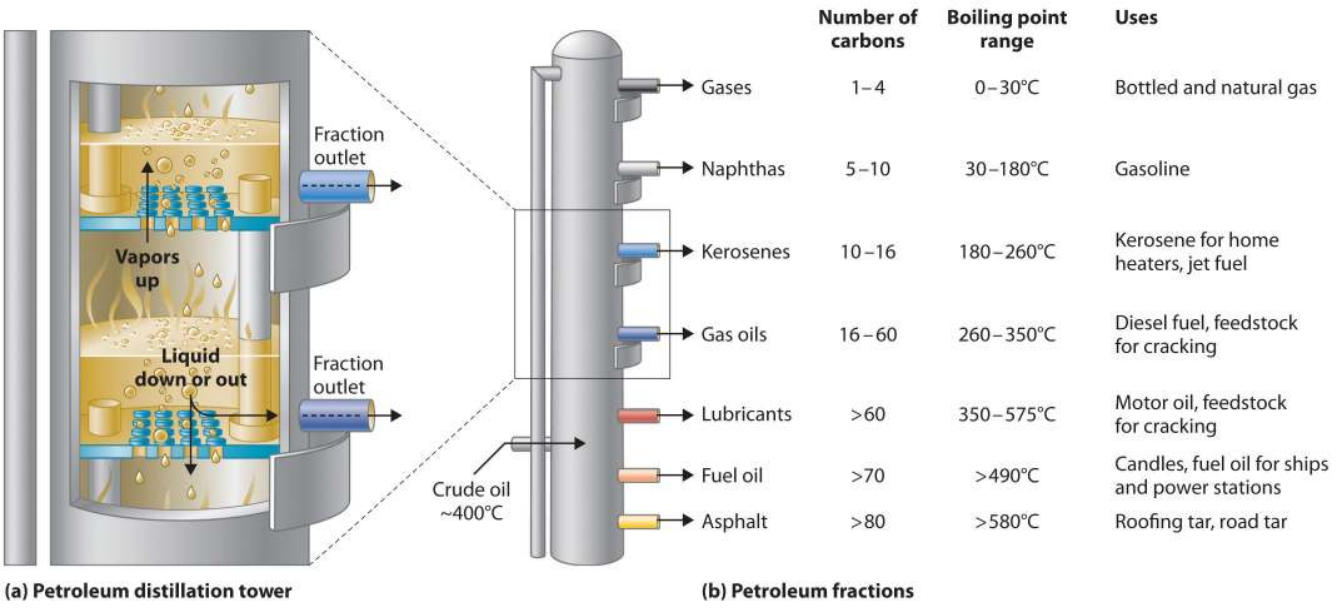


***Figure* 5.9.3** *The Distillation of Petroleum. (a) This is a diagram of a distillation column used for separating petroleum fractions. (b) Petroleum fractions condense at different temperatures, depending on the number of carbon atoms in the molecules, and are drawn off from the column. The most volatile components (those with the lowest boiling points) condense at the top of the column, and the least volatile (those with the highest boiling points) condense at the bottom.*

Octane Ratings of Gasolines

The quality of a fuel is indicated by its octane rating, which is a measure of its ability to burn in a combustion engine without knocking or pinging. Knocking and pinging signal premature combustion (Figure **5.9.4**) which can be caused either by an engine malfunction or by a fuel that burns too fast. In either case, the gasoline-air mixture detonates at the wrong point in the engine cycle, which reduces the power output and can damage valves, pistons, bearings, and other engine components. The various gasoline formulations are designed to provide the mix of hydrocarbons least likely to cause knocking or pinging in a given type of engine performing at a particular level.

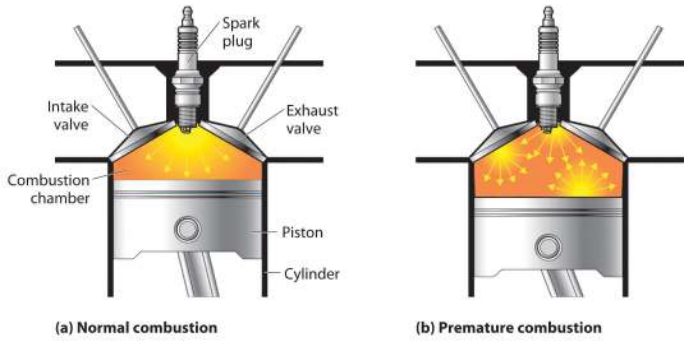


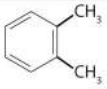
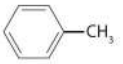
Figure **5.9.4** *The Burning of Gasoline in an Internal Combustion Engine. (a) Normally, fuel is ignited by the spark plug, and combustion spreads uniformly outward. (b) Gasoline with an octane rating that is too low for the engine can ignite prematurely, resulting in uneven burning that causes knocking and pinging.*

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

$$0.89(100) + 0.11(0) = 89 \tag{3.8.1}$$

As given in Table \(\PageIndex{1}\, many compounds that are now available have octane ratings greater than 100, which means they are better fuels than pure isooctane. In addition, antiknock agents, also called octane enhancers, have been developed. One of the most widely used for many years was tetraethyllead [$(C_2H_5)_4Pb$], which at approximately 3 g/gal gives a 10–15-point increase in octane rating. Since 1975, however, lead compounds have been phased out as gasoline additives because they are highly toxic. Other enhancers, such as methyl t-butyl ether (MTBE), have been developed to take their place. They combine a high octane rating with minimal corrosion to engine and fuel system parts. Unfortunately, when gasoline containing MTBE leaks from underground storage tanks, the result has been contamination of the groundwater in some locations, resulting in limitations or outright bans on the use of MTBE in certain areas. As a result, the use of alternative octane enhancers such as ethanol, which can be obtained from renewable resources such as corn, sugar cane, and, eventually, corn stalks and grasses, is increasing.

***Table* 5.9.1** *The Octane Ratings of Some Hydrocarbons and Common Additives.*

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

Alternative Fuels

Alternative means to power vehicles is a hot topic in environmental chemistry. Hybrid vehicles, ethanol, biodiesel (Figure **5.9.5**), natural gas, and hydrogen fuel cells are all options for powering vehicles that reduce the environmental impact of greenhouse gases in the environment. The main concern for these alternative fuels is their efficiency vs. cost when compared to fossil fuels. Table **5.9.2** shows the chemical structure for several fuels, as well as the energy content of each.



Figure **5.9.5***Biofuel station (SECO)*

https://chem.libretexts.org/@go/page/440286

Table 5.9.2 Energy Content of Fuels*.

	Gasoline	No. 2 Diesel	Biodiesel	Ethanol	Hydrogen	Liquefied Natural Gas (LNG)	Liquefied Petroleum Gas
Chemical Structure	C4 to C12	C8 to C25	Methyl esters of C12 to C22 fatty acids	CH_3CH_2OH	H_2	CH_4	C_3H_8 (majority) and C4H10 (minority)
Energy Content (Higher Heat Value)	124,340 Btu/gal (g)	137,380 Btu/gal (g)	127,960 Btu/gal for B100 (g)	84,530 Btu/gal for E100 (g)	61,013 Btu/lb (g)	84,820 Btu/gal (g)	91,410 Btu/gal (g
Energy Contained in Various Alternative Fuels as Compared to One Gallon of Gasoline	100%	113%	103%	77%	100%	64%	73%

*Table created at: http://www.afdc.energy.gov/afdc/fuels/properties.html

Ethanol

Ethanol can be used in varying percent grades by vehicles. Gasohol is 10% ethanol, produces less carbon emissions than typical gasoline, but decreases the miles per gallon (MPG) of the vehicle slightly. E85 is up to 85% ethanol, can be less expensive depending upon where you live, but lowers the MPG up to 30% compared to typical gasoline. Let's look at the bond enthalpy change for the burning of fossil fuels vs. the burning of E85 to understand the drop in MPG.

Summary

- The extraction and processing of natural gas (mainly methane) and petroleum oil were discussed.
- Petroleum is converted to useful products such as gasoline by distillation, cracking, and reforming.
- Alternative means to power vehicles and reduce the effect of greenhouse gases in the environment include hybrid vehicles, ethanol, biodiesel , natural gas, and hydrogen fuel cells.

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- US Department of Energy. Alternative Fuels. Retrieved 6/13/2012 from: http://www.fueleconomy.gov/feg/current.shtml
- US Department of Energy. Alternative and Advanced Fuels. Retrieved 6/13/2012 from: http://www.afdc.energy.gov/afdc/fuels/properties.html
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5.10: Nuclear Energy

Learning Objective

- List the benefits and problems with nuclear energy.

Nuclear power is the use of nuclear reactions that release nuclear energy to generate heat, which most frequently is then used in steam turbines to produce electricity in a nuclear power plant. Nuclear power can be obtained from nuclear fission, nuclear decay and nuclear fusion reactions. Presently, the vast majority of electricity from nuclear power is produced by nuclear fission of uranium and plutonium. Nuclear decay processes are used in niche applications such as radioisotope thermoelectric generators. Generating electricity from fusion power remains at the focus of international research.

Civilian nuclear power supplied 2,563 terawatt hours (TWh) of electricity in 2018, equivalent to about 10% of global electricity generation, and was the second largest low-carbon power source after hydroelectricity. As of December 2019, there are 443 civilian fission reactors in the world, with a combined electrical capacity of 395 gigawatt (GW). There are also 56 nuclear power reactors under construction and 109 reactors planned, with a combined capacity of 60 GW and 120 GW, respectively. The United States has the largest fleet of nuclear reactors, generating over 800 TWh zero-emissions electricity per year with an average capacity factor of 92%. Most reactors under construction are generation III reactors in Asia.

Nuclear power has one of the lowest levels of fatalities per unit of energy generated compared to other energy sources. Coal, petroleum, natural gas and hydroelectricity each have caused more fatalities per unit of energy due to air pollution and accidents. [10] Since its commercialization in the 1970s, nuclear power has prevented about 1.84 million air pollution-related deaths and the emission of about 64 billion tonnes of carbon dioxide equivalent that would have otherwise resulted from the burning of fossil fuels.

There is a debate about nuclear power. Proponents, such as the World Nuclear Association and Environmentalists for Nuclear Energy, contend that nuclear power is safe and it reduces carbon emissions. Nuclear power opponents, such as Greenpeace and NIRS, contend that nuclear power poses many threats to people and the environment.

There are over thirty countries that use nuclear power to generate electricity (see Table **5.10.1**. There were about 450 nuclear power reactors worldwide, producing close to 400,000 MW (MegaWatts) of electrical capacity. Commercial nuclear reactors can be found in North and South America, Europe, Africa, and Asia. The United States has the most reactors of any other countries. There are around ninety-eight reactors in the United States that provide around twenty percent of the electrical energy in the United States. Other countries, like France, employ around sixty nuclear reactors to produce 70% of their electrical power.

Table **5.10.1**: Nuclear Share of Electricity Generation and Number of Operated Reactors in 2019. Source: International Atomic Energy Agency (IAEA)

Country	Number of Operated Reactors	Total Net Electrical Capacity [MW]	Nuclear Electricity Supplied [GW.h]	Nuclear Share [%]
UNITED STATES OF AMERICA	98	99648	809358.57	19.7
UNITED KINGDOM	15	8923	51032.09	15.6
UKRAINE	15	13107	78144.26	53.9
SWITZERLAND	5	3333	25369.65	23.9
SWEDEN	8	8592	64428.86	34.0
SPAIN	7	7121	55856.07	21.4
SOUTH AFRICA	2	1860	13602.57	6.7
SLOVENIA	1	688	5532.98	37.0
SLOVAKIA	4	1814	14282.25	53.9
RUSSIA	39	28448	195535.15	19.7
ROMANIA	2	1300	10368.21	18.5
PAKISTAN	5	1318	9065.80	6.6
NETHERLANDS	1	482	3700.71	3.2
MEXICO	2	1552	10880.73	4.5
KOREA, REPUBLIC OF	25	23833	138809.35	26.2
JAPAN	38	36476	65681.92	7.5
IRAN, ISLAMIC REPUBLIC OF	1	915	5865.73	1.8
INDIA	22	6255	40740.49	3.2
HUNGARY	4	1902	15414.83	49.2
FRANCE	58	63130	382402.75	70.6
FINLAND	4	2794	22914.88	34.7
CZECH REPUBLIC	6	3932	28581.12	35.2
CHINA	48	45518	330122.19	4.9
CANADA	19	13554	94853.85	14.9
BULGARIA	2	2006	15868.88	37.5
BRAZIL	2	1884	15224.11	2.7
BELGIUM	7	5930	41421.66	47.6
ARMENIA	1	375	2028.96	27.8
ARGENTINA	3	1641	7926.96	5.9
Total	449	392779	2586163.02	N

Nuclear Power Plants

After fabrication, fuel assemblies are transported to nuclear power plants where they are used as a source of energy for generating electricity. They are stored onsite until they are needed by the reactor operators. At this stage, the uranium is only mildly radioactive, and essentially all radiation is contained within the metal tubes. When needed, the fuel is loaded into a reactor core (Figure 5.10.2). Typically, about one third of the reactor core (40 to 90 fuel assemblies) is changed out every 12 to 24 months.

The most common type of reactors are the **pressurized water reactors** (PWR) (Figure 5.10.2) in which water is pumped through the reactor core and heated by the fission process. The water is kept under high pressure inside the reactor so it does not boil. The heated water from the reactor passes through tubes inside the steam generator where the heat is transferred to water flowing around the tubes in the steam generator. The water in the steam generator boils and turns to steam. The steam is piped to the turbines. The force of the expanding steam drives the turbines, which spin a magnet in coil of wire – the generator– to produce electricity.

After passing through the turbines, the steam is converted back to water by circulating it around tubes carrying cooling water in the condenser. The condensed steam – now water – is returned to the steam generators to repeat the cycle.

The three water systems (condenser, steam generator, and reactor) are separate from each other and are not permitted to mix. Water in the reactor is radioactive and is contained within the containment structure whereas water in the steam generator and condenser is nonradioactive.

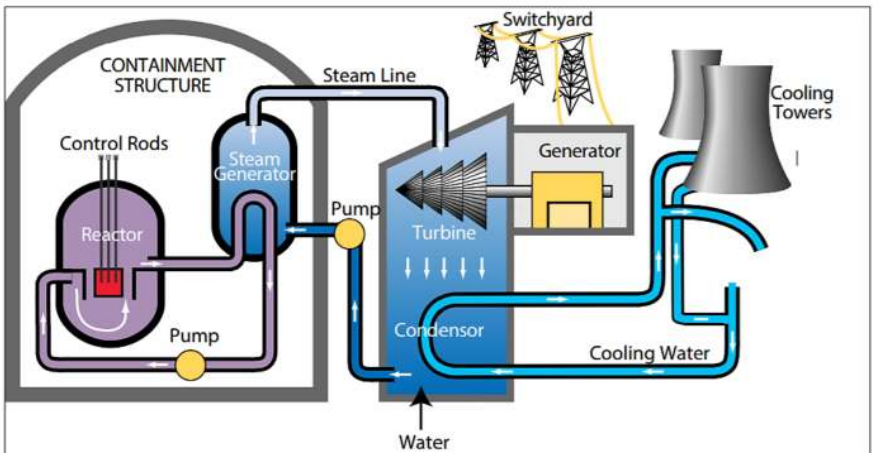


Figure 5.10.1: A schematic diagram of a pressurized water reactor (PWR), the most common type of nuclear reactor. (Public Domain; Tennessee Valley Authority)

The Nuclear Advantage: Minimal Air Pollution

By using fission, nuclear power plants generate electricity without emitting air pollutants like those emitted by fossil fuel-fired power plants. This means that financial costs related to chronic health problems caused by air pollutants such as particulate material, carbon monoxide, nitrogen oxides and ozone among others are significantly reduced. In addition nuclear reactors do not produce carbon dioxide while operating which means that nuclear energy does not contribute to the global warming problem.

Another benefit of nuclear energy over fossil fuels especially coal is that uranium generates far more power per unit weight or volume. This means that less of it needs to be mined and consequently the damage to the landscapes is less especially when compared to the damage that results from coal mining such as mountaintop removal.

Problems with Nuclear Power

The main environmental concern related to nuclear power is the creation of radioactive wastes such as uranium mill tailings, spent (used) reactor fuel, and other radioactive wastes. These materials can remain radioactive and dangerous to human health for thousands of years. Radioactive wastes are classified as low-level and high-level. By volume, most of the waste related to the nuclear power industry has a relatively low-level of radioactivity. Uranium mill tailings contain the radioactive element radium, which decays to produce **radon**, a radioactive gas. Most uranium mill tailings are placed near the processing facility or mill where they come from. Uranium mill tailings are covered with a barrier of material such as clay to prevent radon from escaping into the atmosphere, and they are then covered by a layer of soil, rocks, or other materials to prevent erosion of the sealing barrier.

The other types of low-level radioactive waste are the tools, protective clothing, wiping cloths, and other disposable items that get contaminated with small amounts of radioactive dust or particles at nuclear fuel processing facilities and power plants. These materials are subject to special regulations that govern their handling, storage, and disposal so they will not come in contact with the outside environment.

High-level radioactive waste consists of spent nuclear reactor fuel (i.e., fuel that is no longer useful for producing electricity). The spent reactor fuel is in a solid form consisting of small fuel pellets in long metal tubes called rods. Spent reactor fuel assemblies are initially stored in specially designed pools of water, where the water cools the fuel and acts as a radiation shield. Spent reactor fuel assemblies can also be stored in specially designed dry storage containers. An increasing number of reactor operators now store their older spent fuel in dry storage facilities using special outdoor concrete or steel containers with air cooling. There is currently no permanent disposal facility in the United States for high-level nuclear waste.

When a nuclear reactor stops operating, it must be **decommissioned**. This involves safely removing the reactor and all equipment that has become radioactive from service and reducing radioactivity to a level that permits other uses of the property. The U.S. Nuclear Regulatory Commission has strict rules governing nuclear power plant decommissioning that involve cleanup of radioactively contaminated plant systems and structures, and removal of the radioactive fuel.

The processes for mining and refining uranium ore and making reactor fuel require large amounts of energy. Nuclear power plants have large amounts of metal and concrete, which also require large amounts of energy to manufacture. If fossil fuels are used for mining and refining uranium ore or in constructing the nuclear plant, then the emissions from burning those fuels could be associated with the electricity that nuclear power plants generate.

Nuclear Accidents

A **nuclear meltdown**, or uncontrolled nuclear reaction in a nuclear reactor, can potentially result in widespread contamination of air and water. Some serious nuclear and radiation accidents have occurred worldwide. The most severe accident was the Chernobyl accident of 1986 in the then Soviet Union (now Ukraine) which killed 31 people directly and sickened or caused cancer in thousands more. The Fukushima Daiichi nuclear disaster (2011) in Japan was caused by a 9.0 magnitude earthquake that shut down power supply and a tsunami that flooded the plant's emergency power supply. This resulted in the release of radioactivity although it did not directly result in any deaths at the time of the disaster. Another nuclear accident was the Three Mile Island accident (1979) in Pennsylvania, USA. This accident resulted in a near disastrous core meltdown that was due to a combination of human error and mechanical failure but did not result in any deaths and no cancers or otherwise have been found in follow up studies of this accident. While there are potentially devastating consequences to a nuclear meltdown, the likelihood of one occurring is extremely small. After every meltdown, including the 2011 Fukushima Daiichi disaster, new international regulations were put in place to prevent such an event from occurring again.

Breeder Reactors: Making More Fuel Than They Burn

Because $^{235}_{92}\mathrm{U}$ is only 0.7 percent of naturally occurring uranium, its supply is fairly limited and could well only last for about 50 years of full-scale use. The other 99 percent of the uranium can also be utilized if it is first converted into plutonium by neutron bombardment:

$$^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{239}_{94}\mathrm{Pu} + 2\,{}^{0}_{-1}\mathrm{e}$$

$^{239}_{94}\mathrm{Pu}$ is also fissionable, and so it could be used in a nuclear reactor as well as $^{235}_{92}\mathrm{U}$.

The production of plutonium can be carried out in a breeder reactor which not only produces energy like other reactors but is designed to allow some of the fast neutrons to bombard the $^{235}_{92}\mathrm{U}$, producing plutonium at the same time. More fuel is then produced than is consumed.

Breeder reactors present additional safety hazards to those already outlined. They operate at higher temperatures and use very reactive liquid metals such as sodium in their cooling systems, and so the possibility of a serious accident is higher. In addition the large quantities of plutonium which would be produced in a breeder economy would have to be carefully safeguarded. Plutonium is an α emitter and is very dangerous if taken internally. Its half-life is 24,000 years, and so it will remain in the environment for a long time if dispersed. Moreover, $^{239}_{94}\mathrm{Pu}$ can be separated chemically (not by the much more expensive gaseous diffusion used to

concentrate $^{235}_{92}\text{U}$ from fission products and used to make bombs. Such a material will obviously be attractive to terrorist groups, as well as to countries which are not currently capable of producing their own atomic weapons.

Today many nations are considering an expanded role for nuclear power in their energy portfolios. This expansion is driven by concerns about global warming, growth in energy demand, and relative costs of alternative energy sources. In 2008, 435 nuclear reactors in 30 countries provided 16% of the world's electricity. In January 2009, 43 reactors were under construction in 11 countries, with several hundred more projected to come on line globally by 2030.

Nuclear Fusion

The most important fusion process in nature is the one that powers stars. The fusion of hydrogen and helium, which is the primary energy producer in the sun has been discussed in Chapter 11. This section briefly discusses harnessing energy from nuclear fusion to generate electricity.

The fusion reaction of great interest is known as deuterium–tritium fusion (D–T fusion) wherein a deuterium atom and a tritium atom fuse to produce helium-4 (Figure **5.10.3**).

$$^{2}_{1}\text{H} + {}^{3}_{1}\text{H} \rightarrow {}^{4}_{2}\text{He} + {}^{1}_{0}\text{n} \tag{21.6.13}$$

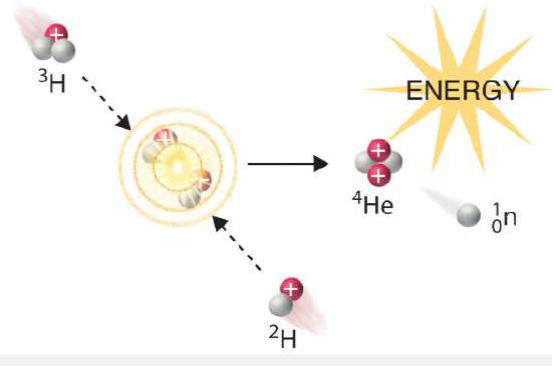


Figure **5.10.2**: Nuclear fusion. The fusion of ^{3}H and ^{2}H produces ^{4}He and a neutron and releases an enormous amount of energy.

Fusion power has the potential to provide sufficient energy to satisfy mounting demand, and to do so sustainably, with a relatively small impact on the environment. Nuclear fusion has many potential attractions. Firstly, its hydrogen isotope fuels are relatively abundant – one of the necessary isotopes, deuterium, can be extracted from seawater, while the other fuel, tritium, would be bred from a lithium blanket using neutrons produced in the fusion reaction itself. Furthermore, a fusion reactor would produce virtually no CO_2 or atmospheric pollutants, and its radioactive waste products would mostly be very short-lived compared to those produced by conventional nuclear reactors (fission reactors).

Useful fusion reactions require very high temperatures for their initiation—about 15,000,000 K or more. At these temperatures, all molecules dissociate into atoms, and the atoms ionize, forming plasma. These conditions occur in an extremely large number of locations throughout the universe—stars are powered by fusion. Humans have already figured out how to create temperatures high enough to achieve fusion on a large scale in thermonuclear weapons. A thermonuclear weapon such as a hydrogen bomb contains a nuclear fission bomb that, when exploded, gives off enough energy to produce the extremely high temperatures necessary for fusion to occur.

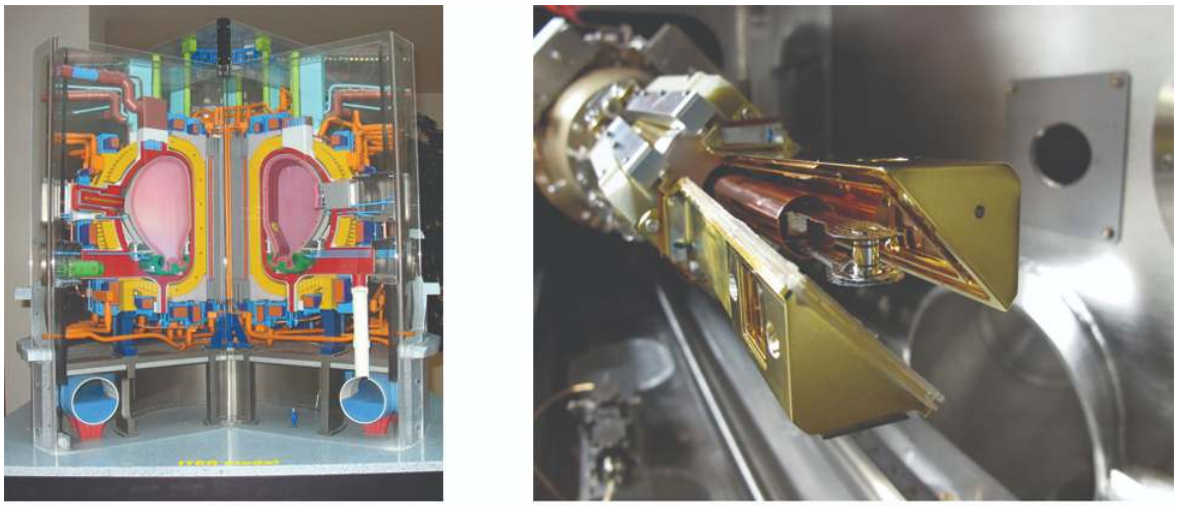


Figure 5.10.3: (a) This model is of the International Thermonuclear Experimental Reactor (ITER) reactor. Currently under construction in the south of France with an expected completion date of 2027, the ITER will be the world's largest experimental Tokamak nuclear fusion reactor with a goal of achieving large-scale sustained energy production. (b) In 2012, the National Ignition Facility at Lawrence Livermore National Laboratory briefly produced over 500,000,000,000 watts (500 terawatts, or 500 TW) of peak power and delivered 1,850,000 joules (1.85 MJ) of energy, the largest laser energy ever produced and 1000 times the power usage of the entire United States in any given moment. Although lasting only a few billionths of a second, the 192 lasers attained the conditions needed for nuclear fusion ignition. This image shows the target prior to the laser shot. (credit a: modification of work by Stephan Mosel)

Another much more beneficial way to create fusion reactions is in a fusion reactor, a nuclear reactor in which fusion reactions of light nuclei are controlled. Because no solid materials are stable at such high temperatures, mechanical devices cannot contain the plasma in which fusion reactions occur. Two techniques to contain plasma at the density and temperature necessary for a fusion reaction are currently the focus of intensive research efforts: containment by a magnetic field and by the use of focused laser beams (Figure 5.10.3). A number of large projects are working to attain one of the biggest goals in science: getting hydrogen fuel to ignite and produce more energy than the amount supplied to achieve the extremely high temperatures and pressures that are required for fusion. The US Department of Energy is funding several sites conducting fusion research as given on the link https://www.usiter.org/fusion/us-fusion-research-sites. One of the research sites is features in the video below Video 5.10.1.



Video 5.10.1: The D-III National Fusion Facility, San Diego California.

Summary

- There is still ongoing debate about nuclear power.
- Proponents, such as the World Nuclear Association and Environmentalists for Nuclear Energy, contend that nuclear power is a safe, energy source that reduces carbon emissions.

- Nuclear power opponents, such as Greenpeace and NIRS, contend that nuclear power poses many threats to people and the environment.
- There are over thirty countries that use nuclear power to generate electricity.

Contributor

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- Libretext: Chemistry of Global Awareness (Gordon)
- Marisa Alviar-Agnew (Sacramento City College)

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5.11: Renewable Energy Sources

Learning Objectives

- Describe the different renewable energy sources.
- List any impacts it may have on the environment.

Energy sources that are more or less continuously made available in a time frame useful to people are called **renewable energy.** Renewable energy sources are often considered alternative sources because, in general, most industrialized countries do not rely on them as their main energy source. Instead, they tend to rely on the conventional energy sources such as fossil fuels or nuclear power that are non-renewable. Because of the energy crisis in the United States during the 1970s, dwindling supplies of fossil fuels and hazards associated with nuclear power, use of renewable energy sources such as solar energy, hydroelectric, wind, biomass, and geothermal has grown. Renewable energy comes from the sun (considered an "unlimited" supply) or other sources that can theoretically be renewed at least as quickly as they are consumed. If used at a sustainable rate, these sources will be available for consumption for thousands of years or longer. Renewable alternatives derive from wind, water, solar or biomass (Figure 5.11.1). Note that wind, water and biomass energy sources are indirect sources of solar energy. One limitation currently associated with most forms of renewable energy is that the energy is not concentrated and not easily portable.



Figure 5.11.1 A variety of voltage sources (clockwise from top left): the Brazos Wind Farm in Fluvanna, Texas (credit: Leaflet, Wikimedia Commons); the Krasnoyarsk Dam in Russia (credit: Alex Polezhaev); a solar farm (credit: U.S. Department of Energy); and a group of nickel metal hydride batteries (credit: Tiaa Monto). The voltage output of each depends on its construction and load, and equals emf only if there is no load.

Energy is an important ingredient in all phases of society. We live in a very interdependent world, and access to adequate and reliable energy resources is crucial for economic growth and for maintaining the quality of our lives. The principal energy resources used in the world are shown in Figure 5.11.2. With the rapid growth of electricity generation, renewables—including solar, wind, and hydroelectric power—are the fastest-growing energy source between 2018 and 2050, surpassing petroleum and other liquids to become the most used energy source in the Reference case. Worldwide renewable energy consumption increases by 3.1% per year between 2018 and 2050, compared with 0.6% annual growth in petroleum and other liquids, 0.4% growth in coal, and 1.1% annual growth in natural gas consumption.

Global natural gas consumption increases more than 40% between 2018 and 2050, and total consumption reaches nearly 200 quadrillion Btu by 2050. In addition to the natural gas used in electricity generation, natural gas consumption increases in the industrial sector. Chemical and primary metals manufacturing, as well as oil and natural gas extraction, account for most of the growing industrial demand.

Global liquid fuels consumption increases more than 20% between 2018 and 2050, and total consumption reaches more than 240 quadrillion Btu in 2050. Demand in OECD (Organisation for Economic Cooperation and Development) countries remains relatively stable during the projection period, but non-OECD demand increases by about 45%.

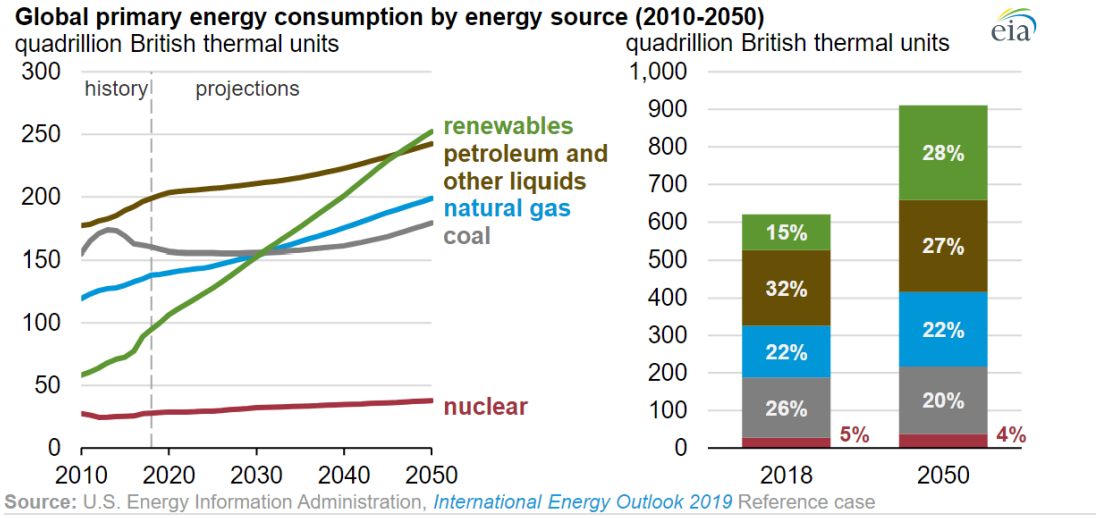


Figure 5.11.2: Global primary energy consumption by energy source (2010-2050)

Why Use Renewable Energy Sources?

Majority of renewable energy sources including solar, wind, water, and biomass can be directly or indirectly attributed to the sun. The fact that the sun will continue burning for another 4-5 billion years makes it inexhaustible as an energy source for human civilization. With appropriate technology, renewable energy sources allow for local, decentralized control over power. Homes, businesses, and isolated communities can use sources such as solar to produce electricity without being near a power plant or being connected to a grid. This eliminates problems such as spills associated with extraction and transportation of fossil fuels that is needed in order to supply these fossil fuels to those areas that are lacking. Most renewable energy sources do not pollute the air with greenhouse gas emissions and other air pollutants associated with fossil fuels. This is especially important in combating climate change.

Solar Energy

Solar energy is the ultimate energy source driving life on earth and many human activities. Though only one billionth of the energy that leaves the sun (Figure 5.11.3) actually reaches the earth's surface, this is more than enough to meet the world's energy requirement. In fact, all other sources of energy, renewable and non-renewable, are actually stored forms of solar energy. The process of directly converting solar energy to heat or electricity is considered a renewable energy source. Solar energy represents an essentially unlimited supply of energy as the sun will long outlast human civilization on earth. The difficulties lie in harnessing the energy. Solar energy has been used for centuries to heat homes and water, and modern technology (photovoltaic cells) has provided a way to produce electricity from sunlight. There are two basic forms of solar energy collectors are passive and active.

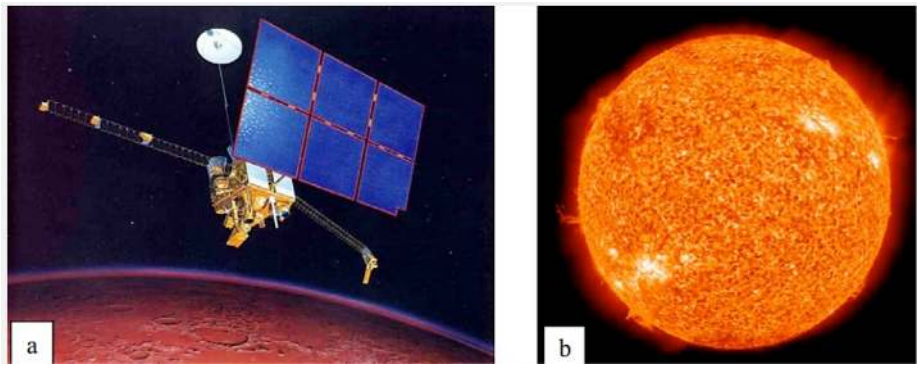


Figure 5.11.3: a) Mars Observer in Mars Orbit showing the solar panel. (Picture: Wikimedia Commons www.jpl.nasa.gov/images/space...t1-browse.jpg,). b) The Sun photographed at 304 angstroms by the Atmospheric Imaging Assembly (AIA 304) of NASA's Solar Dynamics Observatory (SDO). This is a false-color image of the Sun observed in the extreme ultraviolet region of the spectrum. sdo.gsfc.nasa.gov/assets/img/..._4096_0304.jpg, NASA/SDO (AIA)

Solar photovoltaic (PV) devices, or solar cells, change sunlight directly into electricity. PV uses semiconducting materials such as silicon to produce electricity from sunlight: when light hits the cells, the material produces free electrons that migrate across the cell, creating an electric current. Small PV cells can power calculators, watches, and other small electronic devices. Arrangements of many solar cells in PV panels and arrangements of multiple PV panels in PV arrays can produce electricity for an entire house or building (Figure 5.11.4a). Some PV power plants have large arrays that cover many acres to produce electricity for thousands of homes.

Hundreds of thousands of houses and buildings around the world have PV systems on their roofs. Many multi-megawatt PV power plants have also been built. Covering 4% of the world's desert areas with photovoltaics could supply the equivalent of all of the world's electricity. The Gobi Desert alone could supply almost all of the world's total electricity demand.

Solar thermal power plants, like the one in Figure 5.11.4b use concentrating solar collector systems to collect and concentrate sunlight to produce the high temperature heat needed to generate electricity.

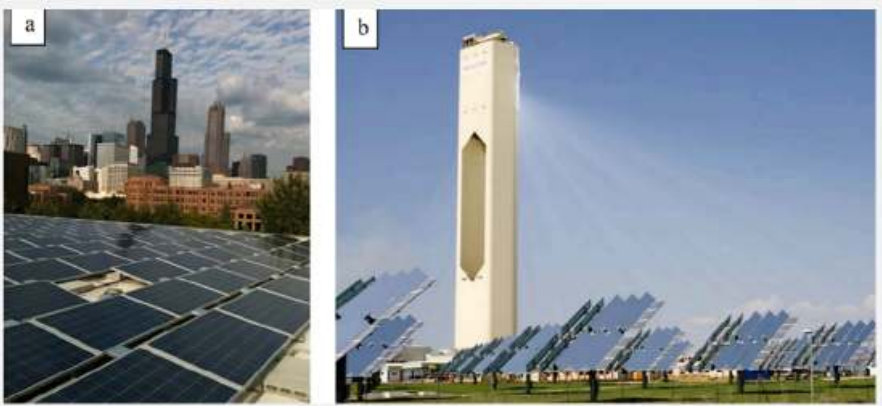


Figure 5.11.4 a) Rooftop Solar Installations on Douglas Hall at the University of Illinois at Chicago has no effect on land resources, while producing electricity with zero emissions. Source: Office of Sustainability. b) Solucar PS10 solar power tower in Andalusia, Spain, is a solar thermal power plant that generates electricity commercially. (Photo by Afloresm Solucar PS10 CC BY 2.0)

Solar power has minimal impact on the environment, depending on where it is placed. The manufacturing of photovoltaic (PV) cells generates some hazardous waste from the chemicals and solvents used in processing. Often solar arrays are placed on roofs of buildings or over parking lots or integrated into construction in other ways. However, large systems may be placed on land and particularly in deserts where those fragile ecosystems could be damaged if care is not taken. Some solar thermal systems use potentially hazardous fluids (to transfer heat) that require proper handling and disposal. Concentrated solar systems may need to be cleaned regularly with water, which is also needed for cooling the turbine-generator. Using water from underground wells may affect the ecosystem in some arid locations.

Biomass Energy

Biomass energy is from the energy stored in materials of biological origin such as plants and animals. Biomass energy is the oldest energy source used by humans. Until the Industrial Revolution prompted a shift to fossil fuels in the mid-18th century, biomass energy was the world's dominant fuel source. Currently, about 12 percent of the world's energy comes from biomass. Biomass is most frequently used as a fuel source in many developing nations, but with the decline of fossil fuel availability and the increase in fossil fuel prices, biomass is increasingly being used as a fuel source even in developed nations.

Direct combustion of solid biomass. The most common source for direct combustion is wood, but energy can also be generated by burning animal manure (dung), herbaceous plant material (non-wood), peat (partially decomposed plant and animal tissues), or converted biomass such as charcoal (wood that has been partially burned to produce a coal-like substance). Using wood and charcoal made from wood, for heating and cooking can replace fossil fuels and may result in lower CO_2 emissions. If wood is harvested from forests or woodlots that have to be thinned or from urban trees that fall down or needed be cut down anyway, then using it for biomass does not impact those ecosystems.

Biomass is also being used on a larger scale, where small power plants are powered by biomass such as woodchips (Figure 5.11.5). For instance, Central State Hospital, Milledgeville, GA has a woodchip burning plant that was the most advanced system available for its time and operating today. Colgate University in Hamilton, New York, has had a wood-burning boiler since the mid-1980's

that processes about 20,000 tons of locally and sustainably harvested wood chips, the equivalent of 1.17 million gallons (4.43 million liters) of fuel oil, avoiding 13,757 tons of emissions, and saving the university over $1.8 million in heating costs. The University's steam-generating wood-burning facility now satisfies more than 75 percent of the campus's heat and domestic hot water needs. For more information about this, click here Colgate University.



Figure 5.11.5 A biomass (woodchip) power plant in Germany. Image from Wikimedia Public Domain.

Gaseous Biomass. Organic material can be converted to methane, the main component of natural gas, by anaerobic decomposition or fermentation, a process that utilizes anaerobic bacteria. Methane is a relatively clean fuel that burns efficiently. It can be generated from any kind of organic waste such as municipal sewage and garbage, livestock manure, kitchen, and garden scraps. In fact, municipal landfills are active sites of methane production contributing annually to methane in the atmosphere and to global warming. This gas can and is currently being captured by numerous landfills around the United States that burn it to generate electricity at power plants or supply it to homes for heating.

Liquid Biofuels. Biofuels are transportation fuels produced from plant sources and used to power vehicles. The most common ones are ethanol and biodiesel.

- **Ethanol**, also known as ethyl alcohol or grain alcohol, is produced by fermenting crops such as corn, sugarcane, and other crops and then mixed with conventional gasoline. As an additive, ethanol lowers reliance on conventional oil and increases the combustion efficiency of gasoline, reducing pollutant emissions.
- **Biodiesel** which is essentially vegetable oil, can also be derived from a wide range of plant sources, including rapeseed, sunflowers, and soybeans, and can be used in most conventional diesel engines. Biodiesel can also be made from used vegetable oil and has been produced on a very local basis. Because it burns more cleanly than its petroleum-based counterpart, biodiesel can reduce pollution from heavy-duty vehicles such as trucks and buses. Compared to petroleum diesel, biodiesel combustion produces less sulfur oxides, particulate matter, carbon monoxide, and unburned and other hydrocarbons, but more nitrogen oxide.

Environmental Impacts of Biomass Energy

A major challenge of biomass is determining if it is really a more sustainable option. The energy content of some biomass energy sources may not be as high as fossil fuels so more must be burned to generate the same energy. It often takes energy to make energy and biomass is one example where the processing to make it may not be offset by the energy it produces. If traditional monoculture crops like corn or soybeans are used, they require major quantities of fossil fuel to manufacture fertilizer, run farm machines, and ship the fuel to markets, so these biofuels do not always offer significant net energy savings over gasoline and diesel fuel. In such instances, biofuels may not be carbon-neutral because the process of producing the biofuels results in more CO_2 added to the atmosphere than that removed by the growing crops.

Burning biomass directly (wood, manure, etc.) produces high particulate material pollution (see chapter 13 on Air Pollution), produces CO_2 and deprives the soil of nutrients it normally would have received from the decomposition of the organic matter. Each type of biomass energy source, therefore, must be evaluated for its full life-cycle impact in order to determine if it is really advancing sustainability and reducing environmental impacts.

Hydrogen: Light and Powerful

Hydrogen gas may be an important clean fuel of the future. Hydrogen is considered an energy carrier, like electricity and batteries, it carries energy that can be converted for use later. Hydrogen gas does not tend to exist freely but rather hydrogen atoms bind to other atoms and molecules becoming incorporated in everything from water to organic compounds. Therefore, to obtain hydrogen gas for fuel, energy is needed to force these substances to release their hydrogen atoms. One such procedure is known as **electrolysis** in which an electric current is passed through water to decompose the water molecule into oxygen and hydrogen (Figure 5.11.6). Hydrogen can also be produced from hydrocarbons such as natural gas and coal, fermentation of plant waste material, and using algae.

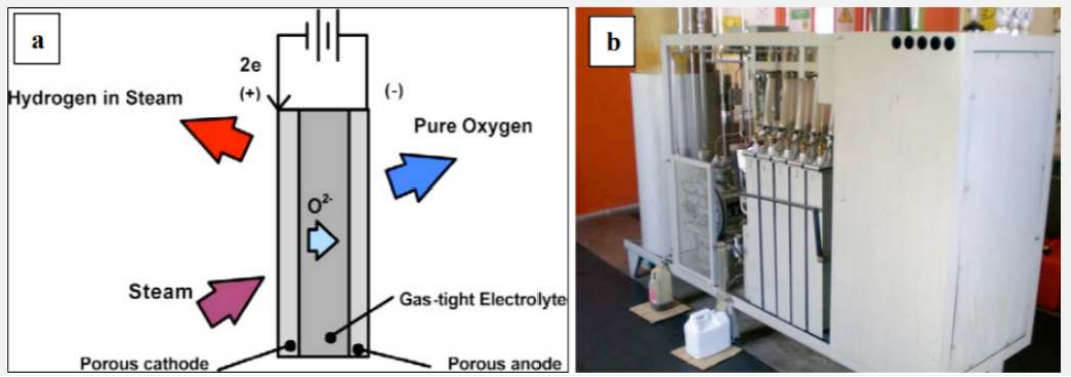


***Figure* 5.11.6** *a) An electric current passed through water resulting in the separation of hydrogen atoms from oxygen to produce the hydrogen fuel. b) An electrolyser used in the production of hydrogen by CambridgeBayWeather. After production the hydrogen is used to inflate weather balloons to which a radiosonde is attached. The oxygen produced is vented to the outside.*

Fuel cells are highly efficient power plants that produce electricity using hydrogen fuel in a chemical reaction that is a reverse of the electrolysis process that produced the hydrogen fuel (Figure 5.11.7). Energy is released by an exothermic electrochemical reaction that combines hydrogen and oxygen ions through an electrolyte material to generate electricity and heat. Experimental fuel cells that can power automobiles have been developed (Figure 5.11.2).



Figure 5.11.7 The electrochemical processes showing how hydrogen fuel is combined with oxygen generating heat energy along with water as a waste product. Some vehicles that use the fuel cell include buses (photo is a hydrogen fuel bus on Tower Bridge London, photo by Sludge G.), cars (The Toyota Fine N car based on fuel cell technology, photo by Chris 73, CC BY-SA 3.0) and motorcycles (Suzuki Burgman Fuel Cell cutaway model shown here, Photo by Mario CC BY-SA 3.0).

Challenges of Hydrogen

Currently, the infrastructure for using hydrogen fuel is lacking and converting a nation such as the United States to hydrogen would require massive and costly development of facilities to produce, store, transport, and provide the fuel. The environmental impact of hydrogen production itself depends on the source of material used to supply the hydrogen. For example, biomass and fossil fuel sources result in carbon-based emissions. Some research suggests that leakage of hydrogen from its production, transport, and use could potentially deplete stratospheric ozone. Research into this is still ongoing.

Other Renewable Sources

Wind Power

Wind is a renewable energy source that uses the power of moving air to generate electricity. Wind turbines use blades to collect the wind's kinetic energy. Wind flows over the blades creating lift (similar to the effect on airplane wings), which causes the blades to turn. The blades are connected to a drive shaft that turns an electric generator, which produces electricity (Figure **5.11.8**). Wind turbines are becoming a more prominent sight across the United States, even in regions that are considered to have less wind potential. Wind turbines (often called windmills) do not release emissions that pollute the air or water (with rare exceptions), and they do not require water for cooling. The U.S. wind industry had 40,181 MW of wind power capacity installed at the end of 2010, with 5,116 MW installed in 2010 alone, providing more than 20 % of installed wind power around the globe. According to the American Wind Energy Association, over 35 % of all new electrical generating capacity in the United States since 2006 was due to wind, surpassed only by natural gas.

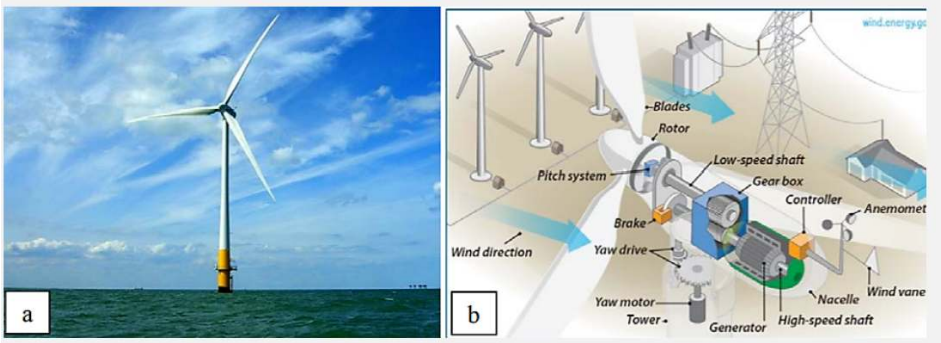


Figure **5.11.8** a) This wind turbine in the Thames Estuary in the UK is an example of induction at work, (credit: Phault, Flickr). Wind pushes the blades of the turbine, spinning a shaft attached to magnets, see image b for parts. The magnets spin around a conductive coil, inducing an electric current in the coil, and eventually feeding the electrical grid.

Most windmills generate about 1kW of electricity, which is only practical for decentralized power generation. California has about 17,000 windmills with a capacity of about 1,400 MW. This is about 80% of all windmills in the U.S. In West Europe windmill generators are quite common. Since a wind turbine has a small physical footprint relative to the amount of electricity it produces, many wind farms are located on crop, pasture, forest land, or coastal areas. They contribute to economic sustainability by providing extra income to farmers and ranchers, allowing them to stay in business and keep their property from being developed for other uses. For example, energy can be produced by installing wind turbines in the Appalachian Mountains of the United States instead of engaging in mountain top removal for coal mining.

Offshore wind turbines on lakes or the ocean may have smaller environmental impacts than turbines on land. Wind turbines do have a few environmental challenges. There are aesthetic concerns to some people when they see them on the landscape. A few wind turbines have caught on fire, and some have leaked lubricating fluids, though this is relatively rare. Some people do not like the sound that wind turbine blades make. Turbines have been found to cause bird and bat deaths particularly if they are located along their migratory path. This is of particular concern if these are threatened or endangered species. There are ways to mitigate that impact and it is currently being researched. There are some small impacts from the construction of wind projects or farms, such as the construction of service roads, the production of the turbines themselves, and the concrete for the foundations. However, overall life cycle analysis has found that turbines make much more energy than the amount used to make and install them.

Geothermal Energy

Geothermal energy uses heat from the Earth's internal geologic processes in order to produce electricity or provide heating. The subsurface temperature of the Earth provides an endless energy resource. One source of geothermal energy is steam. Groundwater percolates down through cracks in the subsurface rocks until it reaches rocks heated by underlying magma, and the heat converts the water to steam. Sometimes this steam makes its way back to the surface in the form of a geyser or hot spring. Wells can be dug to tap the steam reservoir and bring it to the surface, to drive generating turbines and produce electricity (Figure **5.11.9**a). Hot water can be circulated to heat buildings. Regions near tectonic plate boundaries have the best potential for geothermal activity.

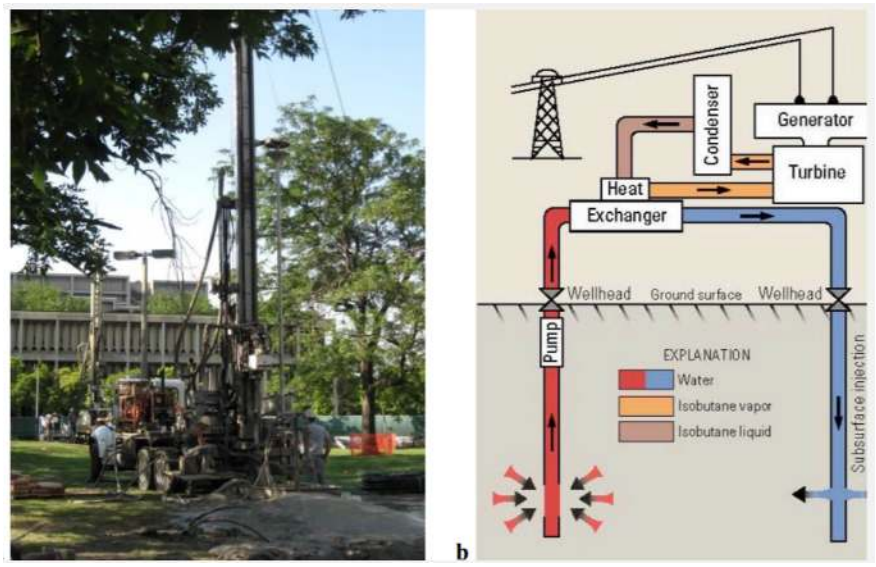


Figure **5.11.9** a) Installing a Geothermal Pipe System Drilling to install geothermal ground source pipe system. Source: Office of Sustainability. b) Electricity generation at a moderate-temperature hydrothermal system. The geothermal water is used to boil a second fluid (isobutane in this example) whose vapor then drives a turbine generator. The wastewater is injected back into the subsurface. Source: USGS.

The environmental impact of geothermal energy depends on how it is being used. Direct use and heating applications have almost no negative impact on the environment. Geothermally heated water can release dissolved gases, including carbon dioxide, methane, ammonia and hydrogen sulfide, although these are usually in very small quantities when compared to those released from fossil fuel plants. In addition, geothermal plants use scrubber systems to clean the air of hydrogen sulfide that is naturally found in the steam and hot water. They emit 97 % less acid rain-causing sulfur compounds than are emitted by fossil fuel plants.

Hydroelectric Power (Hydropower)

This is the second largest source of renewable energy used, next to biomass energy. The majority of hydropower currently comes from dams built across a river to block the flow of river water. The water stored behind the dam contains potential energy and when released, the potential energy is converted to kinetic energy as the water rushes down. This energy is used to turn blades of turbines and causing a generator to generate electricity. Electricity generated in the powerhouse of a dam is transmitted to the electric grid by transmission lines while the water flows into the riverbed below the dam and continues down river. An alternative approach considered less disruptive involves diverting a portion of the river's water through a pipe or channel and passed through a powerhouse to generate electricity and returned to the river. Another approach involves pumping water from a lower reservoir to a higher reservoir and then allowed to flow downhill through a turbine, generating electricity. This approach, however, requires energy input to pump the water. Figure **5.11.10** show a hydroelectric facility (a) and also illustrates the generation of electricity (b).

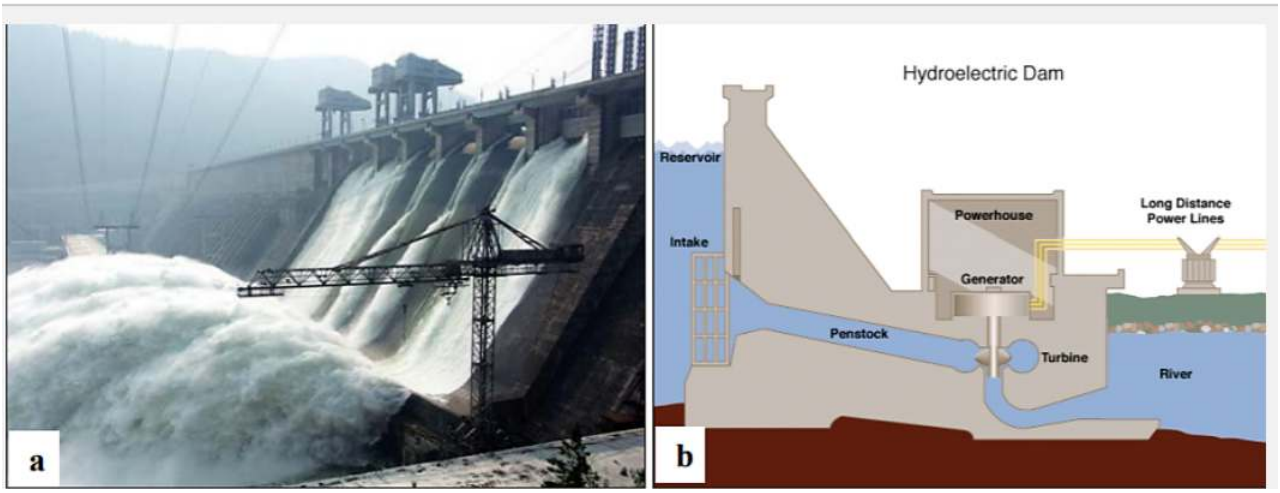


Figure **5.11.10** a) Hydroelectric facility (credit: Denis Belevich, Wikimedia Commons); b) An illustration showing how water is funneled through a portion of the dam to rotate turbines and generate electricity. (Image from Wikimedia, public domain).

Hydropower (hydro-electric) is considered a clean and renewable source of energy since it does not directly produce emissions of air pollutants and the source of power is regenerated. However, hydropower dams, reservoirs, and the operation of generators can have serious environmental impacts. A dam that is used to create a reservoir or to divert water to a run-ofriver hydropower plant can obstruct migration of fish to their upstream spawning areas in areas where salmon must travel upstream to spawn, such as along the Columbia River in Washington and Oregon. Hydro turbines kill and injure some of the fish that pass through the turbine although there are ways to reduce that effect. This problem can be partially alleviated by using 'fish ladders' that help the salmon get up the dams.

A reservoir and operation of the dam can affect the natural water habitat due to changes in water temperatures, chemistry, flow characteristics, and silt loads, all of which can lead to significant changes in the ecology and physical characteristics of the river upstream and downstream.

Potential of Tidal Power

Tidal power involves placing turbines in zones of the ocean with significant tides and currents, and using the power of flowing water to turn the blades of a turbine to generate electricity. Ocean power systems are still being researched and currently still experimental. For example, the Bay of Fundy, which has a 15 m tide, a dam constructed across the estuary would let water enter on the incoming tide, then release the water through turbines at low tide. The energy potential is great http://www.ialtenergy.com/tidal-power-news.html , and so is the environmental cost. Tapping tidal energy resources involves building major dams on inlets and estuaries that are prized for other purposes, so few tidal energy facilities have been developed. Harnessing waves and currents on a significant scale will involve designing turbine structures that are large, inexpensive, and can operate for long periods under the physical stresses and corrosive forces of ocean environments. Though proposed, a tidal power plant has not been constructed at Fundy. There is a 240,000 kW tidal plant at La Rance, France.

Summary

- Renewable sources of energy are derived from wind, water, solar or biomass.
- One limitation currently associated with most forms of renewable energy is that the energy is not concentrated and not easily portable.
- There is a projected increase from 15% (2018) to 28% of global renewable energy consumption.

Contributor

US Energy Information Administration

Libretext: Introduction to Environmental Science (Zendher et al.)

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CHAPTER OVERVIEW

6: Organic Chemistry

Scientists of the 18th and early 19th centuries studied compounds obtained from plants and animals and labeled them *organic* because they were isolated from “organized” (living) systems. Compounds isolated from nonliving systems, such as rocks and ores, the atmosphere, and the oceans, were labeled *inorganic*. For many years, scientists thought organic compounds could be made by only living organisms because they possessed a vital force found only in living systems. The vital force theory began to decline in 1828, when the German chemist Friedrich Wöhler synthesized urea from inorganic starting materials. He reacted silver cyanate (AgOCN) and ammonium chloride (NH_4Cl), expecting to get ammonium cyanate (NH_4OCN). What he expected is described by the following equation.

$$AgOCN + NH_4Cl \rightarrow AgCl + NH_4OCN \tag{6.1}$$

Instead, he found the product to be urea (NH_2CONH_2), a well-known organic material readily isolated from urine. This result led to a series of experiments in which a wide variety of organic compounds were made from inorganic starting materials. The vital force theory gradually went away as chemists learned that they could make many organic compounds in the laboratory.

Today **organic chemistry** is the study of the chemistry of the carbon compounds, and inorganic chemistry is the study of the chemistry of all other elements. It may seem strange that we divide chemistry into two branches—one that considers compounds of only one element and one that covers the 100-plus remaining elements. However, this division seems more reasonable when we consider that of tens of millions of compounds that have been characterized, the overwhelming majority are carbon compounds.

> The word *organic* has different meanings. Organic fertilizer, such as cow manure, is organic in the original sense; it is derived from living organisms. Organic foods generally are foods grown without synthetic pesticides or fertilizers. Organic chemistry is the chemistry of compounds of carbon.

Carbon is unique among the other elements in that its atoms can form stable covalent bonds with each other and with atoms of other elements in a multitude of variations. The resulting molecules can contain from one to millions of carbon atoms. We previously surveyed organic chemistry by dividing its compounds into families based on functional groups. We begin with the simplest members of a family and then move on to molecules that are organic in the original sense—that is, they are made by and found in living organisms. These complex molecules (all containing carbon) determine the forms and functions of living systems and are the subject of biochemistry.



Figure **6.1** All organic compounds contain carbon and most are formed by living things, although they are also formed by geological and artificial processes. (credit left: modification of work by Jon Sullivan; credit left middle: modification of work by Deb Tremper; credit right middle: modification of work by “annszyp”/Wikimedia Commons; credit right: modification of work by George Shuklin)

Organic compounds, like inorganic compounds, obey all the natural laws. Often there is no clear distinction in the chemical or physical properties among organic and inorganic molecules. Nevertheless, it is useful to compare typical members of each class, as in Table **6.1**.

Table **6.1**: General Contrasting Properties and Examples of Organic and Inorganic Compounds

Organic	Hexane		Inorganic	NaCl
low melting points	−95°C		high melting points	801°C
low boiling points	69°C		high boiling points	1,413°C
low solubility in water; high solubility in nonpolar solvents	insoluble in water; soluble in gasoline		greater solubility in water; low solubility in nonpolar solvents	soluble in water; insoluble in gasoline
flammable	highly flammable		nonflammable	nonflammable
aqueous solutions do not conduct electricity	nonconductive		aqueous solutions conduct electricity	conductive in aqueous solution
exhibit covalent bonding	covalent bonds		exhibit ionic bonding	ionic bonds

Keep in mind, however, that there are exceptions to every category in this table. To further illustrate typical differences among organic and inorganic compounds, Table **6.1** also lists properties of the inorganic compound sodium chloride (common table salt, NaCl) and the organic compound hexane (C_6H_{14}), a solvent that is used to extract soybean oil from soybeans (among other uses). Many compounds can be classified as organic or inorganic by the presence or absence of certain typical properties, as illustrated in Table **6.1**.

Today, organic compounds are key components of plastics, soaps, perfumes, sweeteners, fabrics, pharmaceuticals, and many other substances that we use every day. The value to us of organic compounds ensures that organic chemistry is an important discipline within the general field of chemistry. In this chapter, we discuss why the element carbon gives rise to a vast number and variety of compounds, how those compounds are classified, and the role of organic compounds in representative biological and industrial settings.

Contributors and Attributions

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- 6.1: Prelude to Organic Chemistry
  6.2: The Functional Group
  6.3: Aliphatic Hydrocarbons
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- TextMap: The Basics of GOB Chemistry (Ball et al.)

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6.1: Prelude to Organic Chemistry

Scientists of the 18th and early 19th centuries studied compounds obtained from plants and animals and labeled them *organic* because they were isolated from “organized” (living) systems. Compounds isolated from nonliving systems, such as rocks and ores, the atmosphere, and the oceans, were labeled *inorganic*. For many years, scientists thought organic compounds could be made by only living organisms because they possessed a vital force found only in living systems. The vital force theory began to decline in 1828, when the German chemist Friedrich Wöhler synthesized urea from inorganic starting materials. He reacted silver cyanate (AgOCN) and ammonium chloride (NH_4Cl), expecting to get ammonium cyanate (NH_4OCN). What he expected is described by the following equation.

$$AgOCN + NH_4Cl \rightarrow AgCl + NH_4OCN \tag{6.1.1}$$

Instead, he found the product to be urea (NH_2CONH_2), a well-known organic material readily isolated from urine. This result led to a series of experiments in which a wide variety of organic compounds were made from inorganic starting materials. The vital force theory gradually went away as chemists learned that they could make many organic compounds in the laboratory.

Today **organic chemistry** is the study of the chemistry of the carbon compounds, and inorganic chemistry is the study of the chemistry of all other elements. It may seem strange that we divide chemistry into two branches—one that considers compounds of only one element and one that covers the 100-plus remaining elements. However, this division seems more reasonable when we consider that of tens of millions of compounds that have been characterized, the overwhelming majority are carbon compounds.

> The word *organic* has different meanings. Organic fertilizer, such as cow manure, is organic in the original sense; it is derived from living organisms. Organic foods generally are foods grown without synthetic pesticides or fertilizers. Organic chemistry is the chemistry of compounds of carbon.

Carbon is unique among the other elements in that its atoms can form stable covalent bonds with each other and with atoms of other elements in a multitude of variations. The resulting molecules can contain from one to millions of carbon atoms. We previously surveyed organic chemistry by dividing its compounds into families based on functional groups. We begin with the simplest members of a family and then move on to molecules that are organic in the original sense—that is, they are made by and found in living organisms. These complex molecules (all containing carbon) determine the forms and functions of living systems and are the subject of biochemistry.



Figure **6.1.1** All organic compounds contain carbon and most are formed by living things, although they are also formed by geological and artificial processes. (credit left: modification of work by Jon Sullivan; credit left middle: modification of work by Deb Tremper; credit right middle: modification of work by “annszyp”/Wikimedia Commons; credit right: modification of work by George Shuklin)

Organic compounds, like inorganic compounds, obey all the natural laws. Often there is no clear distinction in the chemical or physical properties among organic and inorganic molecules. Nevertheless, it is useful to compare typical members of each class, as in Table **6.1.1**.

Table **6.1.1**: General Contrasting Properties and Examples of Organic and Inorganic Compounds

Organic	Hexane		Inorganic	NaCl
low melting points	−95°C		high melting points	801°C
low boiling points	69°C		high boiling points	1,413°C
low solubility in water; high solubility in nonpolar solvents	insoluble in water; soluble in gasoline		greater solubility in water; low solubility in nonpolar solvents	soluble in water; insoluble in gasoline
flammable	highly flammable		nonflammable	nonflammable
aqueous solutions do not conduct electricity	nonconductive		aqueous solutions conduct electricity	conductive in aqueous solution
exhibit covalent bonding	covalent bonds		exhibit ionic bonding	ionic bonds

Keep in mind, however, that there are exceptions to every category in this table. To further illustrate typical differences among organic and inorganic compounds, Table **6.1.1** also lists properties of the inorganic compound sodium chloride (common table salt, NaCl) and the organic compound hexane (C_6H_{14}), a solvent that is used to extract soybean oil from soybeans (among other uses). Many compounds can be classified as organic or inorganic by the presence or absence of certain typical properties, as illustrated in Table **6.1.1**.

Today, organic compounds are key components of plastics, soaps, perfumes, sweeteners, fabrics, pharmaceuticals, and many other substances that we use every day. The value to us of organic compounds ensures that organic chemistry is an important discipline within the general field of chemistry. In this chapter, we discuss why the element carbon gives rise to a vast number and variety of compounds, how those compounds are classified, and the role of organic compounds in representative biological and industrial settings.

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6.2: The Functional Group

Learning Objectives

- Define *functional group*.
- Identify the functional group(s) present in organic compounds.

With over twenty million known organic compounds in existence, it would be very challenging to memorize chemical reactions for each one. Fortunately, molecules with similar functional groups tend to undergo similar reactions. A **functional group** is defined as an atom or group of atoms within a molecule that has similar chemical properties whenever it appears in various compounds. Even if other parts of the molecule are quite different, certain functional groups tend to react in certain ways.

We've already looked at alkanes, but they are generally unreactive. We primarily use alkanes as a source of energy when they are combusted. While the majority of functional groups involve atoms other than carbon and hydrogen, we will also look at some that include only carbon and hydrogen. Some of the most common functional groups are presented in the following sections.

Organic molecules vary greatly in size and when focusing on functional groups, we want to direct our attention to the atoms involved in the functional group. As a result, the abbreviation **R** is used in some examples. The letter **R** is used in molecular structures to represent the "**R**est of the molecule". It consists of a group of carbon and hydrogen atoms of any size. It is used as an abbreviation since a group of carbon and hydrogen atoms does not affect the functionality of the compound. In some molecules, you will see **R, R', or R"** which indicates that the R groups in the molecule can be different from one another. For example, R might be $–CH_2CH_3$ while R' is $–CH_2CH_2CH_2CH_3$.

The structure of capsaicin, the compound responsible for the heat in peppers, incorporates several functional groups, labeled in the figure below and explained throughout this section.

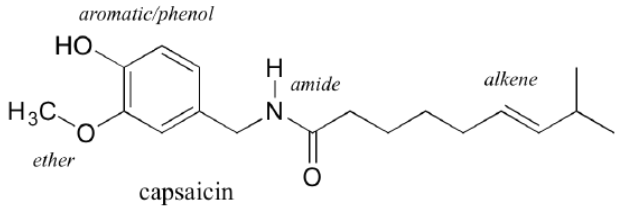


Figure **6.2.1** The structure of capsaicin

The table below summarizes the structures that will be discussed in this chapter:

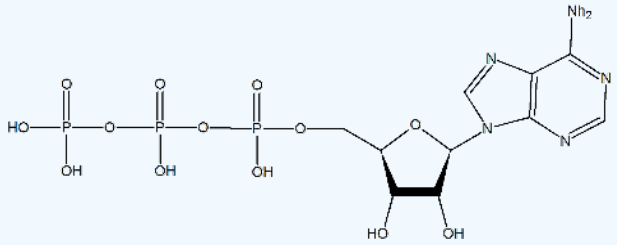
Table **6.2.1** Selected Organic Functional Groups

Compound Name	Structure of Compound and Functional Group (red)	Example	
		Formula	Name
alkene	C═C	C_2H_4	ethene
alkyne	C≡C	C_2H_2	ethyne
alcohol	R—O—H	CH_3CH_2OH	ethanol
ether	R—O—R′	$(C_2H_5)_2O$	diethyl ether
aldehyde	R—C(=O)—H	CH_3CHO	ethanal
ketone	R—C(=O)—R′	$CH_3COCH_2CH_3$	methyl ethyl ketone
carboxylic acid	R—C(=O)—O—H	CH_3COOH	acetic acid
ester	R—C(=O)—O—R′	$CH_3CO_2CH_2CH_3$	ethyl acetate
amine	R—N(—H)—H; R—N(—H)—R′; R—N(—R′)—R″	$C_2H_5NH_2$	ethylamine
amide	R—C(=O)—N(—H)—R′	CH_3CONH_2	acetamide

Figure **6.2.1**

Example 6.2.1

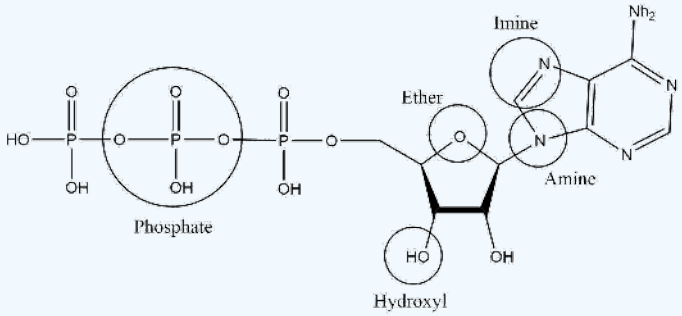
Identify the common functional groups for ATP.



Example **6.2.1**

Solution

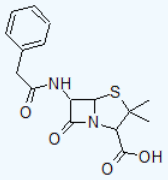
The common functional groups for ATP are **hydroxyl**, **ether** and **amine**. The other functional groups are covered in higher organic chemistry courses.



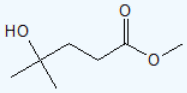
Example **6.2.1** ATP

Exercise 6.2.1

Identify the functional groups (other than alkanes) in the following organic compounds. State whether alcohols and amines are primary, secondary, or tertiary.



penicillin

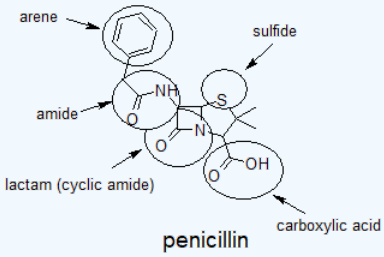




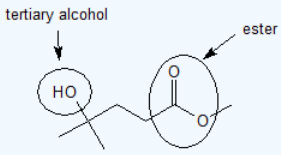
pyruvic acid

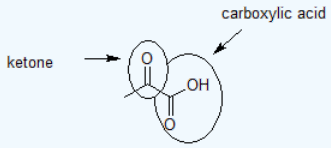


Answer

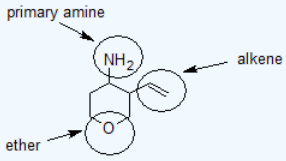


penicillin





pyruvic acid



Summary

- Functional groups consist of a single atom (such as Cl) or a group of atoms (such as CO_2H). It can determine the chemical reactivity of a molecule under a given set of conditions
- The major families of organic compounds are characterized by their functional groups.

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6.3: Aliphatic Hydrocarbons

Learning Objectives

- Define and identify alkanes, alkenes, alkynes, and cyclic hydrocarbons.
- List some properties of hydrocarbons.
- Identify and name simple (straight-chain) alkanes given formulas and write formulas for straight-chain alkanes given their names.
- Define structural and geometric isomers.
- Write condensed structural formulas and draw line-angle formulas given complete structural formulas for alkanes,alkenes, alkynes, and cyclic hydrocarbons.

The simplest organic compounds are those composed of only two elements: carbon and hydrogen. These compounds are called **hydrocarbons**. Hydrocarbons themselves are separated into two types: aliphatic hydrocarbons and aromatic hydrocarbons. **Aliphatic hydrocarbons** are hydrocarbons based on chains of C atoms. There are three types of aliphatic hydrocarbons. **Alkanes** are aliphatic hydrocarbons with only single covalent bonds. **Alkenes** are hydrocarbons that contain at least one C–C double bond, and a**lkynes** are hydrocarbons that contain a C–C triple bond. Occasionally, we find an aliphatic hydrocarbon with a ring of C atoms; these hydrocarbons are called ***cycloalkanes*** (or *cycloalkenes* or *cycloalkynes*). Because alkanes have the maximum number of H atoms possible according to the rules of covalent bonds, alkanes are also referred to as **saturated hydrocarbons**.

Note

The word *saturated* has the same meaning for hydrocarbons as it does for the dietary fats and oils: the molecule has no carbon-to-carbon double bonds (C=C).

Alkanes

The simplest alkanes have their C atoms bonded in a straight chain; these are called *normal* alkanes. They are named according to the number of C atoms in the chain. The smallest alkane is methane:

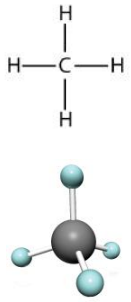


Figure **6.3.1**. Two dimensional model of methane (top); *Three-dimensional representation of methane © Thinkstock. The methane molecule is three dimensional, with the H atoms in the positions of the four corners of a tetrahedron. (bottom)*

The diagrams representing alkanes are called **structural formulas** because they show the structure of the molecule. As molecules get larger, structural formulas become more and more complex. One way around this is to use a **condensed structural formula**, which lists the formula of each C atom in the backbone of the molecule.

condensed structural formula

The condensed formulas show hydrogen atoms right next to the carbon atoms to which they are attached, as illustrated for butane:

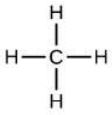
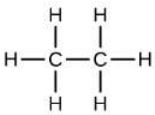
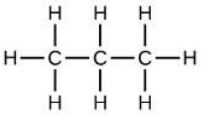
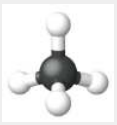
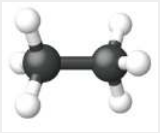
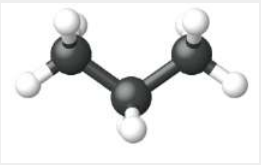


The ultimate condensed formula is a **line-angle formula (or line drawing)** , in which carbon atoms are implied at the corners and ends of lines, and each carbon atom is understood to be attached to enough hydrogen atoms to give each carbon atom four bonds. For example, we can represent pentane ($CH_3CH_2CH_2CH_2CH_3$) and isopentane [$(CH_3)_2CHCH_2CH_3$] as follows:



Pentane Isopentane

Table **6.3.1** Structural formulas for methane, ethane , and propane

Structural Formula			
Ball and Stick Model			
Space Filling model			
Name	Methane	Ethane	Propane
Condensed Structural Formula	CH_4	CH_3CH_3	$CH_3CH_2CH_3$
Molecular Formula	CH_4	C_2H_6	C_3H_8
Line angle drawing			

Example 6.3.1

Provide the molecular formula, the complete structural formula, the condensed structural formula and the line angle formula for a straight chain alkane with 8 carbon atoms.

Solutions

Example **6.3.2** writing formulas for a straight chain alkane with eight carbon atoms.

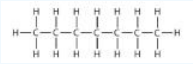
structural formula	Explanation	Answer
ula Molecular Formula	The general formula for an alkane is C_nH_{2n+2} For an alkane with 8 carbon atoms, $C_8H_{(2\times 8)+2} = C_8H_{18}$.	C_8H_{18}.
ula Complete Structural Formula	Eight carbons first linked together and all remaining bonds to hydrogen to fulfill the octet rule.	C_1-C_2-C_3-C_4-C_5-C_6-C_7-C_8
ula Condensed Structural Formula	The terminal carbon atoms (C_1 and C_8) are bonded to three hydrogen atoms each and the six middle carbon atoms are bonded to two hydrogen atoms each. The six middle carbon atoms are all bonded to two hydrogen atoms so the structural formula can be simplified further.	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$ $CH_3(CH_2)_6CH_3$
ula Line Angle Drawing	Eight carbon atoms are implied at the corners and ends of lines, and each carbon atom is understood to be attached to enough hydrogen atoms to give each carbon atom four bonds.	

? Exercise 6.3.1

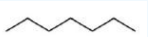
Provide the molecular formula, the complete structural formula, the condensed structural formula, and the line angle formula for a straight chain alkane with 7 carbon atoms.

Answer

molecular formula: C_7H_{16}

complete structural formula: 

condensed structural formula: $CH_3(CH_2)_5CH_3$

line angle drawing: 

Homologous Series

Methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) are the beginning of a series of compounds in which any two members in a sequence differ by one carbon atom and two hydrogen atoms—namely, a CH_2 unit. The first 10 members of this series are given in Table **6.3.1**.

Table **6.3.1** The First 10 Straight-Chain Alkanes

Molecular Formula	Condensed Structural Formula	Name
CH_4	CH_4	methane
C_2H_6	CH_3CH_3	ethane
C_3H_8	$CH_3CH_2CH_3$	propane
C_4H_{10}	$CH_3CH_2CH_2CH_3$	butane
C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$	pentane
C_6H_{14}	$CH_3(CH_2)_4CH_3$	hexane
C_7H_{16}	$CH_3(CH_2)_5CH_3$	heptane
C_8H_{18}	$CH_3(CH_2)_6CH_3$	octane
C_9H_{20}	$CH_3(CH_2)_7CH_3$	nonane
$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	decane

Note

Parentheses in condensed structural formulas indicate that the enclosed grouping of atoms is attached to the adjacent carbon atom.

Consider the series in Figure **6.3.2**. The sequence starts with C_3H_8, and a CH_2 unit is added in each step moving up the series. Any family of compounds in which adjacent members differ from each other by a definite factor (here a CH_2 group) is called a homologous series. The members of such a series, called *homologs*, have properties that vary in a regular and predictable manner. The principle of *homology* gives organization to organic chemistry in much the same way that the periodic table gives organization to inorganic chemistry. Instead of a bewildering array of individual carbon compounds, we can study a few members of a homologous series and from them deduce some of the properties of other compounds in the series.

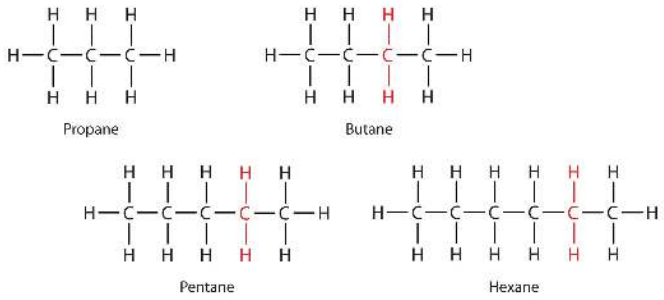


Figure **6.3.2** Members of a homologous series.

The principle of homology allows us to write a general formula for alkanes: $C_nH_{2n\,+\,2}$. Using this formula, we can write a molecular formula for any alkane with a given number of carbon atoms. For example, an alkane with eight carbon atoms has the molecular formula $C_8H_{(2\,\times\,8)\,+\,2} = C_8H_{18}$.

Naming (IUPAC Nomenclature)

A systematic way of naming hydrocarbons and other organic compounds has been devised by the International Union of Pure and Applied Chemistry (IUPAC). These rules, used worldwide, are known as the IUPAC System of Nomenclature. A stem name in Table **6.3.1** indicates the number of carbon atoms in the longest continuous chain (LCC). Atoms or groups attached to this carbon chain, called *substituents*, are then named, with their positions indicated by numbers.

Table **6.3.2***Stems That Indicate the Number of Carbon Atoms in Organic Molecules*

Stem	Number of C Atoms
meth-	1
eth-	2
prop-	3
but-	4
pent-	5
hex-	6
hept-	7
oct-	8
non-	9
dec-	10

Note

A continuous (unbranched) chain of carbon atoms is often called a *straight chain* even though the tetrahedral arrangement about each carbon gives it a zigzag shape. Straight-chain alkanes are sometimes called *normal alkanes*, and their names are given the prefix *n*-. For example, butane is called *n*-butane. We will not use that prefix here because it is not a part of the system established by the International Union of Pure and Applied Chemistry.

Example 6.3.2

What is the name of an eight carbon alkane?

Solution

The stem that refers to eight carbon atoms is **oct** plus the suffix **-ane** for an alkane, so the answer is **Octane**.

Exercise 6.3.2

Provide the name for the following compounds:

a. seven carbon alkane

b. six carbon alkane

Answer

a. heptane

b. hexane

Isomerism-Branched Chain Alkanes

One of the interesting aspects of organic chemistry is that it is three-dimensional. A molecule can have a shape in space that may contribute to its properties. Molecules can differ in the way the atoms are arranged - the same combination of atoms can be assembled in more than one way. These compounds are known as **isomers**. Isomers are molecules with the same molecular formulas, but different arrangements of atoms. We will look at some isomer possibilities for alkanes and alkenes.

We can write the structure of butane (C_4H_{10}) by stringing four carbon atoms in a row,

–C–C–C–C–

and then adding enough hydrogen atoms to give each carbon atom four bonds:

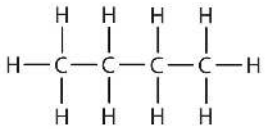


Figure **6.3.2** Complete structural formula of butane

The compound butane has this structure, but there is another way to put 4 carbon atoms and 10 hydrogen atoms together. Place 3 of the carbon atoms in a row and then branch the fourth one off the middle carbon atom:

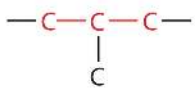
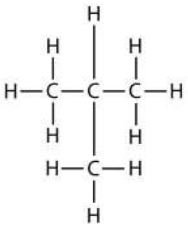


Figure **6.3.3** Incomplete structural formula

Now we add enough hydrogen atoms to give each carbon four bonds.



There is a hydrocarbon that corresponds to this structure, which means that two different compounds have the same molecular formula: C_4H_{10}. The two compounds have different properties—for example, one boils at −0.5°C; the other at −11.7°C. Different compounds having the same molecular formula are called isomers.

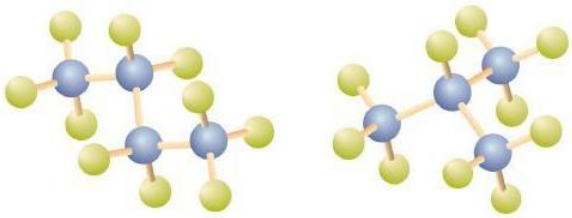
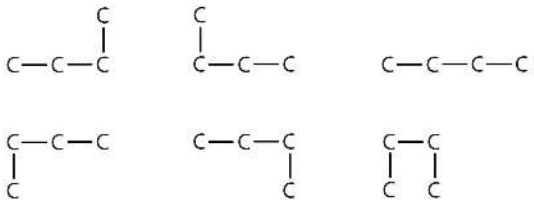


Figure **6.3.4** Butane and isobutane. The ball-and-stick models of these two compounds show them to be isomers; both have the molecular formula C4H10.

Notice that C_4H_{10} is depicted with a bent chain in Figure **6.3.4**. The four-carbon chain may be bent in various ways because the groups can rotate freely about the C–C bonds. However, this rotation does not change the identity of the compound. It is important to realize that bending a chain does *not* change the identity of the compound; all of the following represent the same compound, butane:



The structure of isobutane shows a continuous chain of three carbon atoms only, with the fourth attached as a branch off the middle carbon atom of the continuous chain, which is different from the structures of butane (compare the two structures in Figure **6.3.4**.

Unlike C_4H_{10}, the compounds methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) do not exist in isomeric forms because there is only one way to arrange the atoms in each formula so that each carbon atom has four bonds.

Next beyond C_4H_{10} in the homologous series is pentane. Each compound has the same molecular formula: C_5H_{12}. The compound at the far left is pentane because it has all five carbon atoms in a continuous chain. The compound in the middle is isopentane; like isobutane, it has a one CH_3 branch off the second carbon atom of the continuous chain. The compound at the far right, discovered after the other two, was named neopentane (from the Greek *neos*, meaning "new"). Although all three have the same molecular formula, they have different properties, including boiling points: pentane, 36.1°C; isopentane, 27.7°C; and neopentane, 9.5°C.

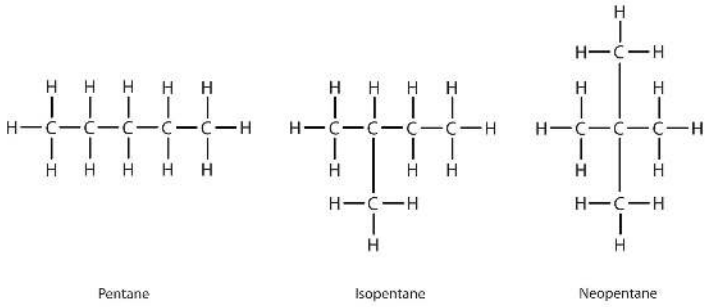


Figure **6.3.5** complete structural formulas for pentane isopentane and neopentane

Naming Branched Alkanes

You have already learned the basics of nomenclature-the names of the first 10 normal hydrocarbons. Here, we will add some steps to the procedure so you can name branched hydrocarbons.

First, given the structure of an alkane, identify the longest continuous chain of C atoms. Note that the longest chain may not be drawn in a straight line. The longest chain determines the parent name of the hydrocarbon. For example, in the molecule

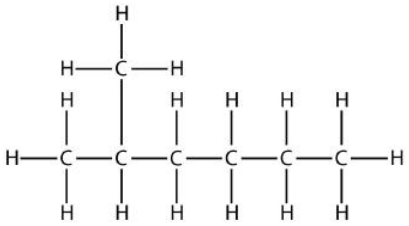


Figure **6.3.6** structural formula for hexane

the longest chain of carbons has six C atoms. Therefore, it will be named as a hexane. However, in the molecule

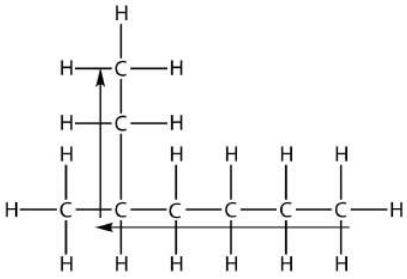


Figure **6.3.7** structural formula for heptane

the longest chain of C atoms is not six, but seven, as shown. So this molecule will be named as a heptane.

The next step is to identify the branches, or **substituents,** on the main chain. The names of the substituents, or *alkyl groups*, are derived from the names of the parent hydrocarbons; however, rather than having the ending *-ane*, the substituent name has the ending *-yl*. Table **6.3.3**, lists the substituent names for the five smallest substituents.

***Table* 6.3.3** *Substituent Names.*

Substituent Formula	Number of C Atoms	Name of Substituent
CH_3	1	*methyl-*
CH_3CH_2	2	*ethyl-*
$CH_3CH_2CH_2$	3	*propyl-*
$CH_3CH_2CH_2CH_2$	4	*butyl-*
$CH_3CH_2CH_2CH_2CH_2$	5	*pentyl-*
and so forth	and so forth	and so forth

In naming the branched hydrocarbon, the name of the substituent is combined with the parent name of the hydrocarbon without spaces. However, there is likely one more step. The longest chain of the hydrocarbon must be numbered, and the numerical position of the substituent must be included to account for possible isomers. As with double and triple bonds, the main chain is numbered to give the substituent the lowest possible number. For example, in this alkane

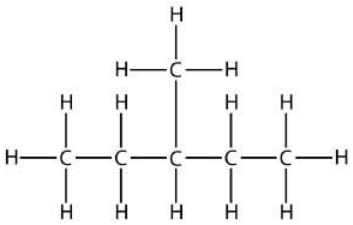


Figure **6.3.7** Structural formula for 3-methylpentane

the longest chain is five C atoms long, so it is a pentane. There is a one-carbon substituent on the third C atom, so there is a methyl group at position 3. We indicate the position using the number, which is followed by a hyphen, the substituent name, and the parent hydrocarbon name-in this case, **3-methylpentane**. That name is specific to that particular hydrocarbon and no other molecule. Organic chemistry nomenclature is very specific!

It is common to write the structural formula of a hydrocarbon without the H atoms, for clarity. So we can also represent 3-methylpentane as

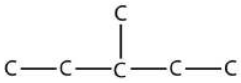
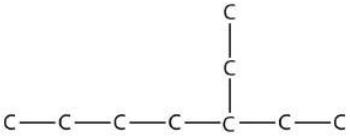


Figure **6.3.8** Structural formula for 3-methylpentane without the hydrogen atoms

where it is understood that any unwritten covalent bonds are bonds with H atoms. With this understanding, we recognize that the structural formula for 3-methylpentane refers to a molecule with the formula of C_6H_{14}.

Example 6.3.3:

Name this molecule.

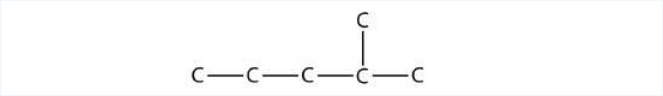


Solution

The longest continuous carbon chain has **seven** C atoms, so this molecule will be named as a **heptane**. There is a **two-carbon substituent** on the main chain, which is an **ethyl group**. To give the substituent the lowest numbering, we number the chain from the *right* side and see that **the substituent is on the third C atom**. So this hydrocarbon is **3-ethylheptane**.

? Exercise 6.3.3

Name this molecule.



Answer

2-methylpentane

Branched hydrocarbons may have more than one substituent. If the substituents are different, then give each substituent a number (using the smallest possible numbers) and list the substituents in alphabetical order, with the numbers separated by hyphens and with no spaces in the name. So the molecule

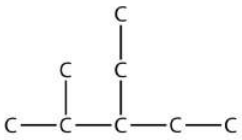


Figure **6.3.8** 3-ethyl-2-methylpentane

is 3-ethyl-2-methylpentane.

If the substituents are the same, then use the name of the substituent only once, but use more than one number, separated by a comma. Also, put a numerical prefix before the substituent name that indicates the number of substituents of that type. The numerical prefixes are listed in Table **6.3.4**. The number of the position values must agree with the numerical prefix before the substituent.

Table **6.3.4** Numerical Prefixes to Use for Multiple Substituents

Number of Same Substituent	Numerical Prefix
2	*di-*
3	*tri-*
4	*tetra-*
5	*penta-*
and so forth	and so forth

Consider this molecule:

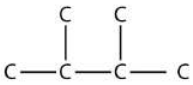
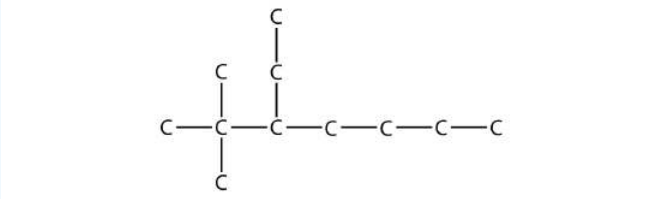


Figure **6.3.9** 2,3-dimethylbutane

The longest chain has four C atoms, so it is a butane. There are two substituents, each of which consists of a single C atom; they are methyl groups. The methyl groups are on the second and third C atoms in the chain (no matter which end the numbering starts from), so we would name this molecule 2,3-dimethylbutane. Note the comma between the numbers, the hyphen between the numbers and the substituent name, and the presence of the prefix *di-* before the *methyl*. Other molecules-even with larger numbers of substituents-can be named similarly.

Example 6.3.4:

Name this molecule.

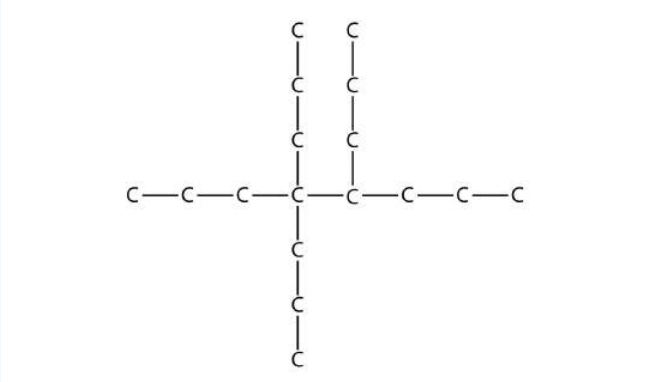


Solution

The longest chain has **seven** C atoms, so we name this molecule as a **heptane**. We find two one-carbon substituents on the second C atom and a **two-carbon substituent** on the third C atom. So this molecule is named **3-ethyl-2,2-dimethylheptane**.

Exercise 6.3.4

Name this molecule.



Answer

4,4,5-tripropyloctane

Properties of Alkanes

All alkanes are composed of carbon and hydrogen atoms, and have similar bonds, structures, and formulas; noncyclic alkanes all have a formula of C_nH_{2n+2}. The number of carbon atoms present in an alkane has no limit. Greater numbers of atoms in the molecules will lead to stronger intermolecular attractions (dispersion forces) and correspondingly different physical properties of the molecules. Properties such as melting point and boiling point (Table **6.3.5**) usually change smoothly and predictably as the number of carbon and hydrogen atoms in the molecules change.

Table **6.3.5** Properties of Some Alkanes

Alkane	Molecular Formula	Melting Point (°C)	Boiling Point (°C)	Phase at STP[4]	Number of Structural Isomers
methane	CH_4	–182.5	–161.5	gas	1
ethane	C_2H_6	–183.3	–88.6	gas	1
propane	C_3H_8	–187.7	–42.1	gas	1
butane	C_4H_{10}	–138.3	–0.5	gas	2
pentane	C_5H_{12}	–129.7	36.1	liquid	3
hexane	C_6H_{14}	–95.3	68.7	liquid	5
heptane	C_7H_{16}	–90.6	98.4	liquid	9
octane	C_8H_{18}	–56.8	125.7	liquid	18
nonane	C_9H_{20}	–53.6	150.8	liquid	35
decane	$C_{10}H_{22}$	–29.7	174.0	liquid	75
tetradecane	$C_{14}H_{30}$	5.9	253.5	solid	1858
octadecane	$C_{18}H_{38}$	28.2	316.1	solid	60,523

Alkanes are relatively stable molecules, but heat or light will activate reactions that involve the breaking of C–H or C–C single bonds. Combustion is one such reaction:

$$\mathrm{CH_4}(g) + 2\,\mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g) + 2\,\mathrm{H_2O}(g)$$

Alkanes burn in the presence of oxygen, a highly exothermic oxidation-reduction reaction that produces carbon dioxide and water. As a consequence, alkanes are excellent fuels. For example, methane, CH_4, is the principal component of natural gas. Butane, C_4H_{10}, used in camping stoves and lighters is an alkane. Gasoline is a liquid mixture of continuous- and branched-chain alkanes, each containing from five to nine carbon atoms, plus various additives to improve its performance as a fuel. Kerosene, diesel oil, and fuel oil are primarily mixtures of alkanes with higher molecular masses. The main source of these liquid alkane fuels is crude oil, a complex mixture that is separated by fractional distillation. Fractional distillation takes advantage of differences in the boiling points of the components of the mixture (Figure **6.3.10**). You may recall that boiling point is a function of intermolecular interactions, which was discussed in the chapter on solutions and colloids.

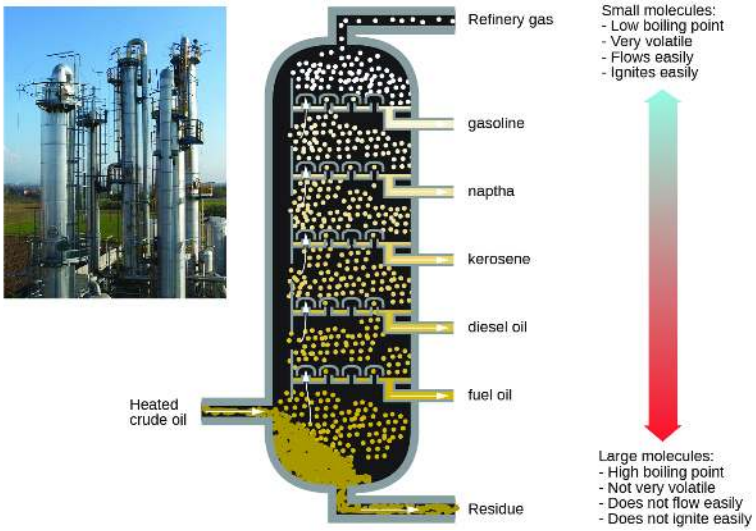


Figure **6.3.10** In a column for the fractional distillation of crude oil, oil heated to about 425 °C in the furnace vaporizes when it enters the base of the tower. The vapors rise through bubble caps in a series of trays in the tower. As the vapors gradually cool, fractions of higher, then of lower, boiling points condense to liquids and are drawn off. (credit left: modification of work by Luigi Chiesa)

In a substitution reaction, another typical reaction of alkanes, one or more of the alkane's hydrogen atoms is replaced with a different atom or group of atoms. No carbon-carbon bonds are broken in these reactions, and the hybridization of the carbon atoms does not change. For example, the reaction between ethane and molecular chlorine depicted here is a substitution reaction:

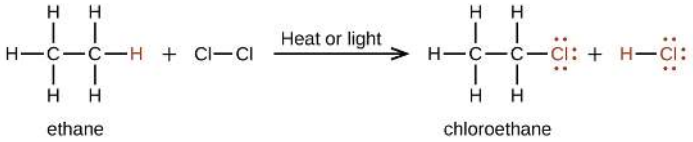


Figure **6.3.11** the reaction between ethane and molecular chlorine

The C–Cl portion of the chloroethane molecule is an example of a functional group, the part or moiety of a molecule that imparts a specific chemical reactivity. The types of functional groups present in an organic molecule are major determinants of its chemical properties and are used as a means of classifying organic compounds as detailed in the remaining sections of this chapter.

Cyclic Hydrocarbons

A **cyclic hydrocarbon** is a hydrocarbon in which the carbon chain joins to itself in a ring. A **cycloalkane** is a cyclic hydrocarbon in which all of the carbon-carbon bonds are single bonds. Like other alkanes, cycloalkanes are saturated compounds. Cycloalkanes have the general formula C_nH_{2n}. The simplest cycloalkane shown below is cyclopropane, a three-carbon ring.

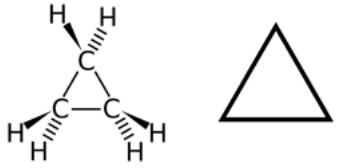


Figure **6.3.11** Cyclopropane the simplest cycloalkane.

The structural formulas of cyclic hydrocarbons can be represented in multiple ways, two of which are shown above. Each atom can be shown as in the structure on the left from the figure above. A convenient shorthand is to omit the element symbols and only show the shape, as in the triangle on the right. Carbon atoms are understood to be the vertices of the triangle.

The carbon atoms in cycloalkanes are still sp^3 hybridized, with an ideal bond angle of $109.5°$. However, an examination of the cyclopropane structure shows that the triangular structure results in a C–C–C bond angle of $60°$. This deviation from the ideal angle is called ring strain and makes cyclopropane a fairly unstable and reactive molecule. Ring strain is decreased for cyclobutane,

with a bond angle of 90°, but is still significant. Cyclopentane has a bond angle of about 108°. This minimal ring strain for cyclopentane makes it a more stable compound.

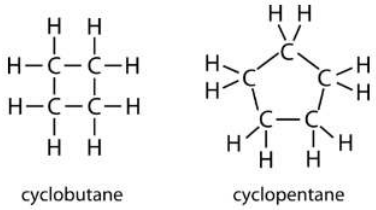


Figure 6.3.12 Cyclobutane and Cyclopentane

Cyclohexane is a six-carbon cycloalkane shown below

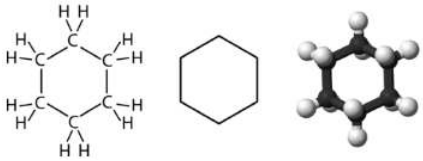


Figure 6.3.13 Cyclohexane

All three of the depictions of cyclohexane are somewhat misleading because the molecule is not planar. In order to reduce the ring strain and attain a bond angle of approximately 109.5°, the molecule is puckered. The puckering of the ring means that every other carbon atom is above and below the plane. The figure below shows two possibilities for the puckered cyclohexane molecule. Each of the structures is called a conformation. The conformation on the right is called the boat conformation, while the one on the left is called the chair conformation.

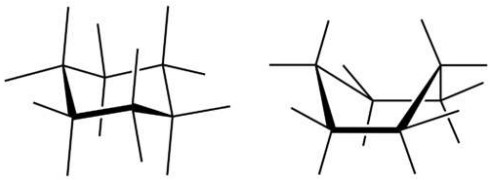


Figure 6.3.14 Chair (left) and boat (right) conformations for cyclohexane.

While both conformations reduce the ring strain compared to a planar molecule, the chair is preferred. This is because the chair conformation results in fewer repulsive interactions between the hydrogen atoms. However, interconversion readily occurs between the two conformations.

Larger cycloalkanes also exist, but are less common. Cyclic hydrocarbons may also be unsaturated. A **cycloalkene** is a cyclic hydrocarbon with at least one carbon-carbon double bond. A **cycloalkyne** is a cyclic hydrocarbon with at least one carbon-carbon triple bond. Shown below are the simplified structural formulas for cyclohexene and cyclooctyne.

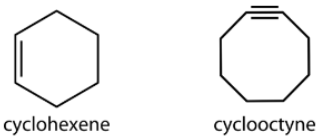


Figure 6.3.15 Cyclohexene(left) and cyclooctyne(right)

Unsaturated Hydrocarbons: Alkenes and Alkynes

Alkenes

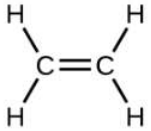
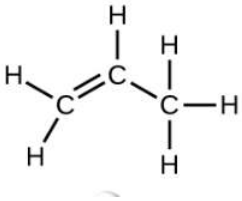
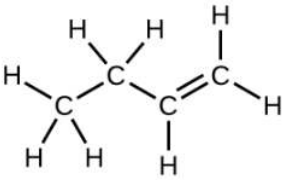
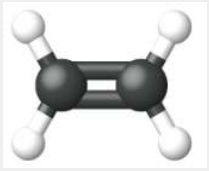
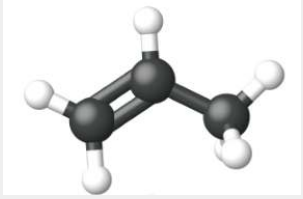
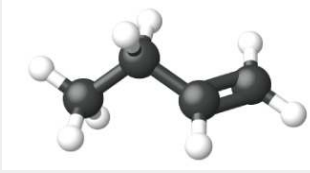
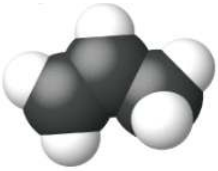
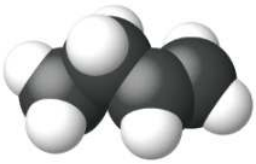
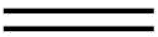
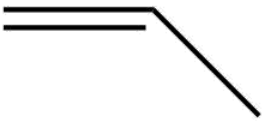
Organic compounds that contain one or more double or triple bonds between carbon atoms are described as unsaturated. Unsaturated hydrocarbons have less than the maximum number of H atoms possible. Unsaturated hydrocarbon molecules that contain one or more double bonds are called alkenes. Carbon atoms linked by a double bond are bound together by two bonds, one σ bond and one π bond. Double and triple bonds give rise to a different geometry around the carbon atom that participates in them, leading to important differences in molecular shape and properties. The differing geometries are responsible for the different properties of unsaturated versus saturated fats.

Note

The word un*saturated* has the same meaning for hydrocarbons as it does for the dietary fats and oils: the molecule has at least one carbon-to-carbon double (C=C) or triple bond (C≡C).

Ethene, C_2H_4, is the simplest alkene. Each carbon atom in ethene, commonly called ethylene, has a trigonal planar structure. The second member of the series is propene (propylene) (Figure **6.3.16**); the butene isomers follow in the series. Four carbon atoms in the chain of butene allows for the formation of isomers based on the position of the double bond, as well as a new form of isomerism.

Structural formulas of Alkenes

Structural Formula			
Ball and Stick Model			
Space Filling model			
Name	ethene	propene	1-butene
Condensed Structural Formula	CH_2CH_2	CH_2CHCH_3	$CH_3CH_2CHCH_2$
Molecular Formula	C_2H_2	C_3H_6	C_4H_8
Line angle drawing			

The name of an alkene is derived from the name of the alkane with the same number of carbon atoms. The presence of the double bond is signified by replacing the suffix *-ane* with the suffix *-ene*. The location of the double bond is identified by naming the smaller of the numbers of the carbon atoms participating in the double bond:

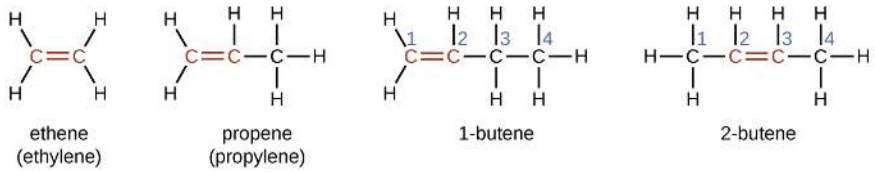


Figure **6.3.16** Four structural formulas and names are shown. The first shows two red C atoms connected by a red double bond illustrated with two parallel line segments. H atoms are bonded above and below to the left of the left-most C atom. Two more H atoms are similarly bonded to the right of the C atom on the right. Beneath this structure the name ethene and alternate name ethylene are shown. The second shows three C atoms bonded together with a red double bond between the red first and second C atoms moving left to right across the three-carbon chain. H atoms are bonded above and below to the left of the C atom to the left. A single H is bonded above the middle C atom. Three more H atoms are bonded above, below, and to the right of the third C atom. Beneath this structure the name propene and alternate name propylene is shown. The third shows four C atoms bonded together, numbered one through four moving left to right with a red double bond between the red first and second carbon in the chain. H atoms are bonded above and below to the left of the C atom to the left. A single H is bonded above the second C atom. H atoms are bonded above and below the third C atom. Three more H atoms are bonded above, below, and to the right of the fourth C atom. Beneath this structure the name 1 dash butene is shown. The fourth shows four C atoms bonded together, numbered one through four moving left to right with a red double bond between the red second and third C atoms in the chain. H atoms are bonded above, below, and to the left of the left-most C atom. A single H atom is bonded above the second C atom. A single H atom is bonded above the third C atom. Three more H atoms are bonded above, below, and to the right of the fourth C atom. Beneath this structure the name 2 dash butene is shown.

Alkynes

Hydrocarbon molecules with one or more triple bonds are called alkynes; they make up another series of unsaturated hydrocarbons. Two carbon atoms joined by a triple bond are bound together by one σ bond and two π bonds. The *sp*-hybridized carbons involved in the triple bond have bond angles of 180°, giving these types of bonds a linear, rod-like shape.

The simplest member of the alkyne series is ethyne, C_2H_2, commonly called acetylene. The Lewis structure for ethyne, a linear molecule, is:

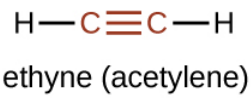


Figure **6.3.17** The structural formula and name for ethyne, also known as acetylene, are shown. In red, two C atoms are shown with a triple bond illustrated by three horizontal line segments between them. Shown in black at each end of the structure, a single H atom is bonded.

The IUPAC nomenclature for alkynes is similar to that for alkenes except that the suffix *-yne* is used to indicate a triple bond in the chain. For example, $\mathbf{CH_3CH_2C \equiv CH}$ is called 1-butyne.

Naming Alkenes and Alkynes

Alkenes and alkynes are named in a similar fashion. The biggest difference is that when identifying the longest carbon chain, it *must* contain the C–C double or triple bond. Furthermore, when numbering the main chain, the double or triple bond gets the lowest possible number. This means that there may be longer or higher-numbered substituents than may be allowed if the molecule were an alkane. For example, this molecule

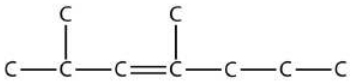
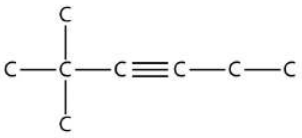


Figure **6.3.18** 2,4-dimethyl-3-heptene

is 2,4-dimethyl-3-heptene (note the number and the hyphens that indicate the position of the double bond).

Example 6.3.5

Name this molecule.

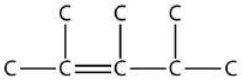


Solution

The longest chain that contains the C–C triple bond has six C atoms, so this is a hexyne molecule. The triple bond starts at the third C atom, so this is a 3-hexyne. Finally, there are two methyl groups on the chain; to give them the lowest possible number, we number the chain from the left side, giving the methyl groups the second position. So the name of this molecule is 2,2-dimethyl-3-hexyne.

? Exercise 6.3.5

Name this molecule.

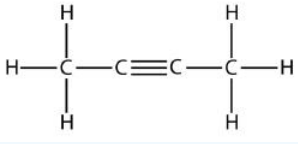
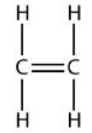
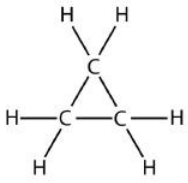


Answer

2,3,4-trimethyl-2-pentene

✓ Example 6.3.6

Identify the molecule as an alkane, an alkene, or an alkyne.

1. 
2. 
3. 

Solution

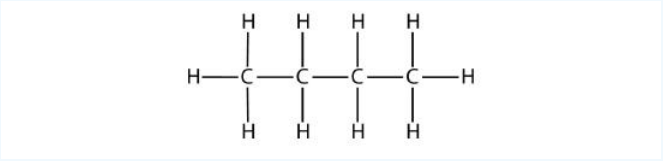
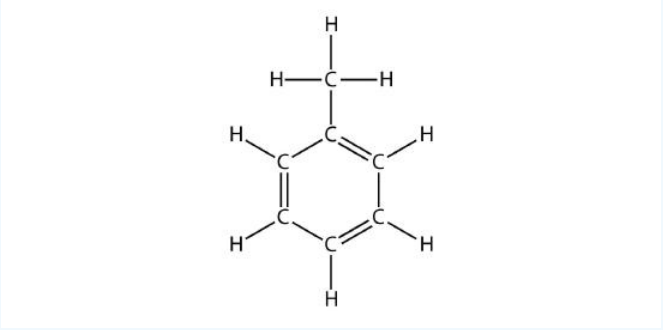
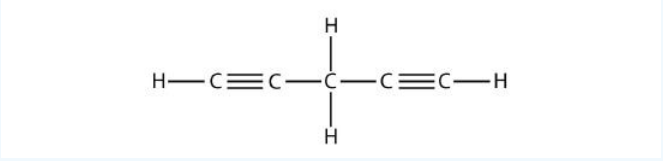
1. The molecule has at least one carbon-to-carbon triple bond (C≡C) so it is an **alkyne**.

2. The molecule has a one carbon-to-carbon double bond (C=C) so it is an **alkene**.

3. The molecule only has carbon-to-carbon single bonds so it is an **alkane**.

Exercise 6.3.6

Identify the molecule as an alkane, an alkene, or an alkyne.

1. 
2. 
3. 

Answer

1. alkane, 2. alkene, 3. alkyne

Properties of Alkenes and Alkynes

Ethylene (the common industrial name for ethene) is a basic raw material in the production of polyethylene and other important compounds. Over 135 million tons of ethylene were produced worldwide in 2010 for use in the polymer, petrochemical, and plastic industries. Ethylene is produced industrially in a process called cracking, in which the long hydrocarbon chains in a petroleum mixture are broken into smaller molecules.

Halogens can also react with alkenes and alkynes, but the reaction is different. In these cases, the halogen reacts with the C–C double or triple bond and inserts itself onto each C atom involved in the multiple bonds. This reaction is called an **addition reaction**. One example is

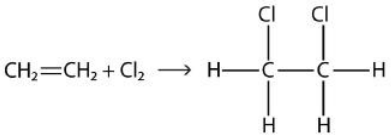


Figure **6.3.19**

$$CH_2=CH_2 + H_2 \xrightarrow{metal\ catalyst} CH_3CH_3$$

The reaction conditions are usually mild; in many cases, the halogen reacts spontaneously with an alkene or an alkyne.

Hydrogen can also be added across a multiple bond; this reaction is called a **hydrogenation reaction**. In this case, however, the reaction conditions may not be mild; high pressures of H_2 gas may be necessary. A platinum or palladium catalyst is usually employed to get the reaction to proceed at a reasonable pace:

$$CH_2=CH_2 + H_2 \xrightarrow{metal\ catalyst} CH_3CH_3$$

Geometric Isomers (Cis-Trans) Isomers

With a molecule such as 2-butene, a different type of isomerism called geometric isomerism can be observed. **Geometric isomers** are isomers in which the order of atom bonding is the same but the arrangement of atoms in space is different. The double bond in an alkene is not free to rotate because of the nature of the pi bond. Therefore, there are two different ways to construct the 2-butene molecule. The image below shows the two geometric isomers, called *cis*-2-butene and *trans*-2-butene.

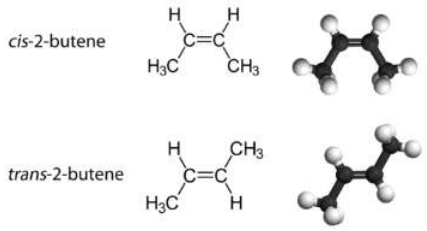


Figure **6.3.20**\ *cis*-2-butene and *trans*-2-butene.

The ***cis* isomer** has the two single hydrogen atoms on the same side of the molecule, while the ***trans* isomer** has them on opposite sides of the molecule. In both molecules, the bonding order of the atoms is the same. In order for geometric isomers to exist, there must be a rigid structure in the molecule to prevent free rotation around a bond. If the double bond in an alkene was capable of rotating, the two geometric isomers above would not exist. In addition, the two carbon atoms must each have two different groups attached in order for there to be geometric isomers. Propene has no geometric isomers because one of the carbon atoms has two single hydrogens bonded to it.

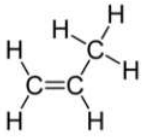


Figure **6.3.21**\ Propene

Physical and chemical properties of geometric isomers are generally different. While *cis*-2-butene is a polar molecule, *trans*-2-butene is nonpolar. Heat or irradiation with light can be used to bring about the conversion of one geometric isomer to another. The input of energy must be large enough to break the pi bond between the two carbon atoms, which is weaker than the sigma bond. At that point,the now single bond is free to rotate and the isomers can interconvert.

As with alkenes, alkynes display structural isomerism beginning with 1-butyne and 2-butyne. However, there are no geometric isomers with alkynes because there is only one other group bonded to the carbon atoms that are involved in the triple bond.

Summary

- Simple alkanes exist as a homologous series, in which adjacent members differ by a CH_2 unit.
- Condensed chemical formulas show the hydrogen atoms (or other atoms or groups) right next to the carbon atoms to which they are attached.
- Line-angle formulas imply a carbon atom at the corners and ends of lines. Each carbon atom is understood to be attached to enough hydrogen atoms to give each carbon atom four bonds.
- Alkanes have both common names and systematic names, specified by IUPAC.
- Names and structures of typical cyclic hydrocarbons are given.
- Structural and geometric isomers are defined.
- Examples of alkane and alkene isomers are given.

Contributors and Attributions

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6.4: Aromatic Compounds- Benzene and Its Relatives

Learning Objective

- Name and identify aromatic compounds.

Benzene is the parent compound of the large family of organic compounds known as aromatic compounds. Unlike cyclohexane, benzene only contains six hydrogen atoms, giving the impression that the ring is unsaturated and each carbon atom participates in one double bond. Two different structures with alternating single and double bonds around the ring can be written for benzene.

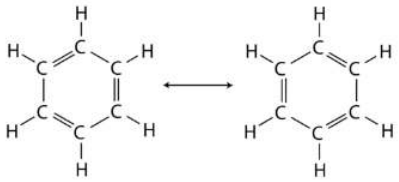


Figure **6.4.1** benzene

In benzene, the true bonding between carbon atoms is neither a single nor a double bond. Rather, all of the bonds are a hybrid of a single and double bond. In benzene, the pi bonding electrons are free to move completely around the ring. **Delocalized electrons** are electrons that are not confined to the bond between two atoms, but are instead allowed to move between three or more. The delocalization of the electrons in benzene can best be shown by showing benzene with a ring inside the hexagon, with the hydrogen atoms understood.



Figure **6.4.2** Delocalized electrons

Delocalization of the electrons makes for a more stable molecule than a similar molecule that does not have delocalized electrons. Benzene is a more stable and less reactive compound than straight-chain hexenes. The sp^2 hybridization of the carbon atoms results in a planar molecule as opposed to the puckered structure of cyclohexane.

There are many derivatives of benzene. The hydrogen atoms can be replaced by many different substituents. Aromatic compounds more readily undergo substitution reactions than addition reactions; replacement of one of the hydrogen atoms with another substituent will leave the delocalized double bonds intact. The following are typical examples of substituted benzene derivatives:

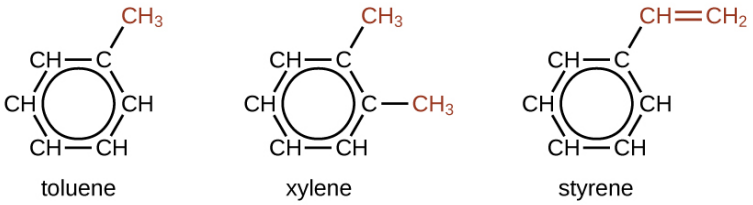


Figure **6.4.3** Three structural formulas are shown. The first is labeled toluene. This molecule has a six carbon hydrocarbon ring in which five of the C atoms are each bonded to only one H atom. At the upper right of the ring, the C atom that does not have a bonded H atom has a red C H subscript 3 group attached. A circle is at the center of the ring. The second is labeled xylene. This molecule has a six carbon hydrocarbon ring in which four of the C atoms are each bonded to only one H atom. At the upper right and right of the ring, the two C atoms that do not have bonded H atoms have C H subscript 3 groups attached. These C H subscript 3 groups appear in red. A circle is at the center of the ring. The third is labeled styrene. This molecule has a six carbon hydrocarbon ring in which five of the carbon atoms are each bonded to only one H atom. At the upper right of the ring, the carbon that does not have a bonded H atom has a red C H double bond C H subscript 2 group attached. A circle is at the center of the ring.

Toluene and xylene are important solvents and raw materials in the chemical industry. Styrene is used to produce the polymer polystyrene. The figure below shows the structural formulas for vanilla and naphthalene. Naphthalene is a chemical which is commonly used in mothballs. The vanilla molecule is extracted from vanilla beans.

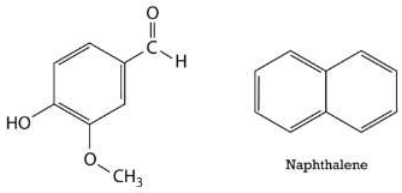


Figure **6.4.4** (left) vanilla molecule ; (right) naphthalene

Nomenclature of Aromatic Compounds

The simplest aromatic compounds are benzene rings with one substituent replacing one of the hydrogen atoms. If this substituent is an alkyl group, it is named first, followed in one word with "benzene". The molecule shown below is therefore called ethylbenzene.

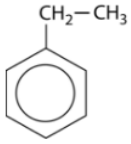


Figure **6.4.5** ethylbenzene

Substituents can be groups other than alkyl groups. If a chlorine atom were substituted for a hydrogen, the name becomes chlorobenzene. An **–NH$_2$** group is called an amino group, so the corresponding molecule is called aminobenzene, often referred to as an aniline. An **–NO$_2$** group is called a nitro group and so the third example below is nitrobenzene.

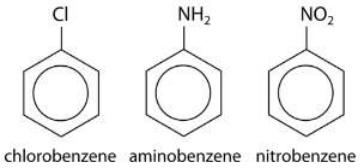


Figure **6.4.6** from left to right: chlorobenzene; aminobenzene; nitrobenzene

If more than one substituent is present, their location relative to each other can be indicated by numbering the positions on the benzene ring.

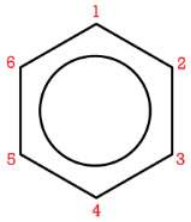


Figure **6.4.7** substituent locations relative to each other can be indicated by numbering the positions on the benzene ring

The number of the carbon location then precedes the name of the substituent in the overall name, with the numbers separated by a comma. As with branched alkanes, the system requires that the numbers be the lowest possible and that prefixes be used for more than one of the same substituent. If there are different substituents, the first in alphabetical order is given the lower number and listed first. The structures below are called 1,2-dimethylbenzene and 1-ethyl-4-methylbenzene.

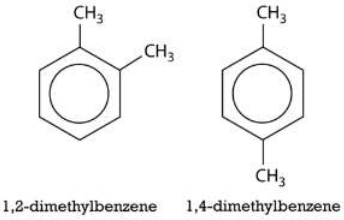


Figure **6.4.8** 1,2-dimethylbenzene (left); 1-ethyl-4-methylbenzene (right)

An alternate system for naming di-substituted benzene rings uses three different prefixes: *ortho*, *meta*, and *para*. If two groups are in the **ortho** position, they are on adjacent carbon atoms. The **meta** positioning refers to being in a 1,3 arrangement. The **para** positioning refers to being in a 1,4 arrangement. Shown below are the three possibilities for dimethylbenzene, also called xylene.

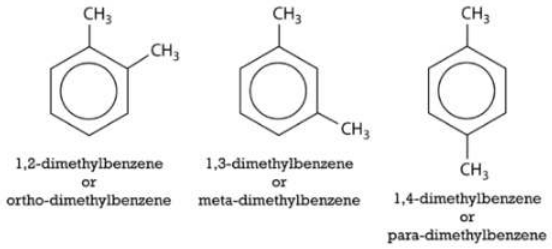


Figure **6.4.9** from left to right: ortho-dimethylbenzene; meta-dimethylbenzene ; para-dimethylbenzene

Lastly, a benzene ring missing one hydrogen atom ($-C_6H_5$) can itself be considered the substituent on a longer chain of carbon atoms. That group is called a *phenyl* group and so the molecule below is called 2-phenylbutane.

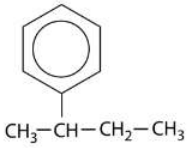


Figure **6.4.10** 2-phenylbutane

Summary

- Aromatic hydrocarbons contain ring structures with delocalized π electron systems.
- Benzene is the parent compound of the large family of organic compounds known as aromatic compounds.
- Naming of aromatic compound i.e. benzene rings with different substituents is described.

Contributors and Attributions

-
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6.5: Halogenated Hydrocarbons- Many Uses, Some Hazards

Learning Objectives

- Identify haloalkanes (alkyl halides) and know their occurrence, uses, and properties.
- Learn how to name simple haloalkanes.

Haloalkanes also known as alkyl halides or halogenoalkanes, are a group of organic compounds in which one or more halogen atoms are substituted for one or more hydrogen atoms in a hydrocarbon. Haloalkanes are widely used commercially and, consequently, are known under many chemical and commercial names. Although these compounds were once widely used as dry cleaning solvents, coolants in refrigerators and air conditioners, and propellants in hairsprays and deodorants, increasing awareness of their toxicity and impact on the environment has led to a widespread decrease in applications for these materials.

The general formulas for organic molecules with functional groups use the letter **R** to stand for the rest of the molecule outside of the functional group. Because there are four possible halogen atoms (fluorine, chlorine, bromine, or iodine) that can act as the functional group, we use the general formula **R–X** to represent an alkyl halide.

Haloalkanes have higher boiling points than alkanes containing the same number of carbons. They are at best only slightly soluble in water but tend to dissolve in organic solvents.

Chloromethane (or methylchloride, CH_3Cl) was a widely used refrigerant, but its use has been discontinued due to its toxicity and flammability. Methyl chloride was also once used for producing lead-based gasoline additives (tetramethyllead).

The most important use of chloromethane today is as a chemical intermediate in the production of silicone polymers. Smaller quantities are used as a solvent in the manufacture of butyl rubber and in petroleum refining.

Large amounts of methyl chloride are produced naturally in the oceans by the action of sunlight on biomass and chlorine in sea foam. However, all methyl chloride that is used in industry is produced synthetically. Most methyl chloride is prepared by reacting methanol with hydrogen chloride, according to the chemical equation

$$CH_3OH + HCl \rightarrow CH_3Cl + H_2O$$

This can be carried out either by bubbling hydrogen chloride gas through boiling methanol with or without a zinc chloride catalyst, or by passing combined methanol and hydrogen chloride vapors over an alumina catalyst at 350 °C (662 °F).

A smaller amount of chloromethane is produced by heating a mixture of methane and chlorine to over 400 °C (752 °F). However, this method also results in more highly chlorinated compounds such as dichloromethane, chloroform, and carbon tetrachloride and is usually only used when these other products are also desired.

Short chain haloalkanes such as dichloromethane (CH_2Cl_2), trichloromethane (chloroform, $CHCl_3$) and tetrachloromethane (carbon tetrachloride, CCl4) are commonly used as hydrophobic solvents in chemistry. They were formerly very common in industry; however, their use has been greatly curtailed due to their toxicity and harmful environmental effects.

Some specific compounds are still used. Halothane (2-bromo-2-chloro-1,1,1-trifluoroethane) is still used in some situations as an inhalation anesthetic. The compound DDT is a very effective pesticide, but is only used when nothing else works because of its harmful effects on the environment.

Naming Alkyl Halides

IUPAC System: The rules for naming simple alkyl halides are listed below.

1. Name the parent compound by finding the longest continuous carbon atom chain that also contains the halogen. Add a prefix for the particular halogen atom. The prefixes for each of the four halogens are *fluoro-*, *chloro-*, *bromo-*, and *iodo-*. If more than one kind of halogen atom is present, put them in alphabetical order. If there is more than one of the same halogen on a given carbon atom, use the prefixes *di-*, *tri-*, or *tetra-* before the prefix for the halogen.
2. As with hydrocarbons, number the carbon chain in a way that makes the sum of halogen numbers as low as possible. If different halogens are in equivalent positions, give the lower number to the one that comes first in alphabetical order.

3. Add the numerical prefix into the name before the halogen prefix.
4. Separate numbers with commas and separate numbers from names or prefixes with a hyphen. There are no spaces in the name.

Listed below are some examples of names and structural formulas of a few alkyl halides.

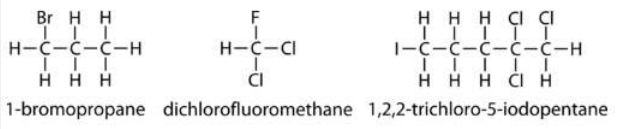


Figure **6.5.1** from left to right: 1-bromopropane; dichlorofluoromethane; 1,2,2-trichloro-5-iodpentane

Note that for the structure based on methane, no number needs to be used since there is only one carbon atom. In the third example, the *chloro-* is listed first alphabetically and the chain is numbered so that the sum of the numbers is as low as possible.

Common Names: The *common names* of alkyl halides consist of two parts: the name of the alkyl group plus the stem of the name of the halogen, with the ending *-ide*.

Alkyl halides with simple alkyl groups (one to four carbon atoms) are often called by common names. Those with a larger number of carbon atoms are usually given IUPAC names.

Example 6.5.1

Give the common and IUPAC names for each compound.

a. $CH_3CH_2CH_2Br$
b. $(CH_3)_2CHCl$

Solution

a. The alkyl group ($CH_3CH_2CH_2$–) is a propyl group, and the halogen is bromine (Br). The common name is therefore propyl bromide. For the IUPAC name, the prefix for bromine (bromo) is combined with the name for a three-carbon chain (propane), preceded by a number identifying the carbon atom to which the Br atom is attached, so the IUPAC name is 1-bromopropane.
b. The alkyl group [$(CH_3)_2CH$–] has three carbon atoms, with a chlorine (Cl) atom attached to the middle carbon atom. The alkyl group is therefore isopropyl, and the common name of the compound is isopropyl chloride. For the IUPAC name, the Cl atom (prefix *chloro-*) attached to the middle (second) carbon atom of a propane chain results in 2-chloropropane.

Exercise 6.5.1

Give common and IUPAC names for each compound.

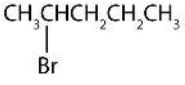
a. CH_3CH_2I
b. $CH_3CH_2CH_2CH_2F$

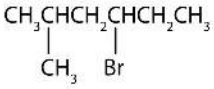
Answers

a. 1-iodoethane, ethyl iodide
b. 1-fluorobutane, butyl fluoride

Example 6.5.2

Give the IUPAC name for each compound.

1. 

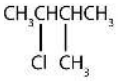


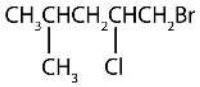
Solution

1. The parent alkane has five carbon atoms in the longest continuous chain; it is pentane. A bromo (Br) group is attached to the second carbon atom of the chain. The IUPAC name is 2-bromopentane.
2. The parent alkane is hexane. Methyl ($CH_{3)}$ and bromo (Br) groups are attached to the second and fourth carbon atoms, respectively. Listing the substituents in alphabetical order gives the name 4-bromo-2-methylhexane.

? Exercise 6.5.2

Give the IUPAC name for each compound.

a. 

- 

Answers

a. 2-chloro-3-methylbutane
b. 1-bromo-2-chloro-4-methylpentane

A wide variety of interesting and often useful compounds have one or more halogen atoms per molecule. For example, methane (CH_4) can react with chlorine (Cl_2), replacing one, two, three, or all four hydrogen atoms with Cl atoms. Several halogenated products derived from methane and ethane (CH_3CH_3) are listed in Table **6.5.1**, along with some of their uses.

Table **6.5.1**: Some Halogenated Hydrocarbons

Formula	Common Name	IUPAC Name	Some Important Uses
Derived from CH_4			
CH_3Cl	methyl chloride	chloromethane	refrigerant; the manufacture of silicones, methyl cellulose, and synthetic rubber
CH_2Cl_2	methylene chloride	dichloromethane	laboratory and industrial solvent
$CHCl_3$	chloroform	trichloromethane	industrial solvent
CCl_4	carbon tetrachloride	tetrachloromethane	dry-cleaning solvent and fire extinguishers (but no longer recommended for use)
$CBrF_3$	halon-1301	bromotrifluoromethane	fire extinguisher systems
CCl_3F	chlorofluorocarbon-11 (CFC-11)	trichlorofluoromethane	foaming plastics
CCl_2F_2	chlorofluorocarbon-12 (CFC-12)	dichlorodifluoromethane	refrigerant
Derived from CH_3CH_3			
CH_3CH_2Cl	ethyl chloride	chloroethane	local anesthetic
$ClCH_2CH_2Cl$	ethylene dichloride	1,2-dichloroethane	solvent for rubber
CCl_3CH_3	methylchloroform	1,1,1-trichloroethane	solvent for cleaning computer chips and molds for shaping plastics

Chlorofluorocarbons and Fluorocarbons

Chlorofluorocarbons (**CFCs**) and **hydrochlorofluorocarbons** (**HCFCs**) are fully or partly halogenated paraffin hydrocarbons that contain only carbon (C), hydrogen (H), chlorine (Cl), and fluorine (F), produced as volatile derivative of methane, ethane, and propane. They are also commonly known by the DuPont brand name **Freon**. The most common representative is dichlorodifluoromethane (R-12 or Freon-12). Many CFCs have been widely used as refrigerants, propellants (in aerosol applications), and solvents. Because CFCs contribute to ozone depletion in the upper atmosphere, the manufacture of such compounds has been phased out under the Montreal Protocol, and they are being replaced with other products such as **hydrofluorocarbons** (HFCs)

Chlorinated or fluorinated alkenes undergo polymerization. Important halogenated polymers include polyvinyl chloride (PVC), and polytetrafluoroethene (PTFE, or Teflon). Billions of kilograms of chlorodifluoromethane are produced annually as precursor to tetrafluoroethylene, the monomer that is converted into Teflon. The production of these materials releases substantial amounts of wastes. PVC and PTFE will be discussed in more detail in Chapter 10.

Summary

- **Haloalkanes** also known as alkyl halides or halogenoalkanes, are a group of organic compounds in which one or more halogen atoms are substituted for one or more hydrogen atoms in a hydrocarbon.
- These compounds are used as dry cleaning, industrial, and laboratory solvents, coolants in refrigerators and air conditioners, and propellants in hairsprays and deodorants
- The use of haloalkanes has been greatly curtailed due to their toxicity and harmful environmental effects.
- Naming of simple haloalkanes is described.

Contributors and Attributions

-
- Marisa Alviar-Agnew (Sacramento City College)
- Libretext: The Basics of GOB Chemistry (Ball et al.)
- Wikipedia

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6.6: Alcohols, Phenols, and Ethers

Learning Objectives

- Describe the structure and properties of alcohols, ethers and phenols.
- Know the name and uses of simple alcohols, phenols and ethers.

An alcohol is an organic compound with a hydroxyl (OH) functional group on an aliphatic carbon atom. Because OH is the functional group of all alcohols, we often represent alcohols by the general formula ROH, where R is an alkyl group. Alcohols are common in nature. Most people are familiar with ethyl alcohol (ethanol), the active ingredient in alcoholic beverages, but this compound is only one of a family of organic compounds known as alcohols. The family also includes such familiar substances as cholesterol and the carbohydrates. Methanol (CH_3OH) and ethanol (CH_3CH_2OH) are the first two members of the homologous series of alcohols.

Nomenclature of Alcohols

Alcohols with one to four carbon atoms are frequently called by common names, in which the name of the alkyl group is followed by the word *alcohol*:

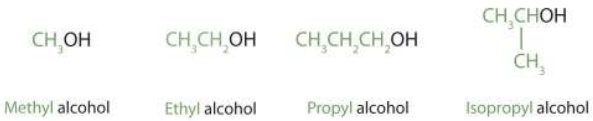
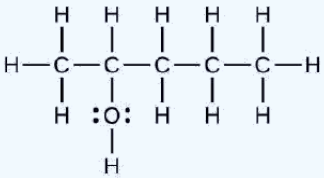


Figure **6.6.1**:left to right: methyl alcohol; ethyl alcohol; propyl alcohol; isopropyl alcohol

According to the International Union of Pure and Applied Chemistry (IUPAC), the name of an alcohol comes from the hydrocarbon from which it was derived. The final *-e* in the name of the hydrocarbon is replaced by *-ol*, and the carbon atom to which the –OH group is bonded is indicated by a number placed before the name.

Example 6.6.1: Naming Alcohols

Consider the following example. How should it be named?

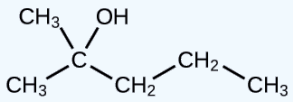


Solution

The carbon chain contains five carbon atoms. If the hydroxyl group was not present, we would have named this molecule pentane. To address the fact that the hydroxyl group is present, we change the ending of the name to *-ol*. In this case, since the –OH is attached to carbon 2 in the chain, we would name this molecule 2-pentanol.

Exercise 6.6.1

Name the following molecule:



Exercise **6.6.1**: The structure shown has a C H subscript 3 group bonded up and to the right to a C atom. The C atom is bonded down and to the right to a C H subscript 2 group. The C H subscript 2 group is bonded up and to the right to a C H subscript 2 group. The C H subscript 2 group is bonded down and to the right to a C H subscript 3 group. The second C atom (from left to right) is bonded to a C H subscript 3 group and an O H group.

Answer

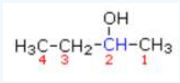
2-methyl-2-pentanol

Note

The IUPAC adopted new nomenclature guidelines in 2013 that require this number to be placed as an “infix” rather than a prefix. For example, the new name for 2-propanol would be propan-2-ol. Widespread adoption of this new nomenclature will take some time, and students are encouraged to be familiar with both the old and new naming protocols.

Example 6.6.2: Naming Alcohols

Consider the following example. How should it be named according to the guidelines adopted in 2013?



Example **6.6.2**:

Solution

The carbon chain contains four carbon atoms. If the hydroxyl group was not present, we would have named this molecule butane. To address the fact that the hydroxyl group is present, we change the ending of the name to *-ol*. In this case, since the –OH is attached to carbon 2 in the chain, we would name this molecule butan-2-ol.

Note

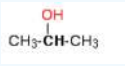
"Always place the OH on the lowest possible number for the chain."

In the previous example, if the carbon atoms were numbered from left to right then the OH would have been placed on the third carbon and the molecule would have been named butan-3-ol, but butan-2-ol is the more preferred name.

Exercise 6.6.2: Naming Alcohols

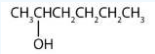
Name the following molecules according to the guidelines adopted in 2013?

a.



Exercise **6.6.2**:

b.



Exercise **6.6.2**:

Answer

a. propan-2-ol

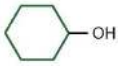
b. hexan-2-ol

Table **6.6.1** names and classifies some of the simpler alcohols. Some of the common names reflect a compound’s classification as secondary (*sec*-) or tertiary (*tert*-). These designations are not used in the IUPAC nomenclature system for alcohols. Note that there are four butyl alcohols in the table, corresponding to the four butyl groups: the butyl group ($CH_3CH_2CH_2CH_2$) discussed before, and three others:



Figure **6.6.2**: from left to right: isobutyl alcohol press; sec-butyl alcohol;tert-butyl alcohol

Table **6.6.1**: Classification and Nomenclature of Some Alcohols

Condensed Structural Formula	Common Name	IUPAC Name
CH_3OH	wood alcohol (methyl alcohol)	methanol
CH_3CH_2OH	grain alcohol (ethyl alcohol)	ethanol
$CH_3CH_2CH_2OH$	propyl alcohol	1-propanol
$(CH_3)_2CHOH$	rubbing alcohol (isopropyl alcohol)	2-propanol
$CH_3CH_2CH_2CH_2OH$	butyl alcohol	1-butanol
$CH_3CH_2CHOHCH_3$	*sec*-butyl alcohol	2-butanol
$(CH_3)_2CHCH_2OH$	isobutyl alcohol	2-methyl-1-propanol
$(CH_3)_3COH$	*tert*-butyl alcohol	2-methyl-2-propanol
	cyclohexyl alcohol	cyclohexanol

Methanol (Methyl Alcohol)

Methanol, also known as **methyl alcohol** among others, is a chemical with the formula CH_3OH (a methyl group linked to a hydroxyl group, often abbreviated MeOH). Methanol acquired the name **wood alcohol** because it was once produced chiefly by the destructive distillation of wood. Today, methanol is mainly produced industrially by hydrogenation of carbon monoxide.

$$CO_{(g)} + 2H_{2(g)} \rightarrow CH_3OH_{(l)}$$

Methanol is the simplest alcohol, consisting of a methyl group linked to a hydroxyl group. It is a light, volatile, colorless, flammable liquid with a distinctive odor similar to that of ethanol (drinking alcohol). At room temperature, it is a polar liquid. With more than 20 million tons produced annually, it is used as a fuel additive and as a precursor to other commodity chemicals, including formaldehyde, acetic acid, methyl tert-butyl ether, as well as a host of more specialized chemicals.

Ethanol (Ethyl Alcohol)

Ethanol (also called **ethyl alcohol**, **grain alcohol**, **drinking alcohol**, or simply **alcohol**) is a chemical compound, a simple alcohol with the chemical formula C_2H_6O. Its formula can be also written as $CH_3{-}CH_2{-}OH$ or C_2H_5OH (an ethyl group linked to a hydroxyl group), and is often abbreviated as **EtOH**. Ethanol is a volatile, flammable, colorless liquid with a slight characteristic odor. It is a psychoactive substance and is the principal type of alcohol found in alcoholic drinks.

Ethanol is naturally produced by the fermentation of sugars by yeasts or via petrochemical processes, and is most commonly consumed as a popular recreational drug. Ethanol is the alcohol produced by some species of yeast that is found in wine, beer, and distilled drinks. It has long been prepared by humans harnessing the metabolic efforts of yeasts in fermenting various sugars:

$$\underset{\text{glucose}}{C_6H_{12}O_6(aq)} \xrightarrow{\text{Yeast}} \underset{\text{ethanol}}{2C_2H_5OH(aq)} + 2CO_2(g)$$

Figure **6.6.3**: Fermentation of glucose to ethanol

Large quantities of ethanol (for industrial use) are synthesized from the addition reaction of water with ethylene using an acid as a catalyst:

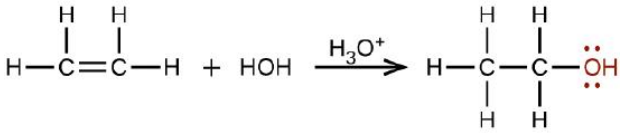


Figure **6.6.4** This reaction shows two carbons connected by a double bond, each with two bonded H atoms plus H O H arrow labeled “H subscript 3 O superscript plus” followed by two carbon atoms connected with a single bond with 5 bonded H atoms and an O H group shown in red at the right end of the molecule. The O of this group is shown with 2 pairs of electron dots.

Ethanol also has medical applications as an antiseptic and disinfectant. The compound is widely used as a chemical solvent, either for scientific chemical testing or in synthesis of other organic compounds, and is a vital substance used across many different kinds of manufacturing industries. Ethanol is also used as a clean-burning fuel source.

Toxicity of Alcohols

With respect to acute toxicity, simple alcohols have low acute toxicities. Doses of several milliliters are tolerated. For pentanols, hexanols, octanols and longer alcohols, LD50 (lethal dose, 50%) range from 2–5 g/kg (rats, oral). Methanol and ethanol are less acutely toxic. Methanol is however far more toxic than ethanol. All alcohols are mild skin irritants.

The metabolism of methanol (and ethylene glycol) is affected by the presence of ethanol, which has a higher affinity for liver alcohol dehydrogenase. In this way methanol will be excreted intact in urine.

The immediate effect of alcohol depends on the drinker's blood alcohol concentration (BAC). BAC can be different for each person depending on their age, sex, pre-existing health condition, even if they drink the same amount of alcohol.

Different BACs have different effects. Table **6.6.2** list the common effects of alcohol on the body depending on the BAC. However, tolerance varies considerably between individuals, as does individual response to a given dosage; the effects of alcohol differ widely between people. Hence in this context, BAC percentages are just estimates used for illustrative purposes.

Table **6.6.2** Blood Alcohol Levels and Effects Source: Wikipedia.

mg/dL	mM	Blood Alcohol Level % v/v	Effects
50	11	0.05%	Euphoria, talkativeness, relaxation
100	22	0.1%	Central nervous system depression, nausea, possible vomiting, impaired motor and sensory function, impaired cognition
>140	30	>0.14%	Decreased blood flow to brain
300	65	0.3%	Stupefaction, possible unconsciousness
400	87	0.4%	Possible death
500	109	>0.55%	Death

Rubbing alcohol refers to either isopropyl alcohol (propan-2-ol) or ethanol based liquids. Rubbing alcohol is undrinkable even if it is ethanol based, due to the bitterants added. Product labels for rubbing alcohol include a number of warnings about the chemical, including the flammability hazards and its intended use only as a topical antiseptic and not for internal wounds or consumption. It should be used in a well-ventilated area due to inhalation hazards. Poisoning can occur from ingestion, inhalation, absorption, or consumption of rubbing alcohol.

Multifunctional Alcohols

A **polyol** is an organic compound containing multiple hydroxyl groups. Examples of polyols discussed in this section include ethylene glycol, propylene glycol, and glycerol.

Alcohols containing two or more hydroxyl groups can be made. Examples include 1,2-ethanediol (ethylene glycol, used in antifreeze) and 1,2,3-propanetriol (glycerine, used as a solvent for cosmetics and medicines):

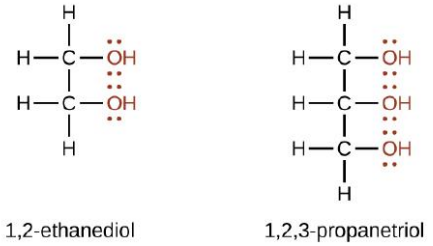


Figure **6.6.5** 1,2-ethanediol; 1,2,3-propanetriol

Ethylene glycol (IUPAC name: ethane-1,2-diol) is an organic compound with the formula $(CH_2OH)_2$. It is mainly used for two purposes, as a raw material in the manufacture of polyester fibers and for antifreeze formulations. It is an odorless, colorless, sweet-tasting, viscous liquid. Ethylene glycol is toxic. Household pets are especially susceptible to ethylene glycol poisoning from vehicle antifreeze leaks.

Figure **6.6.6** from left to right:Ethylene glycol line model; Ethylene glycol ball and stick model*Fluorescent green-dyed antifreeze is visible in the radiator header tank when car radiator cap is removed.*

Propylene glycol (IUPAC name: **propane-1,2-diol**) is a organic compound with the chemical formula $CH_3CH(OH)CH_2OH$. It is a viscous, colorless liquid which is nearly odorless but possesses a faintly sweet taste. Containing two alcohol groups, it is classed as a diol. It is miscible with a broad range of solvents, including water, acetone, and chloroform. In general, glycols are non-irritating, have very low volatility and very low toxicity.

Figure **6.6.7** *A bottle of flavored "e-liquid" for "vaping" shows propylene glycol as the main ingredient. Source: Wikipedia*



Figure **6.6.8** **Propylene glycol**

Forty-five percent of propylene glycol produced is used as chemical feedstock for the production of unsaturated polyester resins. Propylene glycol is also used in various edible items such as coffee-based drinks, liquid sweeteners, ice cream, whipped dairy products and soda.Vaporizers used for delivery of pharmaceuticals or personal-care products often include propylene glycol among the ingredients. In alcohol-based hand sanitizers, it is used as a humectant to prevent the skin from drying. Propylene glycol is used as a solvent in many pharmaceuticals, including oral, injectable and topical formulations, such as for diazepam and lorazepam which are insoluble in water. Certain formulations of artificial tears, such as Systane, use proplyene glycol as an ingredient.Propylene glycol is frequently used as a substitute for ethylene glycol in low toxicity, environmentally friendly automotive antifreeze. It is also used to winterize the plumbing systems in vacant structures.

Glycerol (/ˈɡlɪsərɒl/; also called **glycerine** or **glycerin**; see spelling differences) is a simple polyol compound. It is a colorless, odorless, viscous liquid that is sweet-tasting and non-toxic. The glycerol backbone is found in many lipids which are known as glycerides. It is widely used in the food industry as a sweetener and humectant in pharmaceutical formulations. Glycerol has three hydroxyl groups that are responsible for its solubility in water and its hygroscopic nature.

Figure **6.6.9** Glycerol ball and stick model (top) line model (bottom)

In food and beverages, glycerol serves as a humectant, solvent, and sweetener, and may help preserve foods. It is also used as filler in commercially prepared low-fat foods (e.g., cookies), and as a thickening agent in liqueurs. Glycerol and water are used to preserve certain types of plant leaves. As a sugar substitute, it has approximately 27 kilocalories per teaspoon (sugar has 20) and is

60% as sweet as sucrose. It does not feed the bacteria that form plaques and cause dental cavities.[*citation needed*] As a food additive, glycerol is labeled as E number E422. It is added to icing (frosting) to prevent it from setting too hard.

Glycerol is used in medical, pharmaceutical and personal care preparations, often as a means of improving smoothness, providing lubrication, and as a humectant. Ichthyosis and xerosis have been relieved by the topical use glycerin. It is found in allergen immunotherapies, cough syrups, elixirs and expectorants, toothpaste, mouthwashes, skin care products, shaving cream, hair care products, soaps, and water-based personal lubricants (Figure \(*PageIndex{10}*\)). In solid dosage forms like tablets, glycerol is used as a tablet holding agent.

Table \(\PageIndex{2}\) Blood Alcohol Levels and Effects Source: Wikipedia.

Figure **6.6.10** *Personal lubricants commonly contain glycerol.*

Phenols

Compounds in which an OH group is attached directly to an aromatic ring are designated ArOH and called phenols. Phenols differ from alcohols in that they are slightly acidic in water. They react with aqueous sodium hydroxide (NaOH) to form salts.

$$\mathbf{ArOH\,(aq) + NaOH\,(aq) \rightarrow ArONa\,(aq) + H_2O}$$

The parent compound, C_6H_5OH, is itself called phenol. (An old name, emphasizing its slight acidity, was *carbolic acid*.) Phenol is a white crystalline compound that has a distinctive (“hospital smell”) odor.

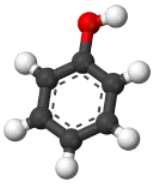


Figure **6.6.11** *Structure of phenol*



Figure **6.6.12**
Approximately two grams of phenol in glass vial. Image used with permisison from Wikipedia

To Your Health: Phenols and Us

Phenols are widely used as antiseptics (substances that kill microorganisms on living tissue) and as disinfectants (substances intended to kill microorganisms on inanimate objects such as furniture or floors). The first widely used antiseptic was phenol. Joseph Lister used it for antiseptic surgery in 1867. Phenol is toxic to humans, however, and can cause severe burns when applied to the skin. In the bloodstream, it is a systemic poison—that is, one that is carried to and affects all parts of the body. Its severe side effects led to searches for safer antiseptics, a number of which have been found.



Figure **6.6.13** *An operation in 1753, painted by Gaspare Traversi, of a surgery before antiseptics were used.*

One safer phenolic antiseptic is 4-hexylresorcinol (4-hexyl-1,3-dihydroxybenzene; resorcinol is the common name for 1,3-dihydroxybenzene, and 4-hexylresorcinol has a hexyl group on the fourth carbon atom of the resorcinol ring). It is much more powerful than phenol as a germicide and has fewer undesirable side effects. Indeed, it is safe enough to be used as the active ingredient in some mouthwashes and throat lozenges.

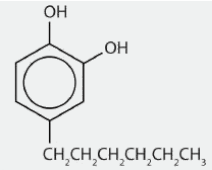


Figure **6.6.14** The compound 4-hexylresorcinol is mild enough to be used as the active ingredient in antiseptic preparations for use on the skin.

In addition to acting as an antiseptic, phenol is also a useful precursor in many chemical syntheses to produce pharmaceuticals, food preservatives, polymers, resins and adhesives. Phenolics are also present in a number of biological systems and natural products such as neurotransmitters, flavouring agents, and vitamins to name a few.

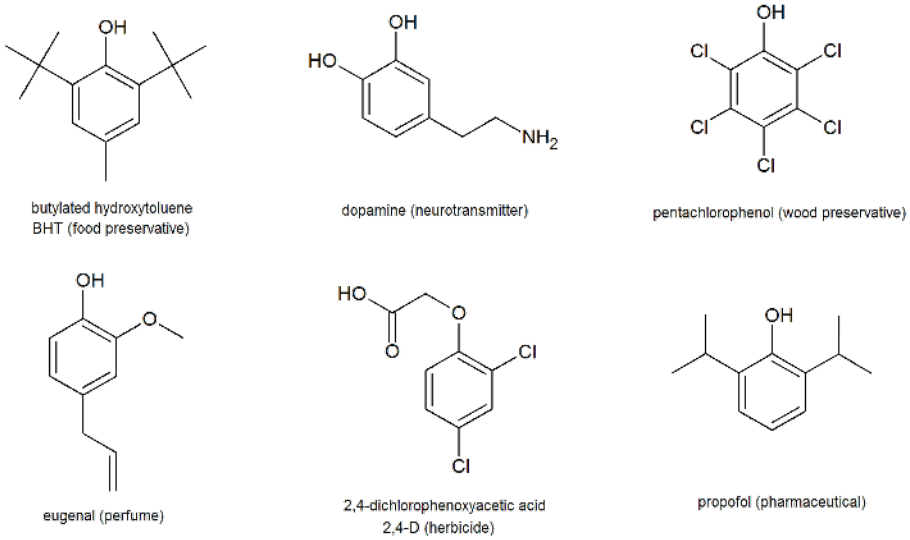


Figure **6.6.15** Top from left to right: line models of BHT; dopamine; pentachlorophenol; Bottom: eugenal; 2,4-dichlorophenoxyacetic acid; propofol

Ethers

Ethers are compounds that contain the functional group –O–. Ethers do not have a designated suffix like the other types of molecules we have named so far. In the IUPAC system, the oxygen atom and the smaller carbon branch are named as an alkoxy substituent and the remainder of the molecule as the base chain, as in alkanes. As shown in the following compound, the red symbols represent the smaller alkyl group and the oxygen atom, which would be named “methoxy.” The larger carbon branch would be ethane, making the molecule methoxyethane. Many ethers as shown below, are referred to with common names instead of the IUPAC system names. For common names, the two branches connected to the oxygen atom are named separately and followed by “ether.”

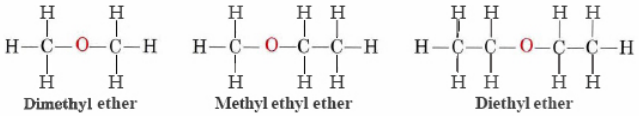


Figure **6.6.16** from left to right: Dimethyl ether; methyl ethyl ether; Diethyl ether

In the general formula for ethers, R—**O**—R, the hydrocarbon groups (R) may be the same or different.

Ether molecules have no hydrogen atom on the oxygen atom (that is, no OH group). Therefore there is no intermolecular hydrogen bonding between ether molecules, and ethers therefore have quite low boiling points for a given molar mass. Indeed, ethers have boiling points about the same as those of alkanes of comparable molar mass and much lower than those of the corresponding alcohols (Table **6.6.3**).

Table **6.6.3** Comparison of Boiling Points of Alkanes, Alcohols, and Ethers

Condensed Structural Formula	Name	Molar Mass	Boiling Point (°C)	Intermolecular Hydrogen Bonding in Pure Liquid?
$CH_3CH_2CH_3$	propane	44	–42	no
CH_3OCH_3	dimethyl ether	46	–25	no
CH_3CH_2OH	ethyl alcohol	46	78	yes
$CH_3CH_2CH_2CH_2CH_3$	pentane	72	36	no
$CH_3CH_2OCH_2CH_3$	diethyl ether	74	35	no
$CH_3CH_2CH_2CH_2OH$	butyl alcohol	74	117	yes

Ether molecules do have an oxygen atom, however, and engage in hydrogen bonding with water molecules. Consequently, an ether has about the same solubility in water as the alcohol that is isomeric with it. For example, dimethyl ether and ethanol (both having the molecular formula C_2H_6O) are completely soluble in water, whereas diethyl ether and 1-butanol (both $C_4H_{10}O$) are barely soluble in water (8 g/100 mL of water).

Diethyl ether, the most widely used compound of this class, is a colorless, volatile liquid that is highly flammable. It was first used in 1846 as an anesthetic, but better anesthetics have now largely taken its place. Diethyl ether and other ethers are presently used primarily as solvents for gums, fats, waxes, and resins. *Tertiary*-butyl methyl ether, $C_4H_9OCH_3$ (abbreviated MTBE—italicized portions of names are not counted when ranking the groups alphabetically—so butyl comes before methyl in the common name), is used as an additive for gasoline. MTBE belongs to a group of chemicals known as oxygenates due to their capacity to increase the oxygen content of gasoline.

To Your Health: Ethers as General Anesthetics

A *general anesthetic* acts on the brain to produce unconsciousness and a general insensitivity to feeling or pain. Diethyl ether ($CH_3CH_2OCH_2CH_3$) was the first general anesthetic to be used.



Figure **6.6.17** *William Morton, a Boston dentist, introduced diethyl ether into surgical practice in 1846. This painting shows an operation in Boston in 1846 in which diethyl ether was used as an anesthetic. Inhalation of ether vapor produces unconsciousness by depressing the activity of the central nervous system. Source: Painting of William Morton by Ernest Board.*

Diethyl ether is relatively safe because there is a fairly wide gap between the dose that produces an effective level of anesthesia and the lethal dose. However, because it is highly flammable and has the added disadvantage of causing nausea, it has been replaced by newer inhalant anesthetics, including the fluorine-containing compounds halothane, enflurane, and isoflurane. Unfortunately, the safety of these compounds for operating room personnel has been questioned. For example, female operating room workers exposed to halothane suffer a higher rate of miscarriages than women in the general population.

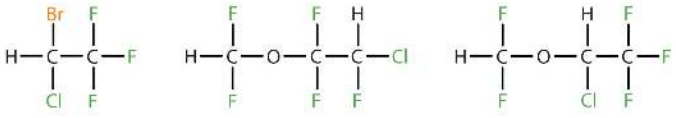
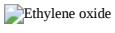


Figure 6.6.18 from left to right: halothane, enflurane, isoflurane. *These three modern, inhalant, halogen-containing, anesthetic compounds are less flammable than diethyl ether.*

A list of important ethers and their uses are given in Table 6.6.4

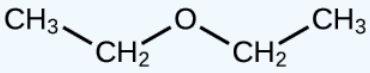
Table 6.6.4 Important Ethers and Their Uses

	Ethylene oxide	Also the simplest epoxide. Most ethylene oxide is used for synthesis of ethylene glycols (antifreeze), including diethylene glycol and triethylene glycol, that accounts for up to 75% of global consumption.
	Dimethyl ether	An aerosol spray propellant. A potential renewable alternative fuel for diesel engines with a cetane rating as high as 56–57.
	Diethyl ether	A common low boiling solvent (b.p. 34.6 °C) and an early anaesthetic. Used as starting fluid for diesel engines. Also used as a refrigerant and in the manufacture of smokeless gunpowder, along with use in perfumery.
	Dimethoxyethane(DME)	A water miscible solvent often found in lithium batteries (b.p. 85 °C):
	Dioxane	A cyclic ether and high-boiling solvent (b.p. 101.1 °C).

Example 6.6.2: classifying functional groups

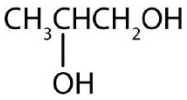
Identify the following compounds as alcohol, phenol or ether.

a.



Example 6.6.2:

b.



Example 6.6.2:

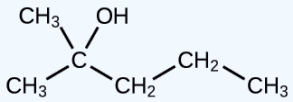
Solution

a. The compound has the general formula R—**O**—R, so it is an ether. b. The compound has two hydroxyl (–OH) groups, so it is an alcophol.

Exercise 6.6.2

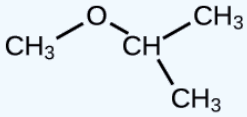
Identify the following compounds as alcohol, phenol or ether.

a.



Exercise **6.6.2**: The structure shown has a C H subscript 3 group bonded up and to the right to a C atom. The C atom is bonded down and to the right to a C H subscript 2 group. The C H subscript 2 group is bonded up and to the right to a C H subscript 2 group. The C H subscript 2 group is bonded down and to the right to a C H subscript 3 group. The second C atom (from left to right) is bonded to a C H subscript 3 group and an O H group.

b.



Exercise **6.6.2**: A molecular structure shows a C H subscript 3 group bonded up and to the right to an O atom. The O atom is bonded down and to the right to a C H group. The C H group is bonded up and to the right to a C H subscript 3 group. The C H group is also bonded down and to the right to another C H subscript 3 group.

Answer

a. alcohol b. ether

Summary

- The –OH group is the functional group of an alcohol. Various alcohols have a wide range of applications in the medical field as well as in the transportation, food, cosmetic industries.
- The name of an alcohol comes from the hydrocarbon from which it was derived.
- The –R–O–R– group is the functional group of an ether. Diethyl ether and other ethers are presently used primarily as solvents for gums, fats, waxes, and resins. Ethylene oxide in particular is used in the manufacture of ethylene glycol (antifreeze).
- Phenols are compounds in which an OH group is attached directly to an aromatic ring. Many phenols are used as antiseptics.

Contributors and Attributions

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- TextMap: The Basics of GOB Chemistry (Ball et al.)
- Marisa Alviar-Agnew (Sacramento City College)
- Wikipedia

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6.7: Aldehydes and Ketones

Learning Objectives

- Describe the structure and properties of aldehydes and ketones.
- Name common aldehydes and ketones.

Aldehydes and ketones are widespread in nature and are often combined with other functional groups. Examples of naturally occurring molecules which contain a aldehyde or ketone functional group are shown in the following two figures. The compounds in Figure **6.7.1** are found chiefly in plants or microorganisms and those in Figure **6.7.2** have animal origins. Aldehydes and ketones are known for their sweet and sometimes pungent odors. The odor from vanilla extract comes from the molecule vanillin. Likewise, benzaldehyde provides a strong scent of almonds and is this author's favorite chemical smell. Because of their pleasant fragrances aldehyde and ketone containing molecules are often found in perfumes. However, not all of the fragrances are pleasing. In particular, 2-Heptanone provides part of the sharp scent from blue cheese and (R)-Muscone is part of the musky smell from the Himalayan musk deer. Lastly, ketones show up in many important hormones such as progesterone (a female sex hormone) and testosterone (a male sex hormone). Notice how subtle differences in structure can cause drastic changes in biological activity. The ketone functionality also shows up in the anti-inflammatory steroid, Cortisone.

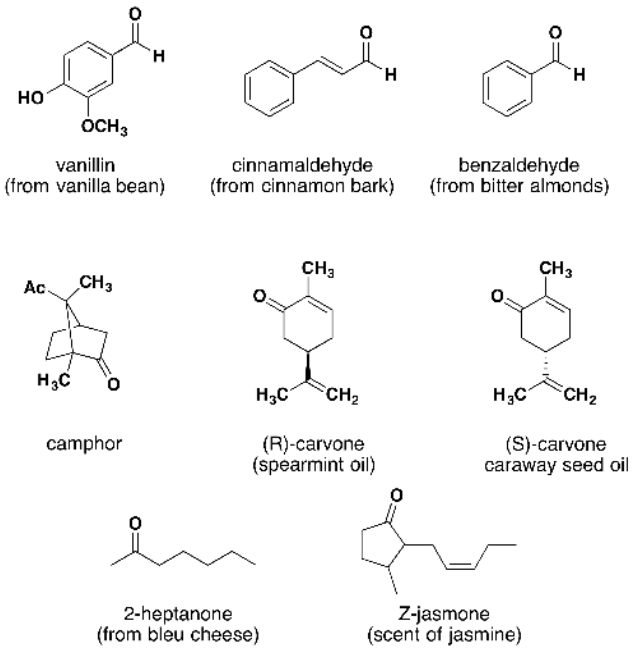


Figure **6.7.1** Aldehyde and ketone containing molecules isolated from plant sources.

Figure **6.7.1**

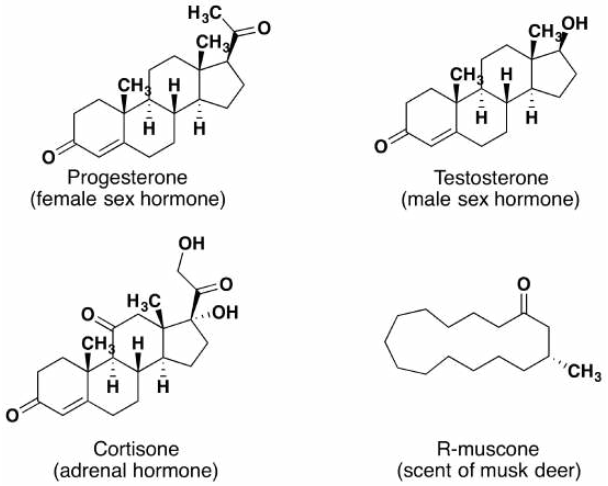


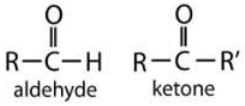
Figure **6.7.2** Aldehyde and ketone containing molecules isolated from animal sources.

Figure **6.7.1**

Aldehydes and **ketones** are two related categories of organic compounds that both contain the **carbonyl group**, shown below



The difference between aldehydes and ketones is the placement of the carbonyl group within the molecule. An **aldehyde** is an organic compound in which the carbonyl group is attached to a carbon atom at the end of a carbon chain. A **ketone** is an organic compound in which the carbonyl group is attached to a carbon atom within the carbon chain. The general formulas for each are shown below.



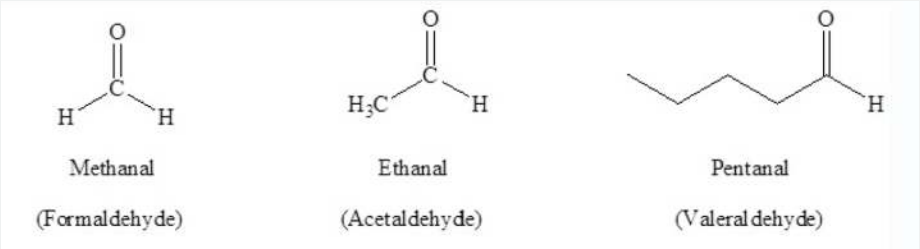
For aldehydes, the **R** group may be a hydrogen atom or any length carbon chain.

Naming Simple Aldehydes and Keones

Aldehydes are named by finding the longest continuous chain that contains the carbonyl group. Change the *-e* at the end of the name of the alkane to *-al*.

For the common name of aldehydes start with the common parent chain name and add the suffix ***-aldehyde***.

The IUPAC system names are given on top while the common name is given on the bottom in parentheses.



For ketones, **R** and **R′** must be carbon chains, of either the same or different lengths. The steps for naming ketones, followed by two examples, are shown below.

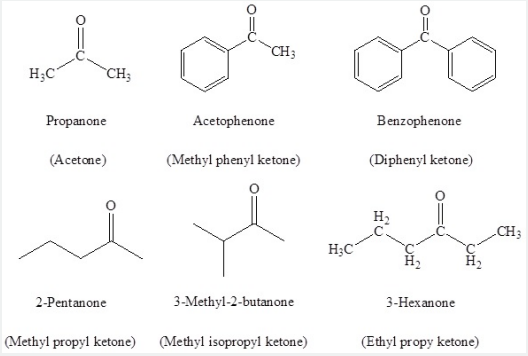
1. Name the parent compound by finding the longest continuous chain that contains the carbonyl group. Change the *-e* at the end of the name of the alkane to *-one*.
2. Number the carbon atoms in the chain in a way that the carbonyl group has the lowest possible number.

3. Add the numerical prefix into the name before the name of the ketone.
4. Use a hyphen between the number and the name of the ketone.

The common name for ketones are simply the **substituent groups listed alphabetically + *ketone*.**

Some common ketones are known by their generic names. Such as the fact that *propanone* is commonly referred to as *acetone*.

The IUPAC system names are given on top while the common name is given on the bottom in parentheses.



Top from left to right:propanone (acetone); acetophenone (methyl phenol ketone); benzophenone (diphenyl ketone; Bottom from left to right: 2 pentanone (methyl propyl ketone); 3 methyl 2 butanone (methyl isopropyl ketone); 3 hexanone (ethyl propyl ketone)

Properties of Aldehydes and Ketones

Aldehydes and ketones can work weak hydrogen bonds with water through the carbonyl oxygen atom. The lower members of both series (3 carbons or fewer) are soluble in water in all proportions. As the length of the carbon chain increases, water solubility decreases. Similar to ethers, neither aldehydes nor ketones can hydrogen bond with themselves. As a result, their boiling points are generally lower than those of alcohols. Unlike alkanes however, aldehydes and ketones are polar molecules due to the more electronegative oxygen atom. The dipole-dipole interactions are stronger than the dispersion forces present in alkanes. The boiling points of aldehydes and ketones are intermediate between those of alkanes and alcohols. For example, the boiling point of ethane is $-89°C$, ethanal is $20°C$, and ethanol is $78°C$.

Methanal, commonly known as formaldehyde, was once commonly used as a biological preservative for dead animals. In recent years formaldehyde has been shown to be a carcinogen and so has been replaced for the purpose by safer alternatives. Aldehydes are currently used in the production of resins and plastics. The simplest ketone, propanone, is commonly called acetone. Acetone is a common organic solvent that was one used in most nail polish removers, but has largely been replaced by other solvents.

Some Common Aldehydes

Formaldehyde, an aldehyde with the formula HCHO, is a colorless gas with a pungent and irritating odor. It is sold in an aqueous solution called formalin, which contains about 37% formaldehyde by weight. Formaldehyde causes coagulation of proteins, so it kills bacteria (and any other living organism) and stops many of the biological processes that cause tissue to decay. Thus, formaldehyde is used for preserving tissue specimens and embalming bodies. It is also used to sterilize soil or other materials. Formaldehyde is used in the manufacture of Bakelite, a hard plastic having high chemical and electrical resistance.

Formaldehyde is produced industrially by the catalytic oxidation of methanol according to the chemical equation:

$$2\ CH_3OH + O_2 \rightarrow 2\ CH_2O + 2\ H_2O$$

Acetaldehyde (systematic name **ethanal**) is an organic chemical compound with the formula CH_3CHO, sometimes abbreviated by chemists as MeCHO (Me = methyl). It is one of the most important aldehydes, occurring widely in nature and being produced on a large scale in industry. Acetaldehyde occurs naturally in coffee, bread, and ripe fruit, and is produced by plants.

In 2003, global production was about 1 million tonnes. Before 1962, ethanol and acetylene were the major sources of acetaldehyde. Since then, ethylene is the dominant feedstock.

The main method of production is the oxidation of ethylene by the Wacker process, which involves oxidation of ethylene using a homogeneous palladium/copper system:

$$2\ CH_2{=}CH_2 + O_2 \rightarrow 2\ CH_3CHO$$

Propionaldehyde or **propanal** is the organic compound with the formula CH_3CH_2CHO. It is a saturated 3-carbon aldehyde and is a structural isomer of acetone. It is a colorless liquid with a slightly irritating, fruity odor. **Butyraldehyde**, also known as **butanal**, is an organic compound with the formula $CH_3(CH_2)_2CHO$. This compound is the aldehyde derivative of butane. It is a colourless flammable liquid with an unpleasant smell. It is miscible with most organic solvents. A major use of butyraldehyde is in the production of bis(2-ethylhexyl) phthalate, a major plasticizer. **Benzaldehyde** (C_6H_5CHO) is an organic compound consisting of a benzene ring with a formyl substituent. It is the simplest aromatic aldehyde and one of the most industrially useful.It is a colorless liquid with a characteristic almond-like odor. The primary component of bitter almond oil, benzaldehyde can be extracted from a number of other natural sources. Synthetic benzaldehyde is the flavoring agent in imitation almond extract, which is used to flavor cakes and other baked goods

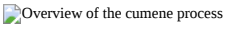
Traces of many aldehydes are found in essential oils and often contribute to their favorable odors, e.g. cinnamaldehyde, cilantro, and vanillin.

Some Common Ketones

In terms of scale, the most important ketones are acetone, methylethyl ketone, and cyclohexanone. They are also common in biochemistry, but less so than in organic chemistry in general.

Dimethyl ketone, CH_3COCH_3, commonly called acetone, is the simplest ketone. **Acetone** is a colorless liquid. Among its many uses are as a solvent for lacquer (including fingernail polish), cellulose acetate, cellulose nitrate, acetylene, plastics, and varnishes; as a paint and varnish remover; and as a solvent in the manufacture of pharmaceuticals and chemicals.

Acetone is produced directly or indirectly from propylene. Approximately 83% of acetone is produced via the cumene process; as a result, acetone production is tied to phenol production. In the cumene process, benzene is alkylated with propylene to produce cumene, which is oxidized by air to produce phenol and acetone:



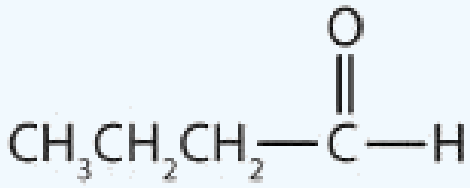
Other processes involve the direct oxidation of propylene (Wacker-Hoechst process), or the hydration of propylene to give 2-propanol, which is oxidized to acetone.

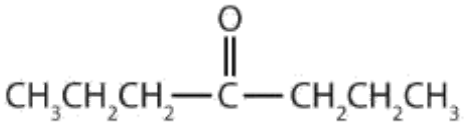
Butanone, also known as **methyl ethyl ketone** (**MEK**), is an organic compound with the formula $CH_3C(O)CH_2CH_3$. This colorless liquid ketone has a sharp, sweet odor reminiscent of butterscotch and acetone. It is produced industrially on a large scale, and also occurs in trace amounts in nature. It is soluble in water and is commonly used as an industrial solvent. Butanone is an effective and common solvent and is used in processes involving gums, resins, cellulose acetate and nitrocellulose coatings and in vinyl films. For this reason it finds use in the manufacture of plastics, textiles, in the production of paraffin wax, and in household products such as lacquer, varnishes, paint remover, a denaturing agent for denatured alcohol, glues, and as a cleaning agent. It has similar solvent properties to acetone but boils at a higher temperature and has a significantly slower evaporation rate.

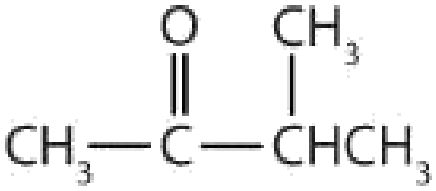
Cyclohexanone is the organic compound with the formula $(CH_2)_5CO$. The molecule consists of six-carbon cyclic molecule with a ketonefunctional group. This colorless oil has an odor reminiscent of that of acetone. Over time, samples of cyclohexanone assume a yellow color. Cyclohexanone is slightly soluble in water and miscible with common organic solvents. Billions of kilograms are produced annually, mainly as a precursor to nylon.

Example 6.7.1

Classify each compound as an aldehyde or a ketone.

a. 

b. 

c. 

Solution

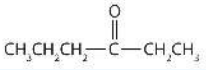
a. This compound has the carbonyl group on an end carbon atom, so it is an aldehyde.

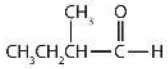
b. This compound has the carbonyl group on an interior carbon atom, so it is a ketone.

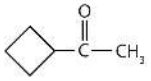
c. This compound has the carbonyl group between two alkyl groups, so it is a ketone.

? Exercise 6.7.1

Classify each compound as an aldehyde or a ketone.

a. 

b. 

c. 

Answer

a. ketone b. aldehyde c. ketone

Summary

- An aldehyde is an organic compound in which the carbonyl group is attached to a carbon atom at the end of a carbon chain.
- A ketone is an organic compound in which the carbonyl group is attached to a carbon atom within the carbon chain.The common names of aldehydes are taken from the names of the corresponding carboxylic acids: formaldehyde, acetaldehyde, and so on. The common names of ketones, like those of ethers, consist of the names of the groups attached to the carbonyl group, followed by the word *ketone*.
- Stem names of aldehydes and ketones are derived from those of the parent alkanes, using an *-al* ending for an aldehydes and an *-one* ending for a ketone.

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-
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6.8: Carboxylic Acids and Esters

Learning Objectives

- Describe the structure and properties of carboxylic acids and esters.
- Name common carboxylic acids and esters.

The odor of vinegar is caused by the presence of acetic acid, a carboxylic acid, in the vinegar. The odor of ripe bananas and many other fruits is due to the presence of esters, compounds that can be prepared by the reaction of a carboxylic acid with an alcohol. Because esters do not have hydrogen bonds between molecules, they have lower vapor pressures than the alcohols and carboxylic acids from which they are derived.

Both carboxylic acids and esters contain a carbonyl group with a second oxygen atom bonded to the carbon atom in the carbonyl group by a single bond. In a carboxylic acid, the second oxygen atom also bonds to a hydrogen atom. In an ester, the second oxygen atom bonds to another carbon atom. The names for carboxylic acids and esters include prefixes that denote the lengths of the carbon chains in the molecules and are derived following nomenclature rules similar to those for inorganic acids and salts (see these examples):

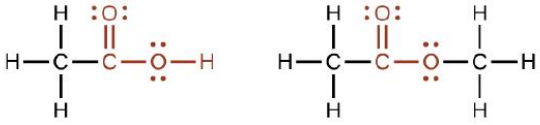


Figure **6.8.1** Two structures are shown. The first structure is labeled, “ethanoic acid,” and, “acetic acid.” This structure indicates a C atom to which H atoms are bonded above, below and to the left. To the right of this in red is a bonded group comprised of a C atom to which an O atom is double bonded above. To the right of the red C atom, an O atom is bonded which has an H atom bonded to its right. Both O atoms have two sets of electron dots. The second structure is labeled, “methyl ethanoate,” and, “methyl acetate.” This structure indicates a C atom to which H atoms are bonded above, below and to the left. In red, bonded to the right is a C atom with a double bonded O atom above and a single bonded O atom to the right. To the right of this last O atom in black is another C atom to which H atoms are bonded above, below and to the right. Both O atoms have two pairs of electron dots.

The functional groups for an acid and for an ester are shown in red in these formulas.

Carboxylic Acids

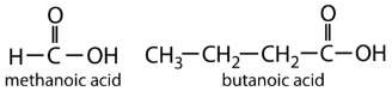
Carboxylic acids occur widely in nature, often combined with alcohols or other functional groups, as in fats, oils, and waxes. They are components of many foods, medicines, and household products (Figure **6.8.1**). Not surprisingly, many of them are best known by common names based on Latin and Greek words that describe their source.



Figure 6.8.2 Carboxylic acids occur in many common household items. (a) Vinegar contains acetic acid, (b) aspirin is acetylsalicylic acid, (c) vitamin C is ascorbic acid, (d) lemons contain citric acid, and (e) spinach contains oxalic acid. © Thinkstock



The carboxyl group contains the C=O of the carbonyl group, with the carbon atom also being bonded to a hydroxyl (–OH) group. A **carboxylic acid** is an organic compound that contains the carboxyl functional group. The general formula for a carboxylic acid can be abbreviated as R–COOH. The carbon atom of the carboxyl group may be attached to a hydrogen atom or to a carbon chain. The naming of a carboxylic acid is as follows: Name the parent compound by finding the longest continuous chain that contains the carboxyl group. Change the *-e* at the end of the name of the alkane to *-oic acid*.



Carboxylic acids are weak acids, meaning they are not 100% ionized in water. Generally only about 1% of the molecules of a carboxylic acid dissolved in water are ionized at any given time. The remaining molecules are undissociated in solution.

We prepare carboxylic acids by the oxidation of aldehydes or alcohols whose –OH functional group is located on the carbon atom at the end of the chain of carbon atoms in the alcohol:

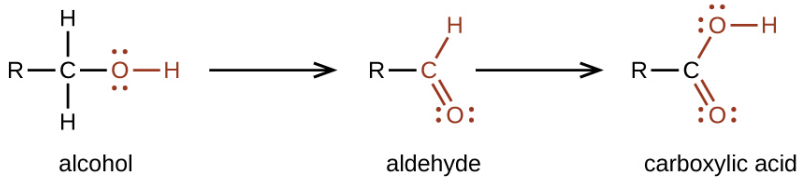
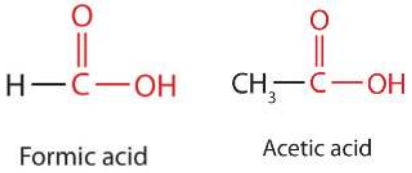


Figure **6.8.3** A chemical reaction with two arrows is shown. On the left, an alcohol, indicated with a C atom to which an R group is bonded to the left, H atoms are bonded above and below, and in red, a single bonded O atom with an H atom bonded to the right is shown. Following the first reaction arrow, an aldehyde is shown. This structure is represented with an R group bonded to a red C atom to which an H atom is bonded above and to the right, and an O atom is double bonded below and to the right. Appearing to the right of the second arrow, is a carboxylic acid comprised of an R group bonded to a C atom to which, in red, an O atom is single bonded with an H atom bonded to its right side. A red O is double bonded below and to the right. All O atoms have two pairs of electron dots.

The simplest carboxylic acid, formic acid (HCOOH, methanoic acid), was first obtained by the distillation of ants (Latin *formica*, meaning “ant”). The bites of some ants inject formic acid, and the stings of wasps and bees contain formic acid (as well as other poisonous materials).

The next higher homolog is acetic acid (CH_3COOH, ethanoic acid), which is made by fermenting cider and honey in the presence of oxygen. This fermentation produces vinegar, a solution containing 4%–10% acetic acid, plus a number of other compounds that add to its flavor. Acetic acid is probably the most familiar weak acid used in educational and industrial chemistry laboratories.



Pure acetic acid solidifies at 16.6°C, only slightly below normal room temperature. In the poorly heated laboratories of the late 19th and early 20th centuries in northern North America and Europe, acetic acid often “froze” on the storage shelf. For that reason, pure acetic acid (sometimes called concentrated acetic acid) came to be known as *glacial acetic acid*, a name that survives to this day.

The third homolog, propionic acid (CH_3CH_2COOH, propionic acid), is seldom encountered in everyday life. The fourth homolog, butyric acid ($CH_3CH_2CH_2COOH$), is one of the most foul-smelling substances imaginable. It is found in rancid butter and is one of the ingredients of body odor. By recognizing extremely small amounts of this and other chemicals, bloodhounds are able to track fugitives.

Many carboxylic acids occur naturally in plants and animals. Citrus fruits such as oranges and lemons contain citric acid (Figure **6.8.4**). Ethanoic and citric acids are frequently added to foods to give them a tart flavor.

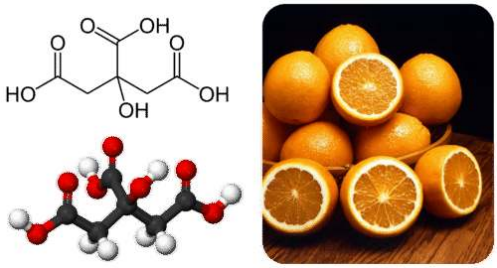
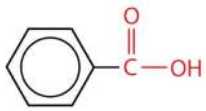


Figure **6.8.4**: Citric acid is a large carboxylic acid with three ionizable hydrogen atoms. It is found in citrus fruits and gives them their sour or tart flavor.

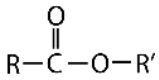
Benzoic, propanoic, and sorbic acids are used as food preservatives because of their ability to kill microorganisms that can lead to spoilage. Methanoic and ethanoic acids are widely used in industry as starting points for the manufacture of paints, adhesives, and coatings.



Benzoic acid

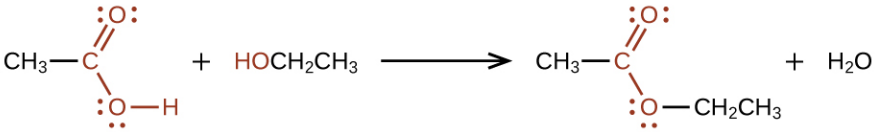
Esters: The Sweet Smell of RCOOR'

An **ester** is an organic compound that is a derivative of a carboxylic acid in which the hydrogen atom of the hydroxyl group has been replaced with an alkyl group. The structure is the product of a carboxylic acid (the **R**-portion) and an alcohol (the **R′**-portion). The general formula for an ester is shown below.



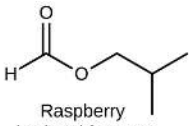
The **R** group can either be a hydrogen or a carbon chain. The **R′** group must be a carbon chain since a hydrogen atom would make the molecule a carboxylic acid.

Esters are produced by the reaction of acids with alcohols. For example, the ester ethyl acetate, $CH_3CO_2CH_2CH_3$, is formed when acetic acid reacts with ethanol:

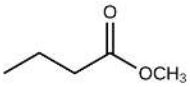


acetic acid ethanol ethyl acetate

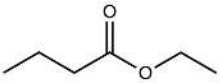
Figure **6.8.5**). Once a flower or fruit has been chemically analyzed, flavor chemists can attempt to duplicate the natural odor or taste. Both natural and synthetic esters are used in perfumes and as flavoring agents.A chemical reaction is shown. On the left, a C H subscript 3 group bonded to a red C atom. The C atom forms a double bond with an O atom which is also in red. The C atom is also bonded to an O atom which is bonded to an H atom, also in red. A plus sign is shown, which is followed by H O C H subscript 2 C H subscript 3. The H O group is in red. Following a reaction arrow, a C H subscript 3 group is shown which is bonded to a red C atom with a double bonded O atom and a single bonded O. To the right of this single bonded O atom, a C H subscript 2 C H subscript 3 group is attached and shown in black. This structure is followed by a plus sign and H subscript 2 O. The O atoms in the first structure on the left and the structure following the reaction arrow have two pairs of electron dots.



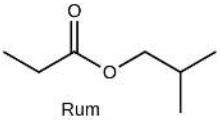
Raspberry
iso-butyl formate



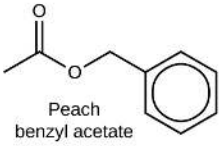
Apple
butyl acetate



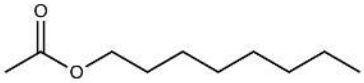
Pineapple
ethyl butyrate



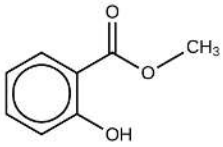
Rum
propyl isobutyrate



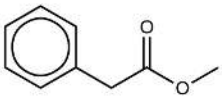
Peach
benzyl acetate



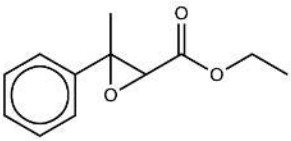
Orange
octyl acetate



Wintergreen
methyl salicylate



Honey
methyl phenylacetate



Strawberry
ethyl methylphenylglycidate

Figure **6.8.6** Esters are responsible for the odors associated with various plants and their fruits. There are nine structures represented in this figure. The first is labeled, “raspberry,” and, “iso-butyl formate.” It shows an H atom with a line going up and to the right which then goes down and to the right. It goes up and to the right again and down and to the right and up and to the right. At the first peak is a double bond to an O atom. At the first trough is an O atom. At the second trough, there is a line going straight down. The second is labeled, “apple,” and, “butyl acetate.” There is a line that goes up and to the right, down and to the right, up and to the right, and down and to the right. At the second peak is a double bond to an O atom. At the end, on the right is O C H subscript 3. The third is labeled, “pineapple,” and, “ethyl butyrate.” It is a line that goes up and to the right, down and to the right, up and to the right, down and to the right, up and to the right, and down and to the right. At the second peak is a double bond to an O atom and at the second trough is an O atom. The fourth is labeled, “rum,” and “propyl isobutyrate.” It shows a line that goes down and to the right, up and to the right, down and to the right, up and to the right, down and to the right and up and to the right. The first complete peak has a double bond to an O atom and the second trough has an O atom. The fifth is labeled, “peach,” and “benzyl acetate.” It shows a line that goes up and to the right, down and to the right, up and to the right and down and to the right. This line connects to a hexagon with a circle inside it. The first peak has a double bond to an O atom and the first trough has an O atom. The sixth is labeled, “orange,” and, “octyl acetate.” It shows a line that goes up and to the right and down and to the right and up and to the right and down and to the right and up and to the right and down and to the right and up and to the right and down and to the right and up and to the right and down and to the right and up and to the right and down and to the right. The first peak has a double bond to an O atom and the first complete trough has and an O atom. The seventh is labeled, “wintergreen,” and “methyl salicylate.” It shows a hexagon with a circle inside of it. On the right, is a bond down and to the right to an O H group. On the right is a bond to a line that goes up and to the right and down and two the right and up and to the right. At the first peak is a double bond to an O atom, the next trough shows and O atom and at the end of the line is a C H subscript 3 group. The eighth is labeled, “honey,” and “methyl phenylacetate.” It shows a hexagon with a circle inside of it. It shows it connecting to a line on the right that goes down and to the right then up and to the right and down and to the right and up and to the right. At the first peak that is not part of the hexagon is a double bond to an O atom. At the last trough is an O atom. The ninth is labeled, “strawberry,” and “ethyl methylphenylglycidate.” This shows a hexagon with a circle inside of it. On the right, it connects to a line that goes up and to the right and down and to the right and up and to the right and down and to the right and up and to the right and down and to the right. At the first peak is a line that extends above and below. Below, it connects to an O atom. At the next trough, the line extends down and to the left to the same O atom. At the next peak is a double bond to an O atom and at the next trough is an O atom.

Chemistry Is Everywhere: Esters, Fragrances, and Flavorings

Esters are very interesting compounds, in part because many have very pleasant odors and flavors. (Remember, never taste anything in the chemistry lab!) Many esters occur naturally and contribute to the odor of flowers and the taste of fruits. Other esters are synthesized industrially and are added to food products to improve their smell or taste; it is likely that if you eat a product whose ingredients include artificial flavorings, those flavorings are esters. Here are some esters and their uses, thanks to their odors, flavors, or both:

Table **6.8.1**: Esters, Fragrances, and Flavorings

Ester	Tastes/Smells Like	Ester	Tastes/Smells Like
allyl hexanoate	pineapple	isobutyl formate	raspberry
benzyl acetate	pear	isobutyl acetate	pear
butyl butanoate	pineapple	methyl phenylacetate	honey
ethyl butanoate	banana	nonyl caprylate	orange
ethyl hexanoate	pineapple	pentyl acetate	apple
ethyl heptanoate	apricot	propyl ethanoate	pear
ethyl pentanoate	apple	propyl isobutyrate	rum

Among the most important of the natural esters are fats (such as lard, tallow, and butter) and oils (such as linseed, cottonseed, and olive oils), which are esters of the trihydroxyl alcohol glycerine, $C_3H_5(OH)_3$, with large carboxylic acids, such as palmitic acid, $CH_3(CH_2)_{14}CO_2H$, stearic acid, $CH_3(CH_2)_{16}CO_2H$, and oleic acid, $\mathbf{CH_3(CH_2)_7CH=CH(CH_2)_7CO_2H}$. Oleic acid is an unsaturated acid; it contains a $\mathbf{C=C}$ double bond. Palmitic and stearic acids are saturated acids that contain no double or triple bonds.

Note

Fats and vegetable oils are esters of long-chain fatty acids and glycerol. Esters of phosphoric acid are of the utmost importance to life.

Esters are common solvents. Ethyl acetate is used to extract organic solutes from aqueous solutions—for example, to remove caffeine from coffee. It also is used to remove nail polish and paint. Cellulose nitrate is dissolved in ethyl acetate and butyl acetate to form lacquers. The solvent evaporates as the lacquer “dries,” leaving a thin film on the surface. High boiling esters are used as softeners (plasticizers) for brittle plastics.

Summary

- A carboxylic acid is an organic compound that contains the carboxyl functional group.
- The general formula for a carboxylic acid can be abbreviated as $\mathbf{R{-}COOH}$.
- Many carboxylic acids are used in the food and beverage industry for flavoring and/or as preservatives.
- An ester has an OR group attached to the carbon atom of a carbonyl group.
- Fats and vegetable oils are esters of long-chain fatty acids and glycerol.
- Esters occur widely in nature and generally have pleasant odors and are often responsible for the characteristic fragrances of fruits and flowers.

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6.9: Nitrogen-Containing Compounds- Amines and Amides

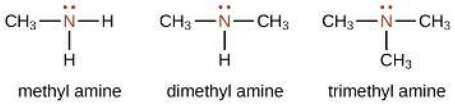
Learning Objectives

- Describe the structure and properties of amines and amides.
- Name simple amines and amides.

The addition of nitrogen into an organic framework leads to two families of molecules. Compounds containing a nitrogen atom bonded in a hydrocarbon framework are classified as amines. Compounds that have a nitrogen atom bonded to one side of a carbonyl group are classified as amides.

Amines

An **amine** is an organic compound that can be considered to be a derivative of ammonia (NH_3). Amines are molecules that contain carbon-nitrogen bonds. Amines are named by naming the alkyl groups attached to the nitrogen atom, followed by the suffix *-amine* as illustrated here for a few simple examples:



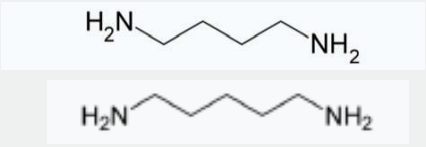
The name of larger molecules involve the class-identifying suffix *–ine* as you will see later in this section(e.g. caffeine and nicotine).

Methylamine and ethylamine are gases at room temperature, while larger amines are liquids. As with other organic compounds that form hydrogen bonds, water solubility is reflected in the length of the carbon chains. Smaller amines are soluble, while larger ones are less soluble.

Amines generally have rather pungent or noxious odors. Ammonia can be considered the simplest amine and has a very distinctive odor. Methylamine has an unpleasant odor associated with dead fish. Amines are often formed biologically during the breakdown of proteins in animal cells, and so many have the smell of death and decay. Putrescine and cadaverine are two such amines and are aptly named for their foul odors. The toxins which many animals use as a form of defense are frequently amines. Amines are used industrially as dyes and in many drugs.

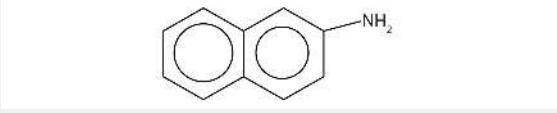
To Your Health: Amines in Death and Life

Amines have “interesting” odors. The simple ones smell very much like ammonia. Higher aliphatic amines smell like decaying fish. Or perhaps we should put it the other way around: Decaying fish give off odorous amines. The stench of rotting fish is due in part to two diamines: putrescine and cadaverine. They arise from the decarboxylation of ornithine and lysine, respectively, amino acids that are found in animal cells.



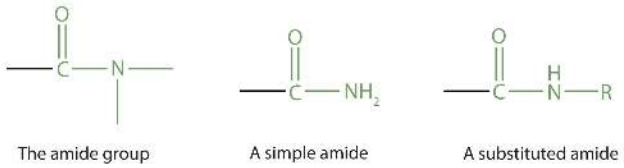
(Figure **6.9.1**) Putrescine(left) Cadaverine (right)

Aromatic amines generally are quite toxic. They are readily absorbed through the skin, and workers must exercise caution when handling these compounds. Several aromatic amines, including β-naphthylamine, are potent carcinogens.



Amides

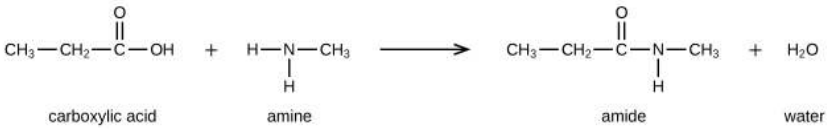
The amide functional group has an nitrogen atom attached to a carbonyl carbon atom. If the two remaining bonds on the nitrogen atom are attached to hydrogen atoms, the compound is a *simple amide*. If one or both of the two remaining bonds on the atom are attached to alkyl or aryl groups, the compound is a *substituted amide*.



Simple amides are named as derivatives of carboxylic acids. The *-ic* ending of the common name or the *-oic* ending of the International Union of Pure and Applied Chemistry (IUPAC) name of the carboxylic acid is replaced with the suffix *-amide*.



Amides can be produced when carboxylic acids react with amines or ammonia in a process called amidation. A water molecule is eliminated from the reaction, and the amide is formed from the remaining pieces of the carboxylic acid and the amine (note the similarity to formation of an ester from a carboxylic acid and an alcohol discussed in the previous section):



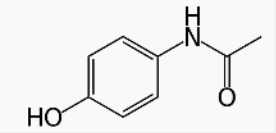
(Figure **6.9.2**) reaction between carboxylic acid and amine to form amide and water

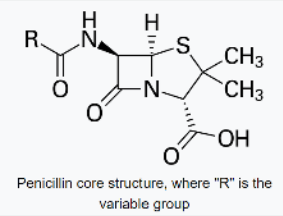
The reaction between amines and carboxylic acids to form amides is biologically important. It is through this reaction that amino acids (molecules containing both amine and carboxylic acid substituents) link together in a polymer to form proteins.

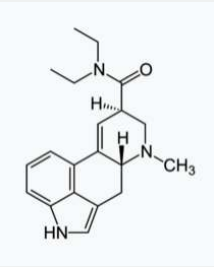
> The carbonyl carbon-to-nitrogen bond is called an *amide linkage*. This bond is quite stable and is found in the repeating units of protein molecules, where it is called a *peptide linkage*.

Amides are pervasive in nature and technology as structural materials. The amide linkage is easily formed, confers structural rigidity, and resists hydrolysis. Nylons are polyamides, as are the very resilient materials Aramid, Twaron, and Kevlar. Amide linkages constitute a defining molecular feature of proteins, the secondary structure of which is due in part to the hydrogen bonding abilities of amides. Amide linkages in a biochemicalcontext are called peptide bonds when they occur in the main chain of a protein and isopeptide bonds when they occur to a side-chain of the protein. Proteins can have structural roles, such as in hair or spider silk, but also nearly all enzymes are proteins. Low molecular weight amides, such as dimethylformamide ($HC(O)N(CH_3)_2$), are common solvents. Many drugs are amides, including paracetamol, penicillin and LSD. Moreover, plant *N*-alkylamides have a wide range of biological functionalities.

Drugs with the Amide Group







(Figure **6.9.3**) Paracetamol (acetaminophen) LSD (Lysergic diethylamide)

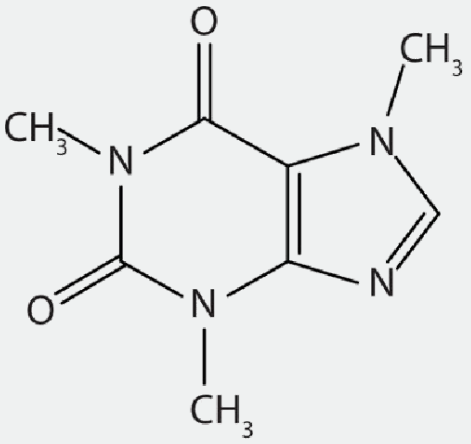
Heterocyclic Compounds: Alkaloids and Others

Looking back at the various cyclic hydrocarbons discussed previously, we see that all the atoms in the rings of these compounds are carbon atoms. In other cyclic compounds, called **heterocyclic compounds** (Greek *heteros*, meaning "other"), nitrogen, oxygen, sulfur, or some other atom is incorporated in the ring. Many heterocyclic compounds are important in medicine and biochemistry. Some compose part of the structure of the nucleic acids, which in turn compose the genetic material of cells and direct protein synthesis.

Many heterocyclic amines occur naturally in plants. Like other amines, these compounds are basic. Such a compound is an **alkaloid**, a name that means "like alkalis." Many alkaloids are physiologically active, including the familiar drugs caffeine, nicotine, and cocaine.

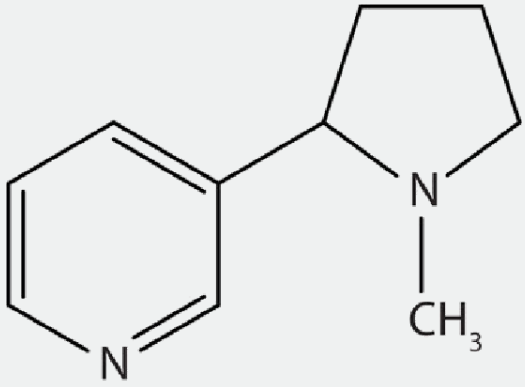
To Your Health: Three Well-Known Alkaloids

Caffeine is a stimulant found in coffee, tea, and some soft drinks. Its mechanism of action is not well understood, but it is thought to block the activity of adenosine, a heterocyclic base that acts as a neurotransmitter, a substance that carries messages across a tiny gap (synapse) from one nerve cell (neuron) to another cell. The effective dose of caffeine is about 200 mg, corresponding to about two cups of strong coffee or tea.



Caffeine

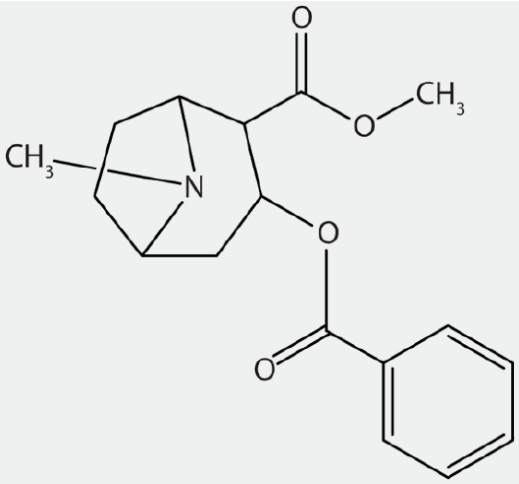
Nicotine acts as a stimulant by a different mechanism; it probably mimics the action of the neurotransmitter acetylcholine. People ingest this drug by smoking or chewing tobacco. Its stimulant effect seems transient, as this initial response is followed by depression. Nicotine is highly toxic to animals. It is especially deadly when injected; the lethal dose for a human is estimated to be about 50 mg. Nicotine has also been used in agriculture as a contact insecticide.



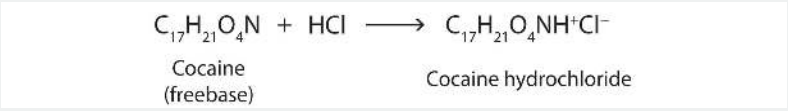
Nicotine

Cocaine acts as a stimulant by preventing nerve cells from taking up dopamine, another neurotransmitter, from the synapse. High levels of dopamine are therefore available to stimulate the pleasure centers of the brain. The enhancement of dopamine action is thought to be responsible for cocaine's "high" and its addictive properties. After the binge, dopamine is depleted in less than an hour. This leaves the user in a pleasureless state and (often) craving more cocaine.

Cocaine is used as the salt cocaine hydrochloride and in the form of broken lumps of the free (unneutralized) base, which is called *crack cocaine*.



Cocaine



Because it is soluble in water, cocaine hydrochloride is readily absorbed through the watery mucous membranes of the nose when it is snorted. Crack cocaine is more volatile than cocaine hydrochloride. It vaporizes at the temperature of a burning cigarette. When smoked, cocaine reaches the brain in 15 s.

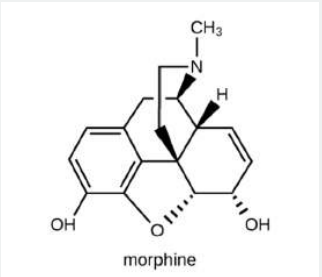
Morphine and Heroin

Morphine, a strong narcotic used to relieve pain, contains two hydroxyl functional groups, located at the bottom of the

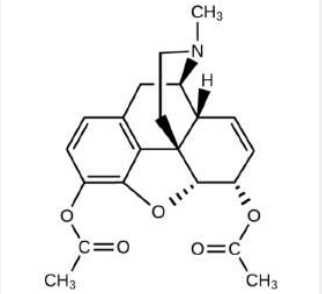


Figure **6.9.4** Poppies can be used in the production of opium, a plant latex that contains morphine from which other opiates, such as heroin, can be synthesized. (credit: Karen Roe)

molecule in this structural formula. Changing one of these hydroxyl groups to a methyl ether group forms codeine, a less potent drug used as a local anesthetic. If both hydroxyl groups are converted to esters of acetic acid, the powerfully addictive drug heroin results (Figure **6.9.4**).



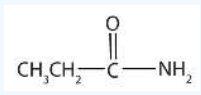
morphine

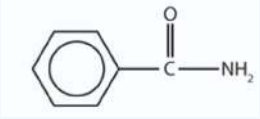


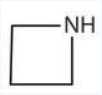
heroin

Example 6.9.1: Amines and Amides

Identify whether each compound is an amide or an amine.

a. 

b. 

c. 

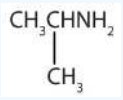
Solutions

a. The compound has the $CONH_2$ functional group so it is an amide.

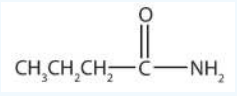
b. The compound has the $CONH_2$ functional group so it is an amide.

c. The compound has the NH functional group so it is an amine.

? Exercise 6.9.1

a. 

b. $CH_3CH_2CH_2CH_2CH_2CH_2NH_2$

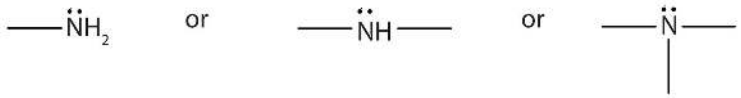
c. 

Answer

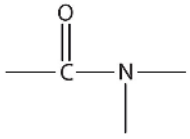
a. amine b. amine c. amide

Summary

- An amine is a derivative of ammonia in which one, two, or all three hydrogen atoms are replaced by hydrocarbon groups. The



amine functional group is as follows:
- Amines are named by naming the alkyl groups attached to the nitrogen atom, followed by the suffix *-amine*.
- Amides have a general structure in which a nitrogen atom is bonded to a carbonyl carbon atom.



(Figure **6.9.5**) Amide

- Like amines, various nomenclature rules may be used to name amides, but all include use of the class-specific suffix *-amide*:
- Heterocyclic amines are cyclic compounds with one or more nitrogen atoms in the ring.

Contributors and Attributions

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6.10: Organic Reactions

Learning Outcomes

- Identify and describe substitution, elimination, addition, hydrolysis, and condensation reactions.
- Predict products of each reaction type.
- Predict products of hydration reactions based on Markovnikov's rule.
- Explain why condensation reactions are also called dehydration reactions.
- Define "polymer".

Organic reactions require the breaking of strong covalent bonds, which takes a considerable input of energy. In order for relatively stable organic molecules to react at a reasonable rate, they often must be modified with the use of highly reactive materials or in the presence of a catalyst. In this lesson, you will learn about several general categories of organic reactions.

Substitution Reactions

A **substitution reaction**, which is the same as a single replacement reaction in inorganic reactions, *is a reaction in which one or more atoms in a molecule are replaced with another atom or group of atoms.* Alkyl halides are formed by the substitution of a halogen atom for a hydrogen atom. When methane reacts with chlorine gas, ultraviolet light can act as a catalyst for the reaction.

$$\mathrm{CH_4\,(g) + Cl_2\,(g) \overset{\text{UV light}}{\rightarrow} CH_3Cl\,(g) + HCl\,(g)} \tag{6.10.1}$$

The reaction produces chloromethane and hydrogen chloride. When the mixture is allowed to react for longer periods of time, further substitution reactions may occur.

$$\mathrm{CH_3Cl\,(g) + Cl_2\,(g) \overset{\text{UV light}}{\rightarrow} CH_2Cl_2\,(g) + HCl\,(g)} \tag{6.10.2}$$

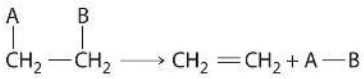
The product above is dichloromethane. Further substitution products trichloromethane and tetrachloromethane, commonly called carbon tetrachloride. A mixture of products occurs in the reaction, with the relative amounts dependent upon the time that the reaction is allowed to proceed. Chlorofluorocarbons are produced by reacting chloroalkanes with **HF**, because the fluorine atom makes a stronger bond to the carbon atom than chlorine does.

$$\mathrm{CCl_4\,(g) + HF\,(g) \overset{SbF_5}{\rightarrow} CCl_3F\,(g) + HCl\,(g)} \tag{6.10.3}$$

The fluorine atom substitutes for a chlorine atom in the reaction.

Elimination Reactions

An **elimination reaction** involves the removal of adjacent atoms from a molecule. This results in the formation of a multiple bond and the release of a small molecule, so they are called elimination reactions. They have the general form



A typical example is the conversion of ethyl chloride to ethylene:

$$\mathrm{CH_3CH_2Cl \rightarrow CH_2 = CH_2 + HCl} \tag{6.10.4}$$

Much of the approximately 26 million tons of ethylene produced per year in the United States is used to synthesize plastics, such as polyethylene. In the above reaction, the A–B molecule eliminated is HCl, whose components are eliminated as H^+ from the carbon atom on the left and Cl^- from the carbon on the right. When an acid is produced, as occurs here, the reaction is generally carried out in the presence of a base (such as NaOH) to neutralize the acid. Other elimination reactions will produce H_2, X_2 (where X = halogen), or H_2O. These reactions are often referred to by more descriptive terms such as dehydrogenation (removing hydrogen) or dechlorination (removing chlorine).

Addition Reactions

An **addition reaction** *is a reaction in which an atom or molecule is added to an unsaturated molecule, making a single product.* An addition reaction can often be thought of as adding a molecule across the double bond of an alkene or across the triple bond of an alkyne. Knowing that "ation" means to add, the specific names of these reactions, such as hydrogenation, hydration, or chlorination, should make sense. Note that hydrogenation (adding H_2) and hydration (adding H_2O) are very different processes.

One type of addition reaction is called hydrogenation. **Hydrogenation** *is a reaction that occurs when molecular hydrogen is added to an alkene to produce an alkane* or *hydrogen is added to an alkyne to produce an alkene or alkane.* The reaction is typically performed with the use of a transition metal catalyst. For example, ethene reacts with hydrogen to form ethane.

$$\mathrm{CH_2{=}CH_2\,(g) + H_2\,(g) \xrightarrow{Pt} CH_3CH_3\,(g)} \tag{6.10.5}$$

Note that the hydrogenation reaction is also a redox reaction. Ethene is reduced, because the oxidation numbers of the carbon atoms change from -2 to -3 as a result of the reaction.

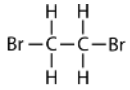
Vegetable oils consist of long carbon chains with carboxyl groups on the end; these molecules are referred to as fatty acids. The carbon chains of the fatty acids in vegetable oils are unsaturated, usually containing multiple double bonds. When hydrogen gas is blown through a sample of the oil, hydrogen atoms add across the double bonds. This conversion changes the substance from a liquid oil into a solid fat. The "hydrogenated" on a food product is an indication that oil (liquid) has been converted into fat (solid) by this process. Margarine is manufactured from unsaturated vegetable oil in this way by hydrogenating some of the double bonds making it a "partially hydrogenated vegetable oil".

Addition reactions are also useful ways to introduce a new functional group into an organic molecule. Alkyl halides can be produced from an alkene by the addition of either the elemental halogen or the hydrogen halide. A monosubstituted alkyl halide can be produced by the addition of a hydrogen halide to an alkene. Shown below is the formation of chloroethane.

$$\mathrm{CH_2{=}CH_2\,(g) + HCl\,(g) \rightarrow CH_3CH_2Cl\,(g)} \tag{6.10.6}$$

When the reactant is the diatomic halogen, the product is a disubstituted alkyl halide as in the addition of bromine to ethene.

$$\mathrm{CH_2{=}CH_2\,(g) + Br_2\,(l) \rightarrow CH_2BrCH_2Br\,(g)} \tag{6.10.7}$$



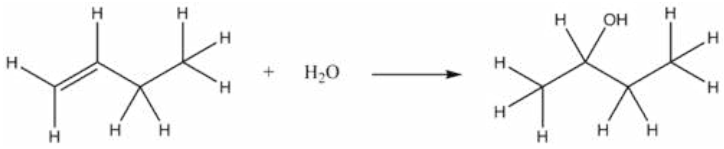
1,2-dibromoethane

The addition of bromine to an unknown organic compound can be used as a test for unsaturation in the compound. Bromine has a distinctive brownish-orange color, while most bromoalkanes are colorless. When bromine is slowly added to a solution of the compound, the orange color will fade if it undergoes an addition reaction to produce an alkyl halide. If the orange color remains, then the original compound was already saturated, and no reaction occurred.

A **hydration reaction** *is a reaction in which water is added to an alkene*. Hydration reactions can take place when the alkene and water are heated to near $\mathbf{100°C}$ in the presence of a strong acid, which acts as a catalyst. Shown below is the hydration of ethene to produce ethanol.

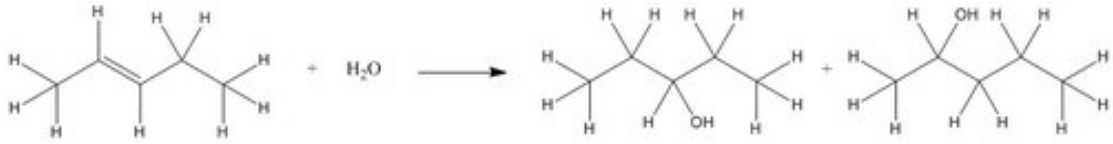
$$\mathrm{CH_2{=}CH_2\,(g) + H_2O\,(l) \rightarrow CH_3CH_2OH\,(g)} \tag{6.10.8}$$

Unlike addition reactions involving $\mathbf{H_2}$ or $\mathbf{Br_2}$, the addition of water can have two possible products because an $\mathbf{-H}$ and an $\mathbf{-OH}$ are being added to the carbons in the double bond. **Markovnikov's rule** helps predict the main product in a hydration reaction. The rule states that the hydrogen atom from water will add to the carbon that originally had more hydrogen atoms. For example, look at the hydration of 1-butene.



https://chem.libretexts.org/@go/page/460393

Note that the first carbon in 1-butene started with two hydrogen atoms and the second carbon started with one hydrogen. Therefore, the hydrogen from water adds to the first carbon and the **–OH** group adds to the second carbon. When there are equal numbers of hydrogen atoms on both carbons in a double bond then the two products will form in approximately equal amounts. For example, the hydration of 2-pentene results in two products. In the first product, the **–OH** group is on the third carbon and in the second product, the **–OH** group is on the second carbon. While these two molecules will have similar properties, there will be differences.



Condensation Reactions

A **condensation reaction** *is a reaction in which two molecules combine to form a single molecule.* A small molecule, often water, is usually removed during a condensation reaction. Amino acids are important biological molecules that have an amine functional group on one end of the molecule and a carboxylic acid functional group on the other end. When two amino acids combine in a condensation reaction, a covalent bond forms between the amine nitrogen of one amino acid and the carboxyl carbon of the second amino acid. A molecule of water is then removed as a second product (see figure below).

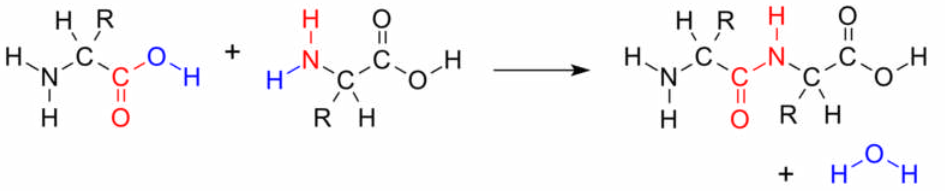
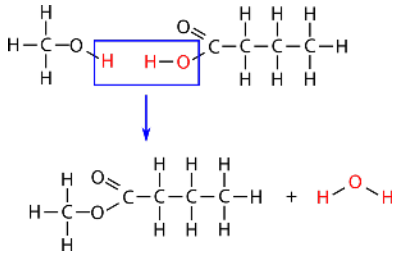


Figure **6.10.1**: Amino acids join together to form a molecule called a dipeptide. The **–OH** from the carboxyl group of one amino acid combines with a hydrogen atom from the amine group of the other amino group to produce water (blue).

This reaction forms a molecule called a dipeptide, and the resulting carbon-nitrogen covalent bond is often called a peptide bond. When repeated numerous times, a long molecule called a protein is eventually produced.

An **esterification** *is a condensation reaction in which an ester is formed from an alcohol and a carboxylic acid.* Esterification is a subcategory of condensation reactions because a water molecule is produced in the reaction. The reaction can be catalyzed by a strong acid, usually sulfuric acid. When the carboxylic acid, butanoic acid, is heated with an excess of methanol and a few drops of sulfuric acid, the ester methyl butanoate is produced. Methyl butanoate has the scent of pineapples. The reaction is shown below with both molecular and structural formulas. Esterification reactions are reversible.

$$CH_3CH_2CH_2COOH + HOCH_3 \overset{H_2SO_4}{\rightarrow} CH_3CH_2CH_2COOCH_3 + H_2O \qquad (6.10.9)$$

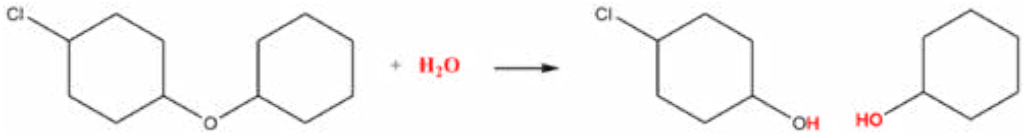


Saponification *describes the alkaline hydrolysis reaction of an ester*. The term saponification originally described the hydrolysis of long-chain esters called fatty acid esters to produce soap molecules, which are the salts of fatty acids. One such soap molecule is sodium stearate, formed from the hydrolysis of ethyl stearate.

$$\underset{\text{ethyl stearate}}{C_{17}H_{35}COOC_2H_5} + NaOH \rightarrow \underset{\text{sodium stearate (soap)}}{C_{17}H_{35}COO^-Na^+} + C_2H_5OH \qquad (6.10.10)$$

Hydrolysis Reactions

Hydrolysis is the reverse of condensation. "Hydro" indicates that water is involved and "lysis" means to break apart. In a hydrolysis reaction, water is added and the molecule breaks apart, usually at a C–O–C linkage.



Polymerization

Polymers are very different than the other kinds of organic molecules that you have seen so far. Whereas other compounds are of relatively low molar mass, polymers are giant molecules of very high molar mass. Polymers are the primary components of all sorts of plastics and related compounds. A **polymer** *is a large molecule formed of many smaller molecules covalently bonded to one another in a repeating pattern*. The *small molecules that make up the polymer are called* **monomers**. Polymers are generally formed by either addition or condensation reactions. Teflon (see figure below) is a non-reactive, non-stick coating used on cookware as well as in containers and pipes for reactive or corrosive chemicals.

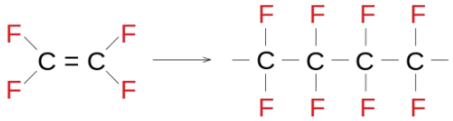


Figure **6.10.2**: Polytetrafluoroethylene (also known as Teflon) is formed from the polymerization of tetrafluoroethylene.

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CHAPTER OVERVIEW

7: Polymers

7.1: Polymerization - Making Big Ones Out of Little Ones
7.2: Polymerization - Addition Polymers
7.3: Polymerization - Condensation Polymers
7.4: Rubber and Other Elastomers
7.5: Properties of Polymers
7.6: Plastics and the Environment
7.7: Naturally Occurring Polymers
7.8: Carbohydrates- A Storehouse of Energy
7.9: Proteins- Polymers of Amino Acids
7.10: Nucleic Acids- Parts, Structure, and Function

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7.1: Polymerization - Making Big Ones Out of Little Ones

Learning Objectives

- Define the terms *monomer* and *polymer*.
- Know the different types of natural polymers.

A **polymer** is a large molecule, or macromolecule, composed of many repeated subunits.The term "polymer" derives from the Greek word *polus (*meaning "many, much") and m*eros* (meaning "part"), and refers to a molecule whose structure is composed of multiple repeating units, from which originates a characteristic of high relative molecular mass and attendant properties. As shown schematically in Figure **7.1.1**.

Due to their broad range of properties, both synthetic and natural polymers play essential and ubiquitous roles in everyday life. Polymers range from familiar synthetic plastics such as polystyrene to natural biopolymers such as DNA and proteins that are fundamental to biological structure and function. Polymers, both natural and synthetic, are created via polymerization of many small molecules, known as monomers. Their consequently large molecular mass relative to small molecule compounds produces unique physical properties, including toughness, viscoelasticity, and a tendency to form glasses and semicrystalline structures rather than crystals. The terms polymer and resin are often synonymous with plastic.

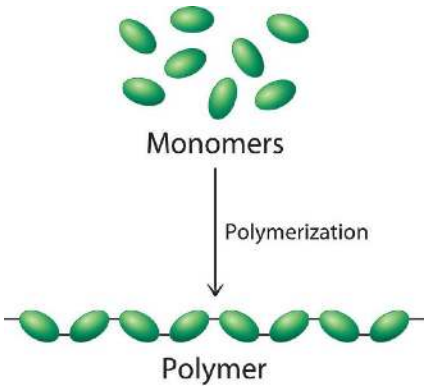
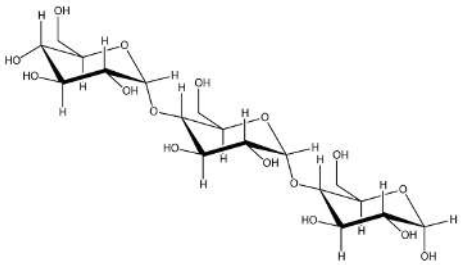


Figure **7.1.1** *Polymer formation during a polymerization reaction, a large number of monomers become connected by covalent bonds to form a single long molecule, a polymer.*

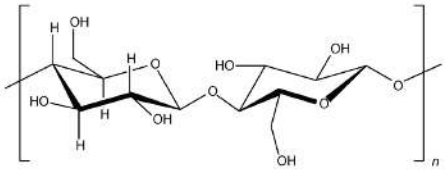
Natural Polymers

Some very important biological materials are polymers. Of the three major food groups, polymers are represented in two: proteins and carbohydrates. **Proteins** are polymers of amino acids, which are monomers that have an amine functional group and a carboxylic acid functional group. Proteins play a crucial role in living organisms.

Linking hundreds of glucose molecules together makes a relatively common material known as *starch*:



Starch is an important source of energy in the human diet. Note how individual glucose units are joined together. They can also be joined together in another way, like this:



This polymer is known as *cellulose*. **Cellulose** is a major component in the cell walls of plants. Curiously, despite the similarity in the building blocks, some animals (such as humans) cannot digest cellulose; those animals that can digest cellulose typically rely on symbiotic bacteria in the digestive tract for the actual digestion. Animals do not have the proper enzymes to break apart the glucose units in cellulose, so it passes through the digestive tract and is considered *dietary fiber*.

Deoxyribonucleic acid* (*DNA*) and *ribonucleic acid* (*RNA*)** are also polymers, composed of long, three-part chains consisting of phosphate groups, sugars with 5 C atoms (ribose or deoxyribose), and N-containing rings referred to as bases. Each combination of the three parts is called a nucleotide; DNA and RNA are essentially polymers of nucleotides that have rather complicated but intriguing structures (F***igure **7.1.2** - Nucleotides). DNA is the fundamental material in chromosomes and is directly responsible for heredity, while RNA is an essential substance in protein synthesis.

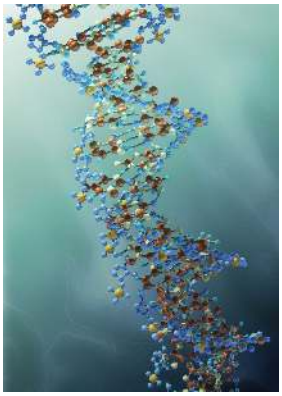


Figure **7.1.2** *Nucleotides © Thinkstock*

The DNA in our cells is a polymer of nucleotides, each of which is composed of a phosphate group, a sugar, and a N-containing base

The above mentioned biopolymers (polymers produced by living organisms) are discussed further in Chapter 16.

Celluloid: Billiard Balls

Celluloids are a class of compounds created from nitrocellulose (partially nitrated cellulose) and camphor, with added dyes and other agents. Generally considered the first thermoplastic, it was first created as Parkesinein (by Alexander Parkes of Birmingham England) in 1856 and as Xylonite in 1869. In the 1860s, an American, John Wesley Hyatt, acquired Parkes's patent and began experimenting with cellulose nitrate with the intention of manufacturing billiard balls, which until that time were made from ivory. In the 1870s the modified plastic was registered as "celluloid".

The main use was in movie and photography film industries, which used only celluloid film stock prior to the adoption of acetate safety film in the 1950s. Celluloid is highly flammable, difficult and expensive to produce and no longer widely used; its most common uses today are in table tennis balls, musical instruments, and guitar picks.

Bakelite (sometimes spelled **Baekelite**) or **polyoxybenzylmethylenglycolanhydride** was the first plastic made from synthetic components. It is a thermosetting phenol formaldehyde resin, formed from a condensation reaction of phenol with formaldehyde. It was developed by the Belgian-American chemist Leo Baekeland in Yonkers, New York, in 1907.

Bakelite was patented on December 7, 1909. The creation of a synthetic plastic was revolutionary for its electrical non conductivity and heat-resistant properties in electrical insulators, radio and telephone casings and such diverse products as kitchenware, jewelry, pipe stems, children's toys, and firearms.

Polymers



***Video* 7.1.2** *Polymers Crash Course*

Summary

- Polymers are giant molecules that consist of long chains of units called monomers connected by covalent bonds.
- Polymerization is the process of linking monomers together to form a polymer.
- Plastic is the general term for polymers made from synthetic materials.
- Several important biological polymers include proteins, starch, cellulose, DNA and RNA.

Contributors and Attributions

- Joshua Halpern, Scott Sinex and Scott Johnson
- TextMap: Beginning Chemistry (Ball et al.)
- Marisa Alviar-Agnew (Sacramento City College)
- Wikipedia

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7.2: Polymerization - Addition Polymers

We reap the benefits of using Styrofoam containers, but don't often consider where they end up. Styrofoam materials do not break down quickly under exposure to the elements. When buried in a landfill, styrofoam will remain intact for a long time. The good news is that there is not a lot of this pollutant found in landfills (maybe about 0.5% by weight of the total mass of garbage). There is no good way to recycle Styrofoam at present, but in the future, a creative scientist may change that.

Polymerization - Addition Polymers

Polymers are very different from the other kinds of organic molecules that you have seen so far. Whereas other compounds are of relatively low molar mass, polymers are giant molecules of very high molar mass. Polymers are the primary components of all sorts of plastics and related compounds. A **polymer** is a large molecule formed of many smaller molecules covalently bonded in a repeating pattern. The small molecules which make up the polymer are called **monomers**. Polymers generally form either from an addition reaction or a condensation reaction.

Addition Polymers

An **addition polymer** is a polymer formed by chain addition reactions between monomers that contain a double bond. Molecules of ethene can polymerize with each other under the right conditions to form the polymer called polyethylene.

$$n\mathrm{CH_2{=}CH_2} \rightarrow -(\mathrm{CH_2CH_2})_n-$$

The letter n stands for the number of monomers that are joined in repeated fashion to make the polymer, and can have a value in the hundreds or even thousands.

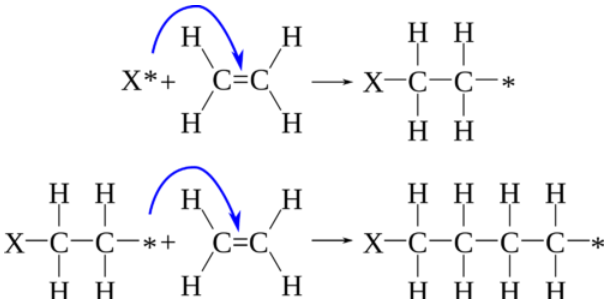


Figure 7.2.1: Polyethylene synthesis.

The reactions above show the basic steps to form an addition polymer:

1. Initiation - a free radical initiator ($\mathrm{X^*}$) attacks the carbon-carbon double bond (first step above). The initiator can be something like hydrogen peroxide. This material can easily split to form two species with a free electron attached to each: $\mathrm{H{-}O{-}O{-}H \rightarrow 2H{-}O\cdot}$. This free radical attacks a carbon-carbon double bond. One of the pi electrons forms a single bond with the initiator while the other pi electron forms a new free radical on the carbon atom.
2. Propagation - the new free radical compound interacts with another alkane, continuing the process of chain growth (second step above).
3. Termination occurs whenever two free radicals come in contact with one another (not shown). The two free electrons form a covalent bond and the free radical on each molecule no longer exists.

Polyethylene can have different properties depending on the length of the polymer chains, and on how efficiently they pack together. Some common products made from different forms of polyethylene include plastic bottles, plastic bags, and harder plastic objects such as milk crates.

Several other kinds of unsaturated monomers can be polymerized, and are components in common household products. Polypropylene is stiffer than polyethylene, and is in plastic utensils and some other types of containers.

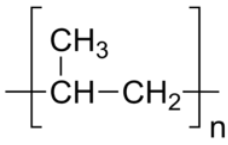


Figure **7.2.2**: Polypropylene structure.

Polystyrene is used in insulation and in molded items such as coffee cups.

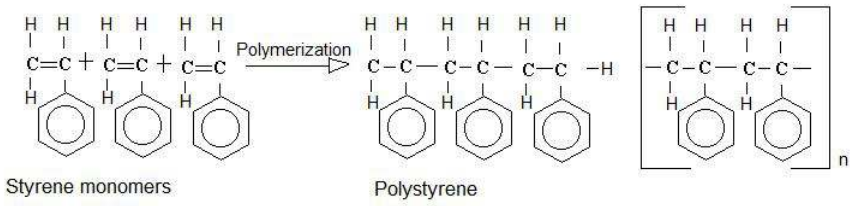


Figure **7.2.3**: Polystyrene synthesis and structure.

Polyvinyl chloride (PVC) is extensively used for plumbing pipes.



Figure **7.2.4**: Polyvinyl chloride.

Polyisoprene is a polymer of isoprene and is better known as rubber. It is produced naturally by rubber trees, but several variants have been developed which demonstrate improvements on the properties of natural rubber.

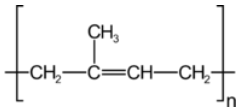


Figure **7.2.5**: Polyisoprene.

Summary

- A polymer is a large molecule formed of many smaller molecules covalently bonded in a repeating pattern; they are the primary components of all sorts of plastics and related compounds.
- The small molecules which make up polymers are called monomers.
- Polymers generally form either from an addition reaction or a condensation reaction.
- An addition polymer is a polymer formed by chain addition reactions between monomers that contain a double bond.
- The basic steps to form an addition polymer are: (1) initiation, (2) propagation, (3) termination

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7.3: Polymerization - Condensation Polymers

Animal intestines and silk were used for all guitar strings for centuries, until modern technology and changes in musical taste brought about significant changes. There are two major types of guitar strings in use today. Steel strings (first developed around 1900) are found on acoustic and electric guitars. They have a bright, crisp sound that lends itself well to diverse music such as jazz, rock 'n' roll, and bluegrass. Nylon strings are a more recent development. During World War II, the silk and animal products needed to manufacture steel guitar strings were not available. Nylon quickly proved to be a more-than-adequate substitute. Now nylon strings are found on all classical guitars. Their sound is somewhat softer than the steel strings, making the tone quality well-suited for the classical genre of music.

Polymerization - Condensation Polymers

A **condensation polymer** is a polymer formed by condensation reactions. Monomers of condensation polymers must contain two functional groups so that each monomer can link up with two other monomers. One type of condensation polymer is called a polyamide. An amide is characterized by the functional group shown below wherein the carbon of a carbonyl group is bonded to the nitrogen of an amine.

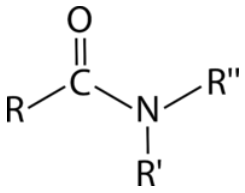


Figure **7.3.1**: Amide.

One pair of monomers that can form a polyamide is that of adipic acid and hexanediamine. Adipic acid is a carboxylic acid with two carboxyl groups on either end of the molecule. Hexanediamine has amino groups on either end of a six-carbon chain. When these molecules react with each other, a molecule of water is eliminated, classifying it as a condensation reaction (see figure below).

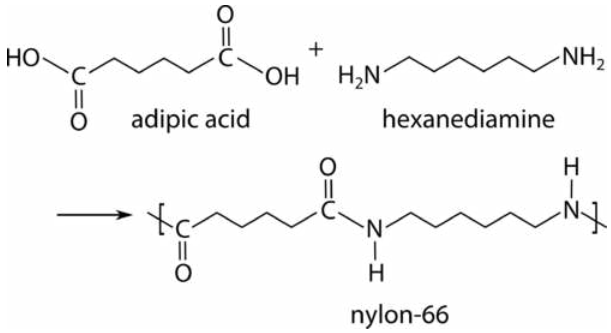


Figure **7.3.2**: Nylon synthesis.

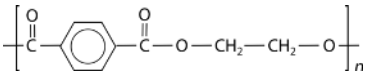
The polymer that results from the repetition of the condensation reaction is a polyamide called nylon-66. Nylon-66 was first invented in 1935 and has been used in all sorts of products. Polyamides, including Nylon-66, are commonly found in fibers and clothing, cooking utensils, fishing line, and carpeting—among many other applications.



Figure **7.3.3**: Nylon spatula.

Polyester is another common type of condensation polymer. Recall that esters are formed from the reaction of an alcohol with a carboxylic acid. When both the acid and alcohol have two functional groups, the ester is capable of being polymerized. One such

polyester is called polyethylene terephthalate (PET) and is formed from the reaction of ethylene glycol with terephthalic acid. The structure of PET is shown below.



PET is used in tires, photographic film, food packaging, and clothing. Polyester fabric is used in permanent-press clothing. Its resistance to wrinkling comes from the cross-linking of the polymer strands.

Summary

- A condensation polymer is a polymer formed by condensation reactions.
- Polyamides and polyesters are common types of condensation polymers.

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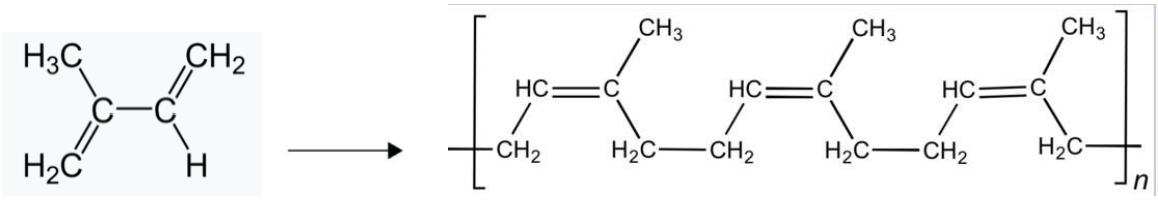
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7.4: Rubber and Other Elastomers

Learning Objectives

- Know the properties of rubber.
- Describe the process of vulcanization.

Natural rubber, also called **India rubber** or ***caoutchouc***, as initially produced, consists of polymers of the organic compound isoprene, with minor impurities of other organic compounds, plus water. Thailand and Indonesia are two of the leading rubber producers. Forms of polyisoprene that are used as natural rubbers are classified as elastomers.



Isoprene Polyisoprene (rubber)

Currently, rubber is harvested mainly in the form of the latex from the rubber tree or others. The latex is a sticky, milky colloid drawn off by making incisions in the bark and collecting the fluid in vessels in a process called "tapping". The latex then is refined into rubber ready for commercial processing. In major areas, latex is allowed to coagulate in the collection cup. The coagulated lumps are collected and processed into dry forms for marketing.

Natural rubber is used extensively in many applications and products, either alone or in combination with other materials. In most of its useful forms, it has a large stretch ratio and high resilience, and is extremely waterproof.

Vulcanization

In 1832–1834 Nathaniel Hayward and Friedrich Ludersdorf discovered that rubber treated with sulfur lost its stickiness. It is likely Hayward shared his discovery with Charles Goodyear, possibly inspiring him to make the discovery of vulcanization. Thomas Hancock (1786–1865), a scientist and engineer, was the first to patent vulcanization of rubber. He was awarded a British patent on May 21, 1845. Three weeks later, on June 15, 1845, Charles Goodyear was awarded a patent in the United States. It was Hancock's friend William Brockedon who coined term 'vulcanization'. Goodyear claimed that he had discovered vulcanization earlier, in 1839.

Sulfur vulcanization is a chemical process for converting natural rubber or related polymers into more durable materials by heating them with sulfur or other equivalent curatives or accelerators. Sulfur forms cross-links (bridges) between sections of polymer chain which results in increased rigidity and durability, as well as other changes in the mechanical and electronic properties of the material. A vast array of products are made with vulcanized rubber, including tires, shoe soles, hoses, and conveyor belts. The term *vulcanization* is derived from Vulcan, the Roman god of fire.

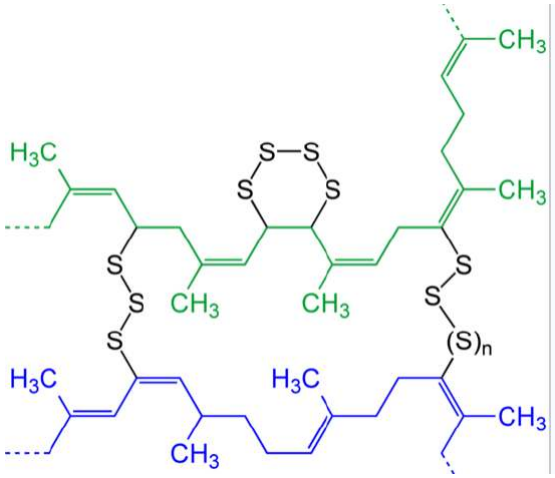


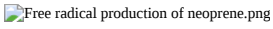
Figure \(\ **PageIndex*{1}*\)** General representation of the chemical structure of vulcanized natural rubber showing the crosslinking of two polymer chains (**blue** and **green**) with sulfur (n = 0, 1, 2, 3 …).

Synthetic Rubber

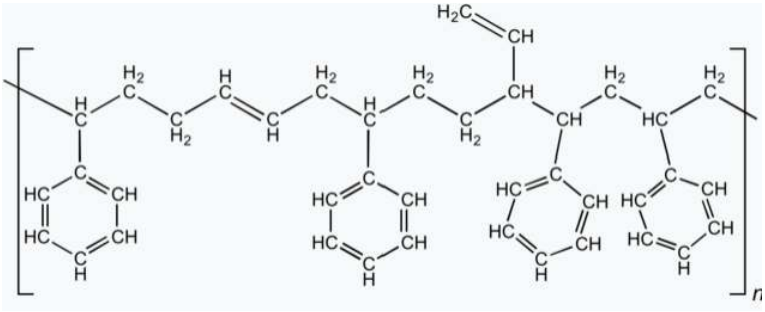
The expanded use of bicycles, and particularly their pneumatic tires, starting in the 1880s, created increased demand for rubber. In 1909 a team headed by Fritz Hofmann, working at the Bayer laboratory in Germany, succeeded in polymerizing isoprene, the first synthetic rubber. A synthetic rubber is any artifiical elastomer. These are mainly polymers synthesized from petroleum by products.

Polybutadiene rubber is a polymer formed from the polymerization of the monomer 1,3-butadiene. Polybutadiene has a high resistance to wear and is used especially in the manufacture of tires, which consumes about 70% of the production. Another 25% is used as an additive to improve the toughness (impact resistance) of plastics such as polystyrene and acrylonitrile butadiene styrene (ABS). Polybutadiene rubber accounted for about a quarter of total global consumption of synthetic rubbers in 2012. It is also used to manufacture golf balls, various elastic objects and to coat or encapsulate electronic assemblies, offering high electrical resistivity.

Neoprene (also **polychloroprene** or **pc-rubber**) is a family of synthetic rubbers that are produced by polymerization of chloroprene. Neoprene exhibits good chemical stability and maintains flexibility over a wide temperature range. Neoprene is sold either as solid rubber or in latex form and is used in a wide variety of applications, such as laptop sleeves, orthopaedic braces (wrist, knee, etc.), electrical insulation, liquid and sheet applied elastomeric membranes or flashings, and automotive fan belts.Neoprene is produced by free-radical polymerization of chloroprene. In commercial production, this polymer is prepared by free radical emulsion polymerization. Polymerization is initiated using potassium persulfate. Bifunctional nucleophiles, metal oxides (e.g. zinc oxide), and thioureas are used to crosslink individual polymer strands.



Styrene-butadiene or **styrene-butadiene rubber** (**SBR**) describe families of synthetic rubbers derived from styrene and butadiene (the version developed by Goodyear is called **Neolite**). These materials have good abrasion resistance and good aging stability when protected by additives. In 2012, more than 5.4 million tonnes of SBR were processed worldwide. About 50% of car tires are made from various types of SBR.



It is a commodity material which competes with natural rubber. The elastomer is used widely in pneumatic tires. Other uses include shoe heels and soles, gaskets, and even chewing gum.

Polymers in Paints

Polymers are one of the key components of modern paints that function as binders. The binder is the film-forming component of paint. It is the only component that is always present among all the various types of formulations. The binder imparts properties such as gloss, durability, flexibility, and toughness. Binders include synthetic or natural resins such as alkyds, acrylics, vinyl-acrylics, vinyl acetate/ethylene (VAE), polyurethanes, polyesters, melamine resins, epoxy, or siloxanes or oils.

Summary

The many uses of natural rubber has led to development and manufacture of synthetic rubber.

Sulfur vulcanization is a chemical process for converting natural rubber or related polymers into more durable materials by heating them with sulfur or other equivalent curatives or accelerators.

Three examples of synthetic rubber used in various applications are polybutadiene, polychloroprene (Neoprene), and styrene-butadiene rubber (SBR)

Contributors and Attributions

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7.5: Properties of Polymers

Learning Objectives

- Know the properties of polymers based on their molecular and intermolecular structures.
- Know the relationship between degree of crystallinity to physical properties of polymers.

The physical properties of a polymer such as its strength and flexibility depend on:

- *chain length* - in general, the longer the chains the stronger the polymer;
- *side groups* - polar side groups (including those that lead to hydrogen bonding) give stronger attraction between polymer chains, making the polymer stronger;
- *branching* - straight, unbranched chains can pack together more closely than highly branched chains, giving polymers that have higher density, are more crystalline and therefore stronger;
- *cross-linking* - if polymer chains are linked together extensively by covalent bonds, the polymer is harder and more difficult to melt.

Crystalline and Amorphous Polymers

When applied to polymers, the term *crystalline* has a somewhat ambiguous usage. A synthetic polymer may be loosely described as crystalline if it contains regions of three-dimensional ordering on atomic (rather than macromolecular) length scales, usually arising from intramolecular folding and/or stacking of adjacent chains. Synthetic polymers may consist of both crystalline and amorphous regions; the degree of crystallinity may be expressed in terms of a weight fraction or volume fraction of crystalline material. Few synthetic polymers are entirely crystalline. The crystallinity of polymers is characterized by their degree of crystallinity, ranging from zero for a completely non-crystalline polymer to one for a theoretical completely crystalline polymer. Polymers with microcrystalline regions are generally tougher (can be bent more without breaking) and more impact-resistant than totally amorphous polymers.Polymers with a degree of crystallinity approaching zero or one will tend to be transparent, while polymers with intermediate degrees of crystallinity will tend to be opaque due to light scattering by crystalline or glassy regions. For many polymers, reduced crystallinity may also be associated with increased transparency.

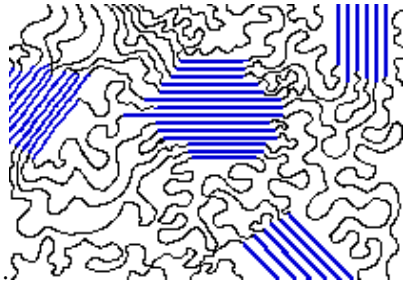


***Figure* 7.5.1** *The crystalline parts of this polymer are shown in blue.*

Depending on the degree of crystallinity, there will be a higher temperature, the *melting point* t_m , at which the crystalline regions come apart and the material becomes a viscous liquid. Such liquids can easily be injected into molds to manufacture objects of various shapes, or extruded into sheets or fibers. Other polymers (generally those that are highly cross-linked) do not melt at all; these are known as *thermosets*. If they are to be made into molded objects, the polymerization reaction must take place within the molds — a far more complicated process. About 20% of the commercially-produced polymers are thermosets; the remainder are thermoplastics.

The Glass Transition Temperature

In some polymers (known as *thermoplastics*) there is a fairly definite softening point that is observed when the thermal kinetic energy becomes high enough to allow internal rotation to occur within the bonds and to allow the individual molecules to slide independently of their neighbors, thus rendering them more flexible and deformable. This defines the *glass transition temperature* t_g . Hard plastics like polystyrene and poly(methyl methacrylate) are used well below their glass transition temperatures, i.e., when

they are in their glassy state. Their T_g values are well above room temperature, both at around 100 °C (212 °F). Rubber elastomers like polyisoprene and polyisobutylene are used above their T_g, that is, in the rubbery state, where they are soft and flexible.

Fiber Formation

Bill Pittendreigh, DuPont, and other individuals and corporations worked diligently during the first few months of World War II to find a way to replace Asian silk and hemp with nylon in parachutes. It was also used to make tires, tents, ropes, ponchos, and other military supplies. It was even used in the production of a high-grade paper for U.S. currency. At the outset of the war, cotton accounted for more than 80% of all fibers used and manufactured, and wool fibers accounted for nearly all of the rest. By August 1945, manufactured fibers had taken a market share of 25%, at the expense of n. After the war, e of shortages of both silk and nylon, nylon parachute material was sometimes repurposed to make dresses.Nylon 6 and 66 fibers are used in carpet manufacture. Nylon is one kind of fibers used in tire cord. Herman E. Schroeder pioneered application of nylon in tires.

Figure **7.5.2** Blue nylon fabric ball gown *by Emma Domb, Science History Institute.*

Fabrics woven or knitted from polyester thread or yarn are used extensively in apparel and home furnishings, from shirts and pants to jackets and hats, bed sheets, blankets, upholstered ure and computer mouse mats. Industrial polyester fibers, yarns and ropes are used in car tire reinforcements, fabrics for conveyor belts, safety belts, coated fabrics and plastic reinforcements with high-energy absorption. Polyester fiber is used as cushioning and insulating material in pillows, comforters and upholstery padding. Polyester fabrics are highly stain-resistant—in fact, the only class of dyes which *can* be used to alter the color of polyester fabric are what are known as disperse dyes.

Figure **7.5.3** *Stretching polyester fabric.*

Acrylic fibers are synthetic fibers made from a polymer (polyacrylonitrile) with an average molecular weight of -100,000, about 1900 monomer units. For a fiber to be called "acrylic" in the US, the polymer must contain at least 85% acrylonitrile monomer. Typical comonomers are vinyl acetate or methyl acrylate. DuPont created the first acrylic fibers in 1941 and trademarked them under the name **Orlon**. It was first developed in the mid-1940s but was not produced in large quantities until the 1950s. Strong and warm, acrylic fiber is often used for sweaters and tracksuits and as linings for boots and gloves, as well as in furnishing fabrics and carpets. It is manufactured as a filament, then cut into short staple lengths similar to wool hairs, and spun into yarn.

Modacrylic is a modified acrylic fiber that contains at least 35% and at most 85% acrylonitrile monomer. The comonomers vinyl chloride, vinylidene chloride or vinyl bromide used in modacrylic give the fiber flame retardant properties. End-uses of modacrylic include faux fur, wigs, hair extensions and protective clothing.

Microfiber (or **microfibre**) is synthetic fiber finer than one denier or decitex/thread, having a diameter of less than ten micrometres. This is smaller than the diameter of a strand of silk (which is approximately one denier), which is itself about 1/5 the diameter of a human hair.



Figure **7.5.4** *Close-up view of microfiber (left) and microfiber household cloth (right).*

The most common types of microfibers are made from polyesters, polyamides (e.g., nylon, Kevlar, Nomex, trogamide), or a conjugation of polyester, polyamide, and polypropylene. Microfiber is used to make mats, knits, and weaves for apparel, upholstery, industrial filters, and cleaning products. The shape, size, and combinations of synthetic fibers are selected for specific characteristics, including softness, toughness, absorption, water repellency, electrostatics, and filtering capabilities.

Environmental and Safety Issues

Microfiber textiles tend to be flammable if manufactured from hydrocarbons (polyester) or carbohydrates (cellulose) and emit toxic gases when burning, more so if aromatic (PET, PS, ABS) or treated with halogenatedflame retardants and azo dyes. Their polyester and nylon stock are made from petrochemicals, which are not a renewable resource and are not biodegradable. However, if made out of polypropylene, they are recyclable (Prolen).

For most cleaning applications they are designed for repeated use rather than being discarded after use. An exception to this is the precise cleaning of optical components where a wet cloth is drawn once across the object and must not be used again as the debris collected are now embedded in the cloth and may scratch the optical surface.

Microfiber that is made from petrochemicals includes polyester and nylon which are not biodegradable. However, microfiber made from polypropylene can be recyclable. Microfiber products may also have the potential of entering the oceanic water supply and food chain similar to other microplastics. Synthetic clothing made of microfibers that are washed can release materials and travel to local wastewater treatment plants, contributing to plastic pollution in water. Fibers retained in wastewater treatment sludge (biosolids) that are land-applied can persist in soils.

There are environmental concerns about this product entering the oceanic food chain similar to other microplastics. A study by the clothing brand Patagonia and University of California, Santa Barbara, found that when synthetic jackets made of microfibers are washed, on average 1.7 grams (0.060 oz) of microfibers are released from the washing machine. These microfibers then travel to local wastewater treatment plants, where up to 40% of them enter into rivers, lakes, and oceans where they contribute to the overall plastic pollution. Microfibers account for 85% of man-made debris found on shorelines worldwide.

However, no pesticides are used for producing synthetic fibers (in comparison to cotton). If these products are made of polypropylene yarn, the yarn is dope-dyed; i.e. no water is used for dyeing (as with cotton, where thousands of liters of water become contaminated).

Summary

- The physical properties of a polymer such as its strength and flexibility depend on chain length, side groups present, branching, and cross-linking.
- Synthetic polymers may consist of both crystalline (more ordered, crystal-like) and amorphous (less ordered) regions; the degree of crystallinity may be expressed in terms of a weight fraction or volume fraction of crystalline material.
- The crystallinity of polymers is characterized by their degree of crystallinity, ranging from zero for a completely non-crystalline polymer to one for a theoretical completely crystalline polymer. Polymers with microcrystalline regions are generally tougher (can be bent more without breaking) and more impact-resistant than totally amorphous polymers.
- Due to their chemical structure, nylon, polyester, and acrylic fibers have physical properties that are comparable or even superior to natural fibers Thus, many of these fibers have a variety of uses and have replaced natural fibers in various products.

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- Stephen Lower, Professor Emeritus (Simon Fraser U.) Chem1 Virtual Textbook IF Figureis used
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7.6: Plastics and the Environment

Learning Objectives

- Know the problems associated with plastics.
- Identify the type of polymer associated with each recycling number.
- Know the different plastic recycling processes.

Problems with Plastics

Due to their low cost, ease of manufacture, versatility, and imperviousness to water, plastics are used in a multitude of products of different scale, including paper clips and spacecraft. They have prevailed over traditional materials, such as wood, stone, horn and bone, leather, metal, glass, and ceramic, in some products previously left to natural materials. However, there are numerous problems encountered with plastic use.

Small-molecule release

Many kinds of polymers contain small molecules — either unreacted monomers, or substances specifically added (plasticizers, uv absorbers, flame retardants, etc.) to modify their properties. Many of these smaller molecules are able to diffuse through the material and be released into any liquid or air in contact with the plastic — and eventually into the aquatic environment. Those that are used for building materials (in mobile homes, for example) can build up in closed environments and contribute to indoor air pollution.

Residual monomer

Formation of long polymer chains is a complicated and somewhat random process that is never perfectly stoichiometric. It is therefore not uncommon for some unreacted monomer to remain in the finished product. Some of these monomers, such as formaldehyde, styrene (from polystyrene, including polystyrene foam food take-out containers), vinyl chloride, and bisphenol-A (from polycarbonates) are known carcinogens. Although there is little evidence that the small quantities that diffuse into the air or leach out into fluids pose a quantifiable health risk, people are understandably reluctant to tolerate these exposures, and public policy is gradually beginning to regulate them.

Perfluorooctanoic acid (PFOA), the monomer from which Teflon is made, has been the subject of a 2004 lawsuit against a DuPont factory that contaminated groundwater. Small amounts of PFOA have been detected in gaseous emissions from hot fluorocarbon products.

Decomposition products

Most commonly-used polymers are not readily biodegradable, particularly under the anaerobic conditions of most landfills. And what decomposition does occur will combine with rainwater to form *leachates* that can contaminate nearby streams and groundwater supplies. Partial photodecomposition, initiated by exposure to sunlight, is a more likely long-term fate for exposed plastics, resulting in tiny broken-up fragments. Many of these materials are less dense than seawater, and once they enter the oceans through coastal sewage outfalls or from marine vessel wastes, they tend to remain there indefinitely.

Open burning of polymeric materials containing chlorine (polyvinyl chloride, for example) is known to release compounds such as dioxins that persist in the environment. Incineration under the right conditions can effectively eliminate this hazard. Disposed products containing **fluorocarbons** (Teflon-coated ware, some personal-care, waterproofing and anti-stick materials) break down into perfluorooctane sulfonate which has been shown to damage aquatic animals.

Hazards to animals

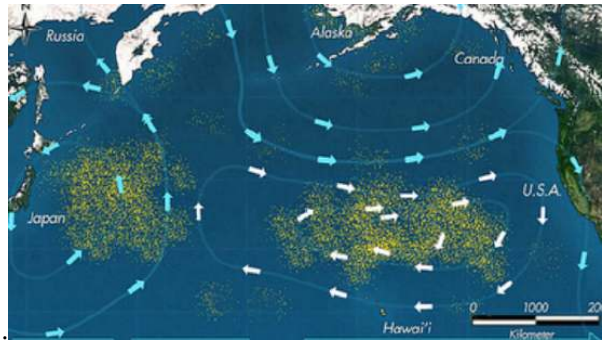
There are two general types of hazards that polymers can introduce into the aquatic environment. One of these relates to the release of small molecules that act as hormone disrupters as described above. It is well established that small aquatic animals such as fish are being seriously affected by such substances in many rivers and estuarine systems, but details of the sources and identities of these molecules have not been identified. One confounding factor is the release of sewage water containing human birth-control drugs (which have a feminizing effect on sexual development) into many waterways.

The other hazard relates to pieces of plastic waste that aquatic animals mistake for food or become entangled in (Figure **7.6.1**) .



Figure **7.6.1** A p*lastic bag (probably mistaken for a jellyfish, the sea turtle's only food) cannot be regurgitated and leads to intestinal blockage and a slow death (left) remains of an albatross that mistook bits of plastic junk for food (right).*

These dangers occur throughout the ocean, but are greatly accentuated in regions known as gyres. These are regions of the ocean in which a combination of ocean currents drives permanent vortices that tend to collect and concentrate floating materials. The most notorious of these are the Great Pacific Gyres that have accumulated astounding quantities of plastic waste.



Recycling

The huge quantity (one estimate is 10^8 metric tons per year) of plastic materials produced for consumer and industrial use has created a gigantic problem of what to do with plastic waste which is difficult to incinerate safely and which, being largely non-biodegradable, threatens to overwhelm the capacity of landfills. An additional consideration is that *de novo* production most of the major polymers consumes non-renewable hydrocarbon resources.



Figure **7.6.2** Plastic water bottles present a special recycling problem because of their widespread use in away-from-home locations.

Plastics recycling has become a major industry, greatly aided by enlightened trash management policies in the major developed nations. However, it is plagued with some special problems of its own:

- Recycling is only profitable when there is a market for the regenerated material. Such markets vary with the economic cycle (they practically disappeared during the recession that commenced in 2008.)
- The energy-related costs of collecting and transporting plastic waste, and especially of processing it for re-use, are frequently the deciding factor in assessing the practicability of recycling.
- Collection of plastic wastes from diverse sources and locations and their transport to processing centers consumes energy and presents numerous operational problems.
- Most recycling processes are optimized for particular classes of polymers. The diversity of plastic types necessitates their separation into different waste streams — usually requiring manual (i.e., low-cost) labor. This in turn encourages shipment of these wastes to low-wage countries, thus reducing the availability of recycled materials in the countries in which the plastics originated.

Some of the major recycling processes include

- Thermal decomposition processes that can accommodate mixed kinds of plastics and render them into fuel oil, but the large inputs of energy they require have been a problem.
- A very small number of condensation polymers can be depolymerized so that the monomers can be recovered and re-used.
- Thermopolymers can be melted and pelletized, but those of widely differing types must be treated separately to avoid incompatability problems.
- Thermosets are usually shredded and used as filler material in recycled thermopolymers.

Other processes

A process has also been developed in which many kinds of plastic can be used as a carbon source in the recycling of

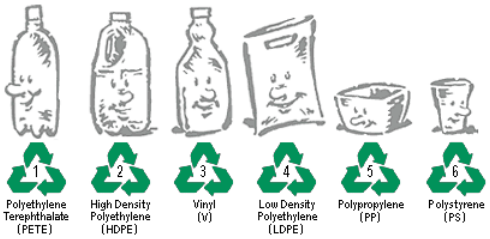
scrap steel. There is also a possibility of mixed recycling of different plastics, which does not require their separation. It is called compatibilization and requires use of special chemical bridging agents compatibilizers. It can help to keep the quality of recycled material and to skip often expensive and inefficient preliminary scanning of waste plastics streams and their separation/purification.

Figure **7.6.3** *Plastic or other polymer compatibilization.*

Recycled Plastics

Seven groups of plastic polymers, each with specific properties, are used worldwide for packaging applications (see Table **7.6.1**). Each group of plastic polymer can be identified by its plastic identification code (PIC), usually a number or a letter abbreviation. For instance, low-density polyethylene can be identified by the number "4" or the letters "LDPE". The PIC appears inside a three-chasing-arrow recycling symbol. The symbol is used to indicate whether the plastic can be recycled into new products.

The PIC was introduced by the Society of the Plastics Industry, Inc., to provide a uniform system for the identification of various polymer types and to help recycling companies separate various plastics for reprocessing. Manufacturers of plastic products are required to use PIC labels in some countries/regions and can voluntarily mark their products with the PIC where there are no requirements. Consumers can identify the plastic types based on the codes usually found at the base or at the side of the plastic products, including food/chemical packaging and containers.



Not all categories are accepted by all local recycling authorities, so residents need to be informed about which kinds should be placed in recycling containers and which should be combined with ordinary trash.

Table **7.6.1** The Major Groups of Plastic Polymers. Source: Wikipedia

Plastic identification code	Type of plastic polymer	Properties	Common packaging applications	Melting temperatures (°C)
	Polyethylene terephthalate(PET, PETE)	Clarity, strength, toughness, barrier to gas and moisture.	Soft drink, water and salad dressing bottles; peanut butter and jam jars; ice cream cone lids; small consumer electronics	Tm = 250
	High-density polyethylene(HDPE)	Stiffness, strength, toughness, resistance to moisture, permeability to gas	Water pipes, Gas & Fire Pipelines, Electrical & Communications conduit, hula hoop rings, five gallon buckets, milk, juice and water bottles; grocery bags, some shampoo/toiletry bottles	Tm = 130
	Polyvinyl chloride(PVC)	Versatility, ease of blending, strength, toughness.	Blister packaging for non-food items; cling films for non-food use. May be used for food packaging with the addition of the plasticisers needed to make natively rigid PVC flexible. Non-packaging uses are electrical cable insulation; rigid piping; vinyl records.	Tm = 240
	Low-density polyethylene(LDPE)	Ease of processing, strength, toughness, flexibility, ease of sealing, barrier to moisture	Frozen food bags; squeezable bottles, e.g. honey, mustard; cling films; flexible container lids	Tm = 120
	Polypropylene(PP)	Strength, toughness, resistance to heat, chemicals, grease and oil, versatile, barrier to moisture.	Reusable microwaveable ware; kitchenware; yogurt containers; margarine tubs; microwaveable disposable take-away containers; disposable cups; soft drink bottle caps; plates.	Tm = 173
	Polystyrene(PS)	Versatility, clarity, easily formed	Egg cartons; packing peanuts; disposable cups, plates, trays and cutlery; disposable take-away containers	Tm = 240

	Other (often polycarbonateor ABS)	Dependent on polymers or combination of polymers	Beverage bottles, baby milk bottles. Non-packaging uses for polycarbonate, compact discs, "unbreakable" glazing, electronic apparatus housing, lenses (including sunglasses), prescription glasses, automotive headlamps, riot shields, instrument panels.	Polycarbonate: Tm = 225

Tire Recycling

The large number of rubber tires that are disposed of, together with the increasing reluctance of landfills to accept them, has stimulated considerable innovation in the re-use of this material, especially in the construction industry.

Plastics and Fire Hazards

The term *fire (or flame)-retardant* as applied to organic (i.e., containing carbon) materials, is intended to refer to *reduced* fire hazard, as all will burn under certain circumstances. Fabric flammability is an important textile issue, especially for stage drapery that will be used in a public space such as a school, theatre or special event venue. In the United States, Federal regulations require that drapery fabrics used in such spaces be certified as flame or fire-retardant. For draperies and other fabrics used in public places, this is known as the NFPA 701 Test, which follows standards developed by the National Fire Protection Association (NFPA). Although all fabrics will burn, some are naturally more resistant to fire than others. Those that are more flammable can have their fire resistance drastically improved by treatment with fire-retardant chemicals. Inherently flame-retardant fabrics such as polyester are commonly used for flame retardant curtain fabrics.

The deaths in fiery crashes of race car drivers Fireball Roberts at Charlotte, and Eddie Sachs and Dave MacDonald at Indianapolis in 1964 led to the use of flame-resistant ics such as Nomex. Nomex and related aramid polymers are related to nylon, but have aromatic backbones, and hence are more rigid and more durable. Nomex is an example of a *meta* variant of the aramids (Kevlar is a *para* aramid). Unlike Kevlar, Nomex strands cannot align during filament polymerization and has less strength. However, it has excellent thermal, chemical, and radiation resistance for a polymer material.

A Nomex hood is a common piece of racing and firefighting equipment. It is placed on the head on top of a firefighter's face mask. The hood protects the portions of the head not covered by the helmet and face mask from the intense heat of the fire.

Figure **7.6.4** A firefighter in Toronto, Canada wears a Nomex hood in 2007.

Wildland firefighters wear Nomex shirts and trousers as part of their personal protective equipment during wildfire suppression activities.

Racing car drivers wear driving suits constructed of Nomex and or other fire retardant materials, along with Nomex gloves, long underwear, balaclavas, socks, helmet lining and shoes, to protect them in the event of a fire.

Military pilots and aircrew wear flight suits made of over 92 percent Nomex to protect them from the possibility of cockpit fires and other mishaps. Recently, troops riding in ground vehicles have also begun wearing Nomex. Kevlar thread is often used to hold the fabric together at seams.

Military tank drivers also typically use Nomex hoods as protection against fire.

Plasticizers and Pollution

Plasticizers (UK: **plasticisers**) or **dispersants** are additives that increase the plasticity or decrease the viscosity of a material. These substances are compounded into certain types of plastics to render them more flexible by lowering the glass transition

temperature. They accomplish this by taking up space between the polymer chains and acting as lubricants to enable the chains to more readily slip over each other. Many (but not all) are small enough to be diffusible and a potential source of health problems.

Polyvinyl chloride polymers are one of the most widely-plasticized types, and the odors often associated with flexible vinyl materials such as garden hoses, waterbeds, cheap shower curtains, raincoats and upholstery are testament to their ability to migrate into the environment.

The well-known "new car smell" is largely due to plasticizer release from upholstery and internal trim.

According to 2014 data, the total global market for plasticizers was 8.4 million metric tonnes including 1.3 million metric tonnes in Europe.

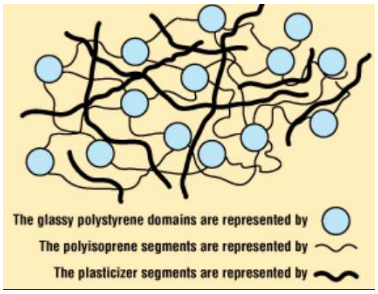


Figure **7.6.5** Shares of global plasticizer consumption in 2014 (8 million metric tons).

Substantial concerns have been expressed over the safety of some plasticizers, especially because some low molecular weight ortho-phthalates have been classified as potential endocrine disruptors with some developmental toxicity reported.

Summary

- Plastics are found everywhere due to its low cost, versatility, ease of use etc.
- Plastics pose a threat to the environment due to residual or degradation products that contribute to air and water pollution.
- Plastics hazards to animals and marine life as these living creatures mistake them for food.
- Plastic polymers are classified into seven groups for recycling purposes.

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7.7: Naturally Occurring Polymers

There are a number of naturally occurring polymeric substances that have a high degree of technical importance. Some of these, such as natural rubber (Section 13-4), cellulose, and starch (Section 20-7), have regular structures and can be regarded as being made up of single monomer units. Others, such as wool, silk (Section 25-8A), and deoxyribonucleic acid (Section 25-13A) are copolymers. Because we already have considered the chemistry of most of these substances, we shall confine our attention here to wool and collagen, which have properties related to topics discussed previously in this chapter.

7.7.1: Wool

The structure of wool is more complicated than that of silk fibroin (Figure 25-13) because wool, like insulin (Figure 25-8) and lysozyme (Figure 25-15), contains a considerable quantity of cystine, which provides $-S-S-$ (disulfide) cross-links between the peptide chains. These disulfide linkages play an important part in determining the mechanical properties of wool fibers because if the disulfide linkages are reduced, as with ammonium mercaptoethanoate solution, the fibers become much more pliable.

$$\underset{\substack{\text{(wool cystine}\\\text{cross-link)}}}{RCH_2{-}S{-}S{-}CH_2R} + \underset{\substack{\text{ammonium}\\\text{mercaptoethanoate}}}{2HSCH_2CO_2^{\ominus}\,NH_4^{\oplus}} \longrightarrow$$

$$RCH_2SH + HSCH_2R + NH_4^{\oplus}\,O_2CCH_2{-}S{-}S{-}CH_2CO_2^{\ominus}\,NH_4^{\oplus}$$

Advantage is taken of this reaction in the curling of hair, the reduction and curling being followed by restoration of the disulfide linkages through treatment with a mild oxidizing agent.

7.7.2: Collagen

The principal protein of skin and connective tissue is called collagen and is primarily constituted of glycine, proline, and hydroxyproline. Collagen is made up of tropocollagen, a substance with very long and thin molecules (14×2900 Å, MW about 300,000). Each tropocollagen molecule consists of three twisted polypeptide strands. When collagen is boiled with water, the strands come apart and the product is ordinary cooking gelatin. Connective tissue and skin are made up of fibrils, 200 Å to 1000 Å wide, which are indicated by x-ray diffraction photographs to be composed of tropocollagen molecules running parallel to the long axis. Electron micrographs show regular bands, 640 Å apart, across the fibrils, and it is believed that these correspond to tropocollagen molecules, all heading in the same direction but regularly staggered by about a fourth of their length (Figure 29-10).

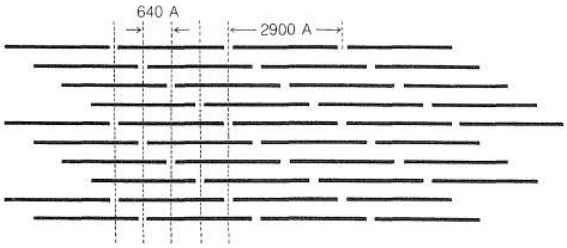


Figure 29-10: Schematic diagram of collagen molecules in a fibril so arranged as to give the 640-Å spacing visible in electron micrographs.

The conversion of collagen fibrils to leather presumably involves formation of cross-links between the tropocollagen molecules. Various substances can be used for the purpose, but chromium salts act particularly rapidly.

7.7.3: Contributors and Attributions

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7.8: Carbohydrates- A Storehouse of Energy

Learning Objective

- Know the difference between starch, cellulose and glycogen.
- List the key steps in carbohydrate digestion.

All carbohydrates consist of carbon, hydrogen, and oxygen atoms and are polyhydroxy aldehydes or ketones or are compounds that can be broken down to form such compounds. Examples of carbohydrates include starch, fiber, the sweet-tasting compounds called sugars, and structural materials such as cellulose. Different carbohydrates that will be discussed below include the simple sugars, oligosaccharides and polysaccharides (Figure **7.8.1**.

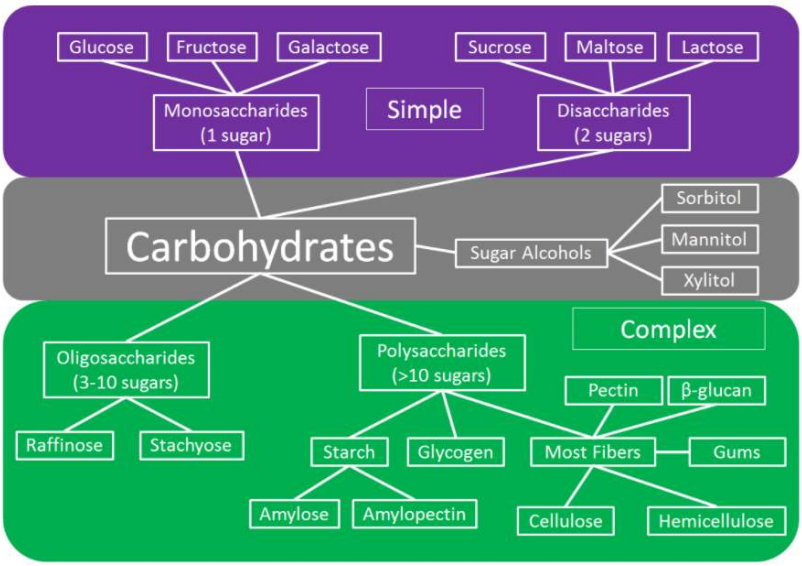
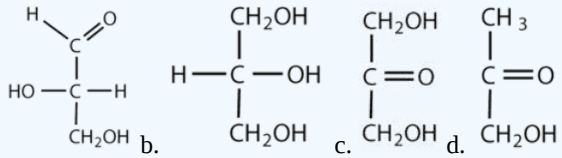


Figure **7.8.1** *Overview of carbohydrates*

Example 7.8.1

Which compounds would be classified as carbohydrates?

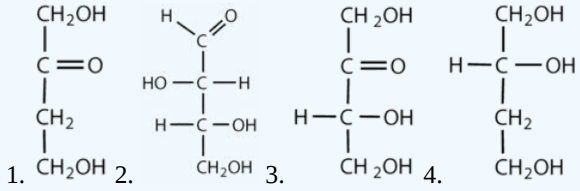


Solution

a. This is a carbohydrate because the molecule contains an aldehyde functional group with OH groups on the other two carbon atoms.
b. This is not a carbohydrate because the molecule does not contain an aldehyde or a ketone functional group.
c. This is a carbohydrate because the molecule contains a ketone functional group with OH groups on the other two carbon atoms.
d. This is not a carbohydrate; although it has a ketone functional group, one of the other carbons atoms does not have an OH group attached.

? Exercise 7.8.1

Which compounds would be classified as carbohydrates?



Some Simple Sugars

The naturally occurring **monosaccharides** contain three to seven carbon atoms per molecule (one sugar unit) . Monosaccharides (or simple sugars) of specific sizes may be indicated by names composed of a stem denoting the number of carbon atoms and the suffix *-ose*. For example, the terms *triose*, *tetrose*, *pentose*, and *hexose* signify monosaccharides with, respectively, three, four, five, and six carbon atoms. Monosaccharides are also classified as aldoses or ketoses. Those monosaccharides that contain an aldehyde functional group are called aldoses; those containing a ketone functional group on the second carbon atom are ketoses. Combining these classification systems gives general names that indicate both the type of carbonyl group *and* the number of carbon atoms in a molecule. Thus, monosaccharides are described as aldotetroses, aldopentoses, ketopentoses, ketoheptoses, and so forth.

Although a variety of monosaccharides are found in living organisms, three hexoses are particularly abundant: D-glucose, D-galactose, and D-fructose (Figure **7.8.2**). Glucose and galactose are both aldohexoses, while fructose is a ketohexose.

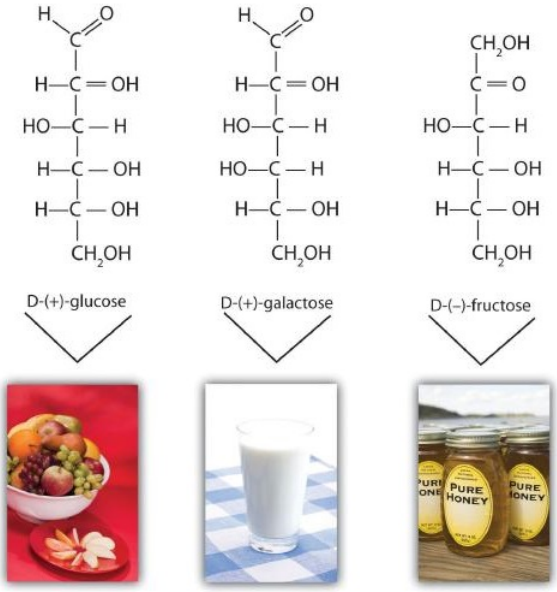


Figure **7.8.2**: Structures of Three Important Hexoses. Each hexose is pictured with a food source in which it is commonly found. Source: Photos © Thinkstock.

In aqueous solution, the predominant forms are not the straight-chain structure shown above. Rather, they adopt a cyclic structure. The representative ring structures of glucose, fructose, and galactose are shown in Figure **7.8.3**. Notice that all are 6-carbon sugars (hexoses). However, fructose has a five member ring, while glucose and galactose have 6 member rings. Also notice that the only structural difference between glucose and galactose is the position of the alcohol (OH) group that is shown in red.

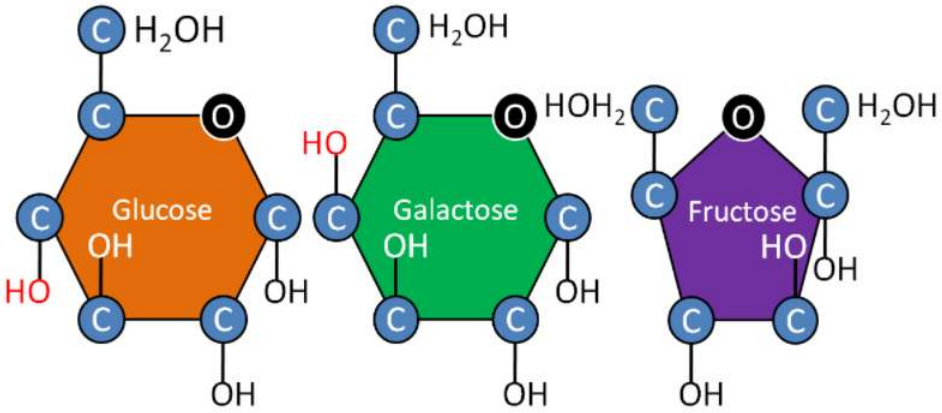


Figure **7.8.3** *The ring structures of glucose, galactose, and fructose.*

A **disaccharide** contains two monosaccharides joined together. Examples include and . They are composed of two monosaccharide units bound together by a bond known as a formed via a , resulting in the loss of a atom from one monosaccharide and a from the other. The of unmodified disaccharides is $C_{12}H_{22}O_{11}$. Although there are numerous kinds of disaccharides, a handful of disaccharides are particularly notable.

Sucrose, which may be obtained by condensing a molecule of α-glucose with one of the cyclic forms of fructose called β-fructose. The structure of sucrose is shown in Figure **7.8.4**.

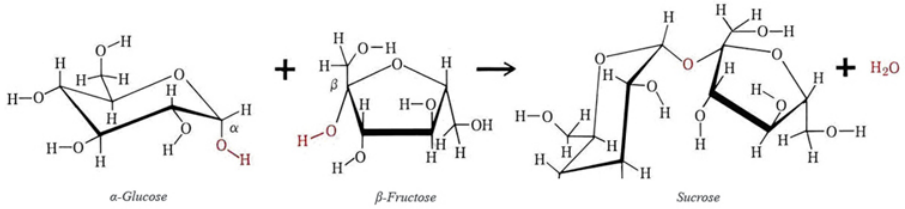


Figure **7.8.4** *The formation of sucrose from glucose and fructose.*

Other, less familiar, examples of disaccharides are lactose, which occurs in milk, and maltose, which are shown in Figure **7.8.5**. In order to digest a disaccharide like sucrose or lactose, the human body must have an enzyme which can catalyze hydrolysis of the linkage between the two monosaccharide units. Many Asians, Africans, and American Indians are incapable of synthesizing lactase, the enzyme that speeds hydrolysis of lactose. If such persons drink milk, the undigested lactose makes them sick.

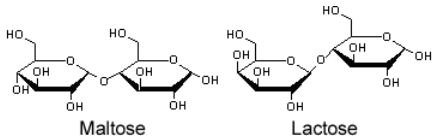


Figure **7.8.5** Two other common disaccharides, maltose and lactose.

The polysaccharides are the most abundant carbohydrates in nature and serve a variety of functions, such as energy storage or as components of plant cell walls. Polysaccharides are very large polymers composed of tens to thousands of monosaccharides joined together by glycosidic linkages. The three most abundant polysaccharides are starch, glycogen, and cellulose. These three are referred to as *homopolymers* because each yields only one type of monosaccharide (glucose) after complete hydrolysis. *Heteropolymers* may contain sugar acids, amino sugars, or noncarbohydrate substances in addition to monosaccharides. Heteropolymers are common in nature (gums, pectins, and other substances) but will not be discussed further in this textbook. The polysaccharides are nonreducing carbohydrates, are not sweet tasting, and do not undergo mutarotation.

Starch

Starch is the most important source of carbohydrates in the human diet and accounts for more than 50% of our carbohydrate intake. It occurs in plants in the form of granules, and these are particularly abundant in seeds (especially the cereal grains) and tubers, where they serve as a storage form of carbohydrates. The breakdown of starch to glucose nourishes the plant during periods of

reduced photosynthetic activity. We often think of potatoes as a “starchy” food, yet other plants contain a much greater percentage of starch (potatoes 15%, wheat 55%, corn 65%, and rice 75%). Commercial starch is a white powder.

Starch is a mixture of two polymers: amylose and amylopectin. Natural starches consist of about 10%–30% amylose and 70%–90% amylopectin. Amylose is a linear polysaccharide composed entirely of D-glucose units joined by the α-1,4-glycosidic linkages we saw in maltose (part (a) of Figure **7.8.6**). Experimental evidence indicates that amylose is not a straight chain of glucose units but instead is coiled like a spring, with six glucose monomers per turn (part (b) of Figure **7.8.6**). When coiled in this fashion, amylose has just enough room in its core to accommodate an iodine molecule. The characteristic blue-violet color that appears when starch is treated with iodine is due to the formation of the amylose-iodine complex. This color test is sensitive enough to detect even minute amounts of starch in solution.

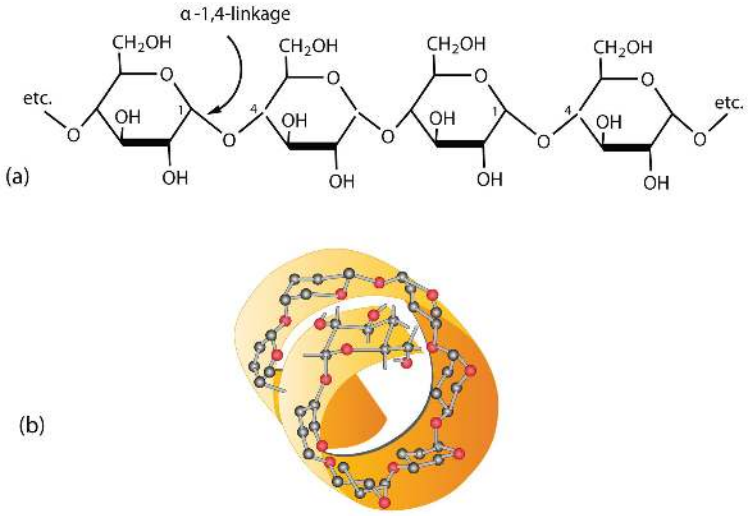


Figure **7.8.6** Amylose. (a) Amylose is a linear chain of α-D-glucose units joined together by α-1,4-glycosidic bonds. (b) Because of hydrogen bonding, amylose acquires a spiral structure that contains six glucose units per turn.

Amylopectin is a branched-chain polysaccharide composed of glucose units linked primarily by α-1,4-glycosidic bonds but with occasional α-1,6-glycosidic bonds, which are responsible for the branching. A molecule of amylopectin may contain many thousands of glucose units with branch points occurring about every 25–30 units (Figure **7.8.7**). The helical structure of amylopectin is disrupted by the branching of the chain, so instead of the deep blue-violet color amylose gives with iodine, amylopectin produces a less intense reddish brown.

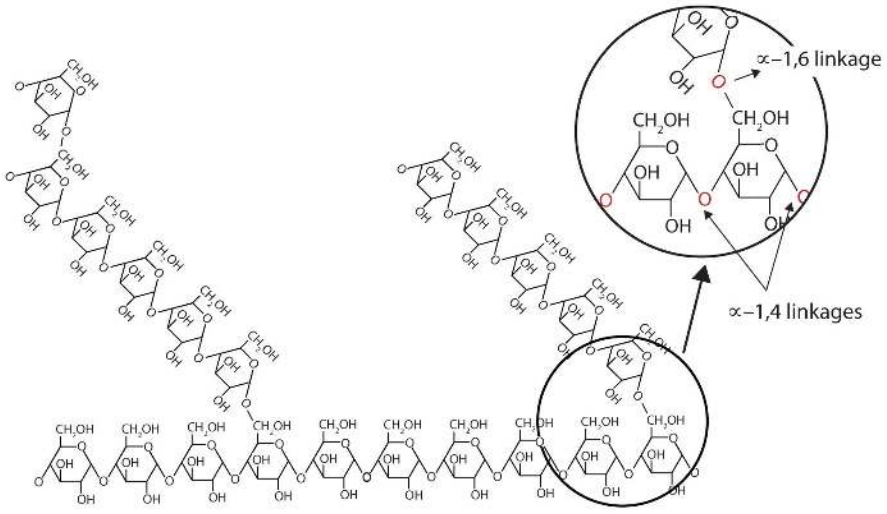


Figure **7.8.7** Representation of the Branching in Amylopectin and Glycogen. Both amylopectin and glycogen contain branch points that are linked through α-1,6-linkages. These branch points occur more often in glycogen.

Dextrins are glucose polysaccharides of intermediate size. The shine and stiffness imparted to clothing by starch are due to the presence of dextrins formed when clothing is ironed. Because of their characteristic stickiness with wetting, dextrins are used as adhesives on stamps, envelopes, and labels; as binders to hold pills and tablets together; and as pastes. Dextrins are more easily digested than starch and are therefore used extensively in the commercial preparation of infant foods.

The complete hydrolysis of starch yields, in successive stages, glucose:

$$\text{starch} \rightarrow \text{dextrins} \rightarrow \text{maltose} \rightarrow \text{glucose}$$

In the human body, several enzymes known collectively as amylases degrade starch sequentially into usable glucose units.

Glycogen

Glycogen is the energy reserve carbohydrate of animals. Practically all mammalian cells contain some stored carbohydrates in the form of glycogen, but it is especially abundant in the liver (4%–8% by weight of tissue) and in skeletal muscle cells (0.5%–1.0%). Like starch in plants, glycogen is found as granules in liver and muscle cells. When fasting, animals draw on these glycogen reserves during the first day without food to obtain the glucose needed to maintain metabolic balance.

Glycogen is structurally quite similar to amylopectin, although glycogen is more highly branched (8–12 glucose units between branches) and the branches are shorter. When treated with iodine, glycogen gives a reddish brown color. Glycogen can be broken down into its D-glucose subunits by acid hydrolysis or by the same enzymes that catalyze the breakdown of starch. In animals, the enzyme phosphorylase catalyzes the breakdown of glycogen to phosphate esters of glucose.

> *About 70% of the total glycogen in the body is stored in muscle cells. Although the percentage of glycogen (by weight) is higher in the liver, the much greater mass of skeletal muscle stores a greater total amount of glycogen.*

Cellulose

Cellulose, a fibrous carbohydrate found in all plants, is the structural component of plant cell walls. Because the earth is covered with vegetation, cellulose is the most abundant of all carbohydrates, accounting for over 50% of all the carbon found in the vegetable kingdom. Cotton fibrils and filter paper are almost entirely cellulose (about 95%), wood is about 50% cellulose, and the dry weight of leaves is about 10%–20% cellulose. The largest use of cellulose is in the manufacture of paper and paper products. Although the use of noncellulose synthetic fibers is increasing, rayon (made from cellulose) and cotton still account for over 70% of textile production.

Like amylose, cellulose is a linear polymer of glucose. It differs, however, in that the glucose units are joined by β-1,4-glycosidic linkages, producing a more extended structure than amylose (part (a) of Figure **7.8.8**). This extreme linearity allows a great deal of hydrogen bonding between OH groups on adjacent chains, causing them to pack closely into fibers (part (b) of Figure **7.8.8**). As a result, cellulose exhibits little interaction with water or any other solvent. Cotton and wood, for example, are completely insoluble in water and have considerable mechanical strength. Because cellulose does not have a helical structure, it does not bind to iodine to form a colored product.

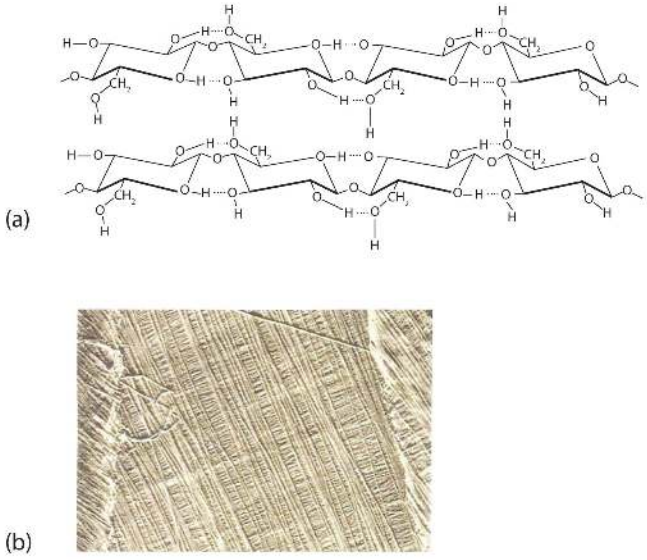


Figure **7.8.8** Cellulose. (a) There is extensive hydrogen bonding in the structure of cellulose. (b) In this electron micrograph of the cell wall of an alga, the wall consists of successive layers of cellulose fibers in parallel arrangement.

Cellulose yields D-glucose after complete acid hydrolysis, yet humans are unable to metabolize cellulose as a source of glucose. Our digestive juices lack enzymes that can hydrolyze the β-glycosidic linkages found in cellulose, so although we can eat potatoes, we cannot eat grass. However, certain microorganisms can digest cellulose because they make the enzyme cellulase, which catalyzes the hydrolysis of cellulose. The presence of these microorganisms in the digestive tracts of herbivorous animals (such as cows, horses, and sheep) allows these animals to degrade the cellulose from plant material into glucose for energy. Termites also contain cellulase-secreting microorganisms and thus can subsist on a wood diet. This example once again demonstrates the extreme stereospecificity of biochemical processes.

Summary

- Starch is a storage form of energy in plants. It contains two polymers composed of glucose units: amylose (linear) and amylopectin (branched).
- Glycogen is a storage form of energy in animals. It is a branched polymer composed of glucose units. It is more highly branched than amylopectin.
- Cellulose is a structural polymer of glucose units found in plants. It is a linear polymer with the glucose units linked through β-1,4-glycosidic bonds.

Sources

Wikipedia

Contributors and Attributions

- Template:ContribLindshield
- Libretext: The Basics of GOB Chemistry (Ball et al.)
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- Marisa Alviar-Agnew (Sacramento City College)

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7.9: Proteins- Polymers of Amino Acids

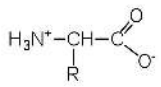
Learning Objectives

- Identify different amino acids.
- Describe how short chain proteins (polypeptides) are formed from amino acids.

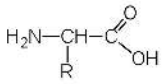
Proteins may be defined as compounds of high molar mass consisting largely or entirely of chains of amino acids. Their masses range from several thousand to several million daltons (Da). In addition to carbon, hydrogen, and oxygen atoms, all proteins contain nitrogen and sulfur atoms, and many also contain phosphorus atoms and traces of other elements. Proteins serve a variety of roles in living organisms and are often classified by these biological roles. Muscle tissue is largely protein, as are skin and hair. Proteins are present in the blood, in the brain, and even in tooth enamel. Each type of cell in our bodies makes its own specialized proteins, as well as proteins common to all or most cells. We begin our study of proteins by looking at the properties and reactions of amino acids, which is followed by a discussion of how amino acids link covalently to form peptides and proteins. We end the chapter with a discussion of enzymes—the proteins that act as catalysts in the body.

The proteins in all living species, from bacteria to humans, are constructed from the same set of 20 amino acids, so called because each contains an amino group attached to a carboxylic acid. The amino acids in proteins are α-amino acids, which means the amino group is attached to the α-carbon of the carboxylic acid. Humans can synthesize only about half of the needed amino acids; the remainder must be obtained from the diet and are known as essential amino acids. However, two additional amino acids have been found in limited quantities in proteins: Selenocysteine was discovered in 1986, while pyrrolysine was discovered in 2002.

The amino acids are colorless, nonvolatile, crystalline solids, melting and decomposing at temperatures above 200°C. These melting temperatures are more like those of inorganic salts than those of amines or organic acids and indicate that the structures of the amino acids in the solid state and in neutral solution are best represented as having both a negatively charged group and a positively charged group. Such a species is known as a zwitterion.



α-Amino acid drawn as a zwitterion

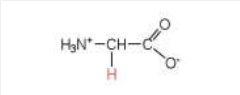
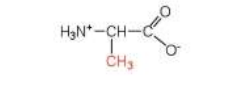
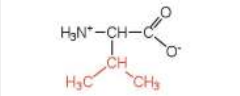
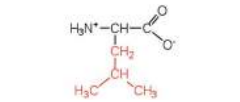
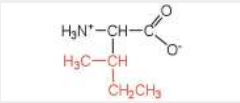
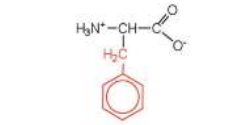
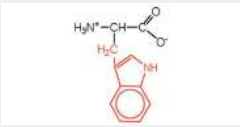
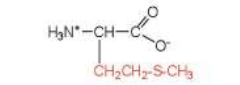
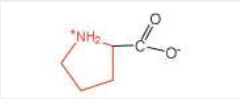
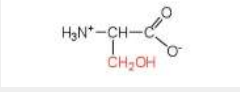
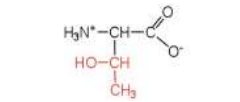
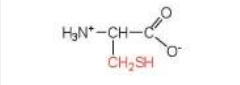


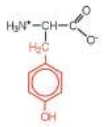
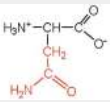
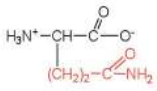
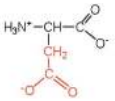
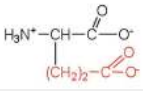
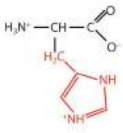
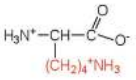
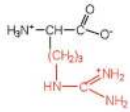
α-Amino acid drawn as an uncharged molecule; not an accurate respresentation of amino acid structure

Classification

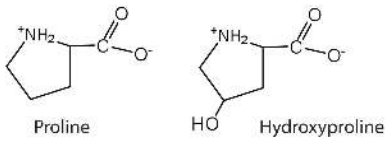
In addition to the amino and carboxyl groups, amino acids have a side chain or R group attached to the α-carbon. Each amino acid has unique characteristics arising from the size, shape, solubility, and ionization properties of its R group. As a result, the side chains of amino acids exert a profound effect on the structure and biological activity of proteins. Although amino acids can be classified in various ways, one common approach is to classify them according to whether the functional group on the side chain at neutral pH is nonpolar, polar but uncharged, negatively charged, or positively charged. The structures and names of the 20 amino acids, their one- and three-letter abbreviations, and some of their distinctive features are given in Table **7.9.1**.

Table **7.9.1**: Common Amino Acids Found in Proteins

Common Name	Abbreviation	Structural Formula (at pH 6)	Molar Mass	Distinctive Feature
Amino acids with a nonpolar R group				
glycine	gly (G)		75	the only amino acid lacking a chiral carbon
alanine	ala (A)		89	—
valine	val (V)		117	a branched-chain amino acid
leucine	leu (L)		131	a branched-chain amino acid
isoleucine	ile (I)		131	an essential amino acid because most animals cannot synthesize branched-chain amino acids
phenylalanine	phe (F)		165	also classified as an aromatic amino acid
tryptophan	trp (W)		204	also classified as an aromatic amino acid
methionine	met (M)		149	side chain functions as a methyl group donor
proline	pro (P)		115	contains a secondary amine group; referred to as an *α-imino acid*
Amino acids with a polar but neutral R group				
serine	ser (S)		105	found at the active site of many enzymes
threonine	thr (T)		119	named for its similarity to the sugar threose
cysteine	cys (C)		121	oxidation of two cysteine molecules yields *cystine*

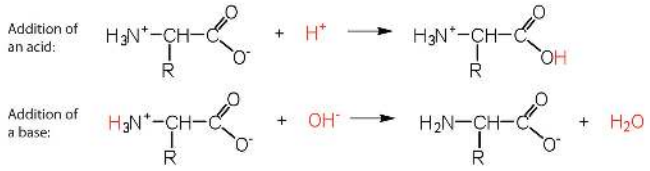
Common Name	Abbreviation	Structural Formula (at pH 6)	Molar Mass	Distinctive Feature
tyrosine	tyr (Y)		181	also classified as an aromatic amino acid
asparagine	asn (N)		132	the amide of aspartic acid
glutamine	gln (Q)		146	the amide of glutamic acid
Amino acids with a negatively charged R group				
aspartic acid	asp (D)		132	carboxyl groups are ionized at physiological pH; also known as aspartate
glutamic acid	glu (E)		146	carboxyl groups are ionized at physiological pH; also known as glutamate
Amino acids with a positively charged R group				
histidine	his (H)		155	the only amino acid whose R group has a pK_a (6.0) near physiological pH
lysine	lys (K)		147	—
arginine	arg (R)		175	almost as strong a base as sodium hydroxide

The first amino acid to be isolated was asparagine in 1806. It was obtained from protein found in asparagus juice (hence the name). Glycine, the major amino acid found in gelatin, was named for its sweet taste (Greek *glykys*, meaning “sweet”). In some cases an amino acid found in a protein is actually a derivative of one of the common 20 amino acids (one such derivative is hydroxyproline). The modification occurs *after* the amino acid has been assembled into a protein.



Zwitterions

The structure of an amino acid allows it to act as both an acid and a base. An amino acid has this ability because at a certain pH value (different for each amino acid) nearly all the amino acid molecules exist as zwitterions. If acid is added to a solution containing the zwitterion, the carboxylate group captures a hydrogen (H^+) ion, and the amino acid becomes positively charged. If base is added, ion removal of the H^+ ion from the amino group of the zwitterion produces a negatively charged amino acid. In both circumstances, the amino acid acts to maintain the pH of the system—that is, to remove the added acid (H^+) or base (OH^-) from solution.



The Peptide Bond: Peptides and Proteins

Two or more amino acids can join together into chains called peptides. Previously, we discussed the reaction between ammonia and a carboxylic acid to form an amide. In a similar reaction, the amino group on one amino acid molecule reacts with the carboxyl group on another, releasing a molecule of water and forming an amide linkage as shown in Figure **7.9.1**

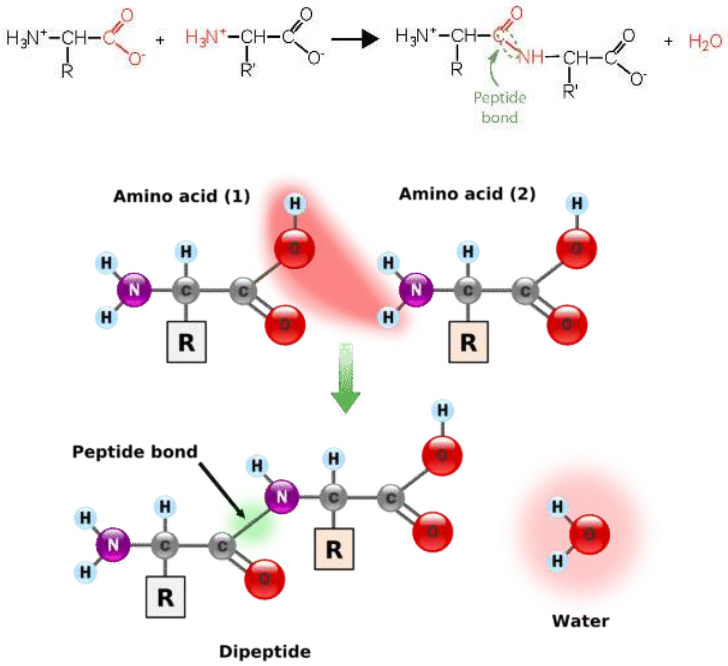
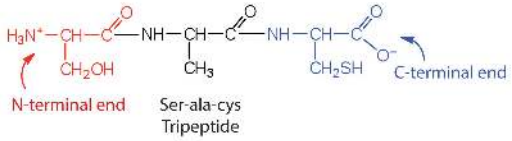


Figure **7.9.1** *Amino acids undergo condensation to form a molecule called a dipeptide. The* **C–N** *bond is called a peptide bond.*

An amide bond joining two amino acid units is called a peptide bond. Note that the product molecule still has a reactive amino group on the left and a reactive carboxyl group on the right. These can react with additional amino acids to lengthen the peptide. The process can continue until thousands of units have joined, resulting in large proteins.

A chain consisting of only two amino acid units is called a *dipeptide*; a chain consisting of three is a *tripeptide*. By convention, peptide and protein structures are depicted with the amino acid whose amino group is free (the N-terminal end) on the left and the amino acid with a free carboxyl group (the C-terminal end) to the right.

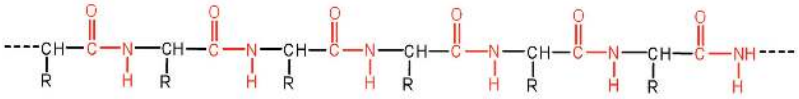


The general term *peptide* refers to an amino acid chain of unspecified length. However, chains of about 50 amino acids or more are usually called proteins or polypeptides. In its physiologically active form, a protein may be composed of one or more polypeptide chains.

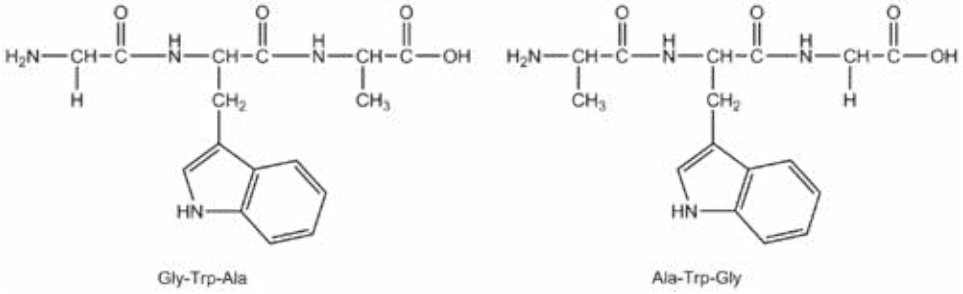
Peptide cells in our bodies have an intricate mechanism for the manufacture of proteins. Humans have to use other techniques in order to synthesize the same proteins in a lab. The chemistry of peptide synthesis is complicated. Both active groups on an amino acid can react and the amino acid sequence must be a specific one in order for the protein to function. Robert Merrifield developed the first synthetic approach for making proteins in the lab, a manual approach which was lengthy and tedious (and, he won the Nobel Prize in Chemistry in 1984 for his work). Today, however, automated systems can crank out a peptide in a very short period of time.

The Sequence of Amino Acids

The particular sequence of amino acids in a longer chain is called an amino acid sequence. By convention, the amino acid sequence is listed in the order such that the free amine group is on the left end of the molecule and the free carboxyl group is on the right end of the molecule.



For example, suppose that a sequence of the amino acids glycine, tryptophan, and alanine is formed with the free amine group as part of the glycine and the free carboxyl group as part of the alanine. The amino acid sequence can be easily written using the abbreviations as Gly-Trp-Ala. This is a different sequence from Ala-Trp-Gly because the free amine and carboxyl groups would be on different amino acids in that case.



Bradykinin

For peptides and proteins to be physiologically active, it is not enough that they incorporate certain amounts of specific amino acids. The order, or *sequence*, in which the amino acids are connected is also of critical importance. Bradykinin is a nine-amino acid peptide (Figure **7.9.2**) produced in the blood that has the following amino acid sequence:

arg-pro-pro-gly-phe-ser-pro-phe-arg

This peptide lowers blood pressure, stimulates smooth muscle tissue, increases capillary permeability, and causes pain. When the order of amino acids in bradykinin is reversed,

arg-phe-pro-ser-phe-gly-pro-pro-arg

the peptide resulting from this synthesis shows none of the activity of bradykinin.

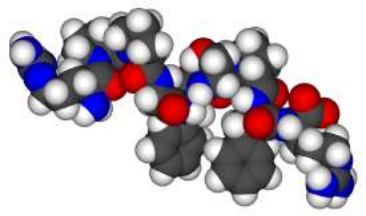


Figure **7.9.2** Space-filling model of bradykinin. (Public Domain; Fvasconcellos)

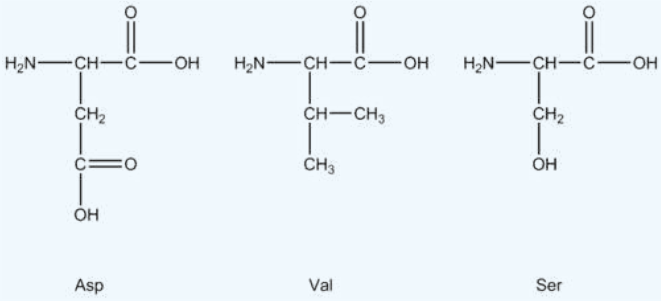
Just as millions of different words are spelled with our 26-letter English alphabet, millions of different proteins are made with the 20 common amino acids. However, just as the English alphabet can be used to write gibberish, amino acids can be put together in the *wrong sequence* to produce nonfunctional proteins. Although the correct sequence is ordinarily of utmost importance, it is not always absolutely required. Just as you can sometimes make sense of incorrectly spelled English words, a protein with a small percentage of "incorrect" amino acids may continue to function. However, it rarely functions as well as a protein having the correct sequence. There are also instances in which seemingly minor errors of sequence have disastrous effects. For example, in some people, every molecule of hemoglobin (a protein in the blood that transports oxygen) has a single incorrect amino acid unit out of about 300 (a single valine replaces a glutamic acid). That "minor" error is responsible for sickle cell anemia, an inherited condition that usually is fatal.

Example 7.9.1

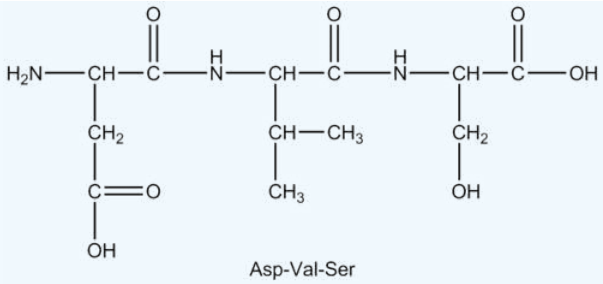
Draw the polypeptide Asp-Val-Ser.

Solution

1. Identify the structures of each of the three given amino acids and draw them in the same order as given in the name.



2. Leaving the order the same, connect the amino acids to one another by forming peptide bonds. Note that the order given in the name is the same way the amino acids are connected in the molecule. The first one listed is always the **N**-terminus of the polypeptide.



Asp-Val-Ser

Example 7.9.2

List all of the possible polypeptides that can be formed from cysteine (Cys), leucine (Leu), and arginine (Arg).

Solution

Although there are only three amino acids, the order in which they are bonded changes the identity, properties, and function of the resulting polypeptide. There are six possible polypeptides formed from these three amino acids.

Cys-Leu-Arg

Cys-Arg-Leu

Leu-Cys-Arg

Leu-Arg-Cys

Arg-Cys-Leu

Arg-Leu-Cys

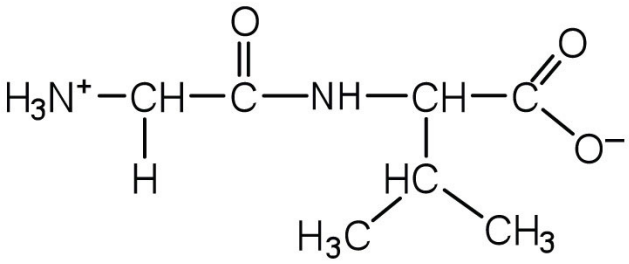
Exercise 7.9.1

Draw the structure for each peptide.

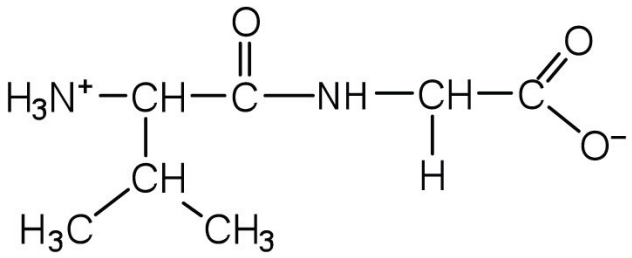
a. gly-val
b. val-gly

Answers

a.



b.



Summary

- The amino group of one amino acid can react with the carboxyl group on another amino acid to form a peptide bond that links the two amino acids together.
- Additional amino acids can be added on through the formation of addition peptide (amide) bonds.
- A chain consisting of only two amino acid units is called a *dipeptide*; a chain consisting of three is a *tripeptide*.
- Chains of about 50 amino acids or more are usually called proteins or polypeptides.
- A sequence of amino acids in a peptide or protein is written with the N-terminal amino acid first and the C-terminal amino acid at the end (writing left to right).
- The order, or *sequence*, in which the amino acids are connected is also of critical importance in order for a peptide or protein to be physiologically active.

Contributors and Attributions

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-
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7.10: Nucleic Acids- Parts, Structure, and Function

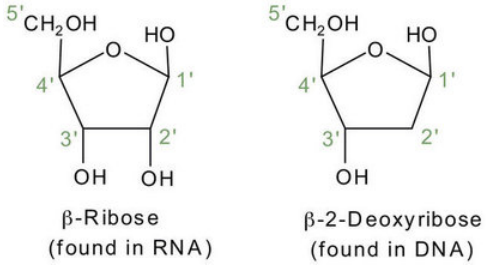
Learning Objectives

- Describe the two types of nucleic acids and the function of each type.
- Describe the secondary structure of DNA and the importance of complementary base pairing.
- Describe how a new copy of DNA is synthesized.

The repeating, or monomer, units that are linked together to form nucleic acids are known as nucleotides. The deoxyribonucleic acid (DNA) of a typical mammalian cell contains about 3×10^9 nucleotides. Nucleotides can be further broken down to phosphoric acid (H_3PO_4), a pentose sugar (a sugar with five carbon atoms), and a nitrogenous base (a base containing nitrogen atoms).

$$\text{nucleic acids} \xrightarrow[\text{down into}]{\text{can be broken}} \text{nucleotides} \xrightarrow[\text{down into}]{\text{can be broken}} H_3PO_4 + \text{nitrogen base} + \text{pentose sugar}$$

If the pentose sugar is ribose, the nucleotide is more specifically referred to as a *ribonucleotide*, and the resulting nucleic acid is ribonucleic acid (RNA). If the sugar is 2-deoxyribose, the nucleotide is a *deoxyribonucleotide*, and the nucleic acid is DNA.



The nitrogenous bases found in nucleotides are classified as pyrimidines or purines. Pyrimidines are heterocyclic amines with two nitrogen atoms in a six-member ring and include uracil, thymine, and cytosine. Purines are heterocyclic amines consisting of a pyrimidine ring fused to a five-member ring with two nitrogen atoms. Adenine and guanine are the major purines found in nucleic acids (Figure **7.10.1**).

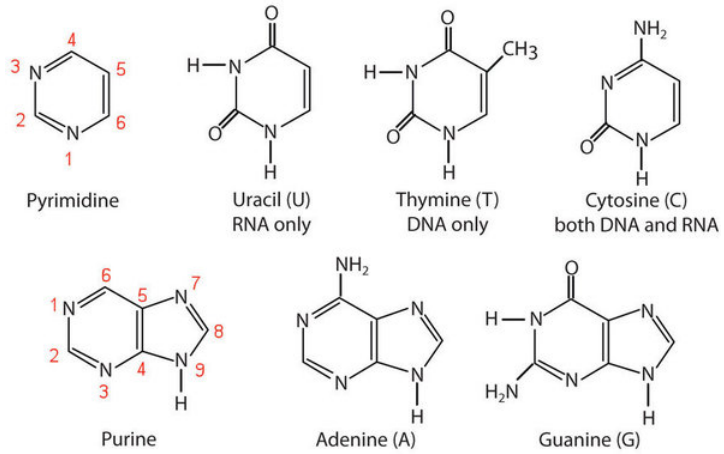


Figure **7.10.1** The Nntrogenous bases found in DNA and RNA.

The formation of a bond between C1′ of the pentose sugar and N1 of the pyrimidine base or N9 of the purine base joins the pentose sugar to the nitrogenous base. In the formation of this bond, a molecule of water is removed. Table **7.10.1** summarizes the similarities and differences in the composition of nucleotides in DNA and RNA.

> The numbering convention is that primed numbers designate the atoms of the pentose ring, and unprimed numbers designate the atoms of the purine or pyrimidine ring.

Table **7.10.1** Composition of Nucleotides in DNA and RNA.

Composition	DNA	RNA
purine bases	adenine and guanine	adenine and guanine
pyrimidine bases	cytosine and thymine	cytosine and uracil
pentose sugar	2-deoxyribose	ribose
inorganic acid	phosphoric acid (H_3PO_4)	H_3PO_4

The names and structures of the major ribonucleotides and one of the deoxyribonucleotides are given in Figure **7.10.2**.

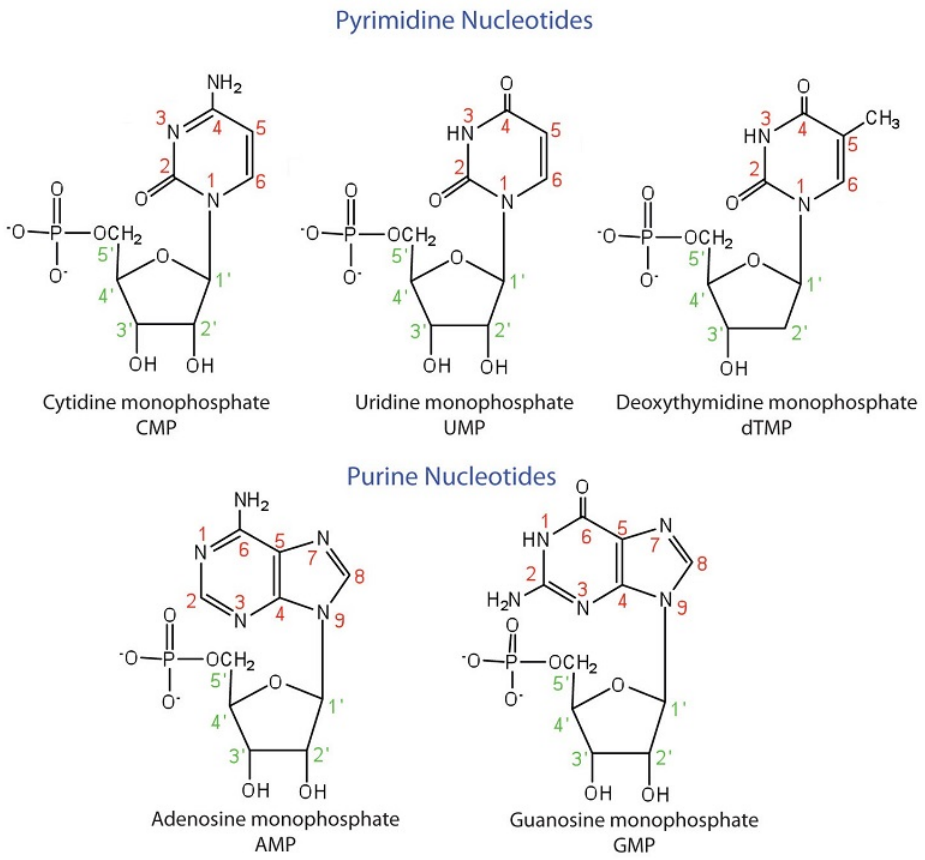


Figure **7.10.2** The pyrimidine and purine nucleotides

Apart from being the monomer units of DNA and RNA, the nucleotides and some of their derivatives have other functions as well. Adenosine diphosphate (ADP) and adenosine triphosphate (ATP), shown in Figure **7.10.3**, have a role in cell metabolism. Moreover, a number of coenzymes, including flavin adenine dinucleotide (FAD), nicotinamide adenine dinucleotide (NAD^+), and coenzyme A, contain adenine nucleotides as structural components.

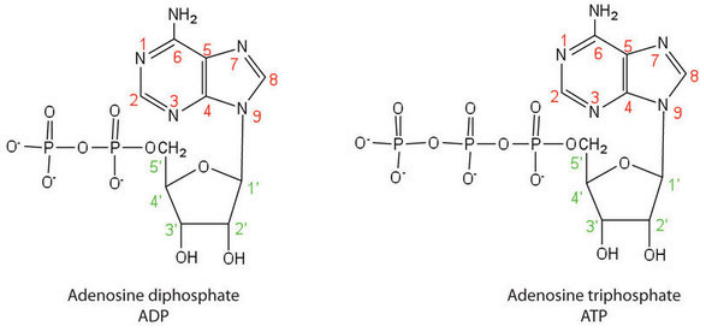


Figure **7.10.3** *Structures of two important adenine-containing nucleotides.*

Nucleic acids are large polymers formed by linking nucleotides together and are found in every cell. Deoxyribonucleic acid (DNA) is the nucleic acid that stores genetic information. If all the DNA in a typical mammalian cell were stretched out end to end, it would extend more than 2 m. Ribonucleic acid (RNA) is the nucleic acid responsible for using the genetic information encoded in DNA to produce the thousands of proteins found in living organisms.

Primary Structure of Nucleic Acids

Nucleotides are joined together through the phosphate group of one nucleotide connecting in an ester linkage to the OH group on the third carbon atom of the sugar unit of a second nucleotide. This unit joins to a third nucleotide, and the process is repeated to produce a long nucleic acid chain (Figure **7.10.4**). The backbone of the chain consists of alternating phosphate and sugar units (2-deoxyribose in DNA and ribose in RNA). The purine and pyrimidine bases branch off this backbone.

> *Each phosphate group has one acidic hydrogen atom that is ionized at physiological pH. This is why these compounds are known as nucleic acids.*

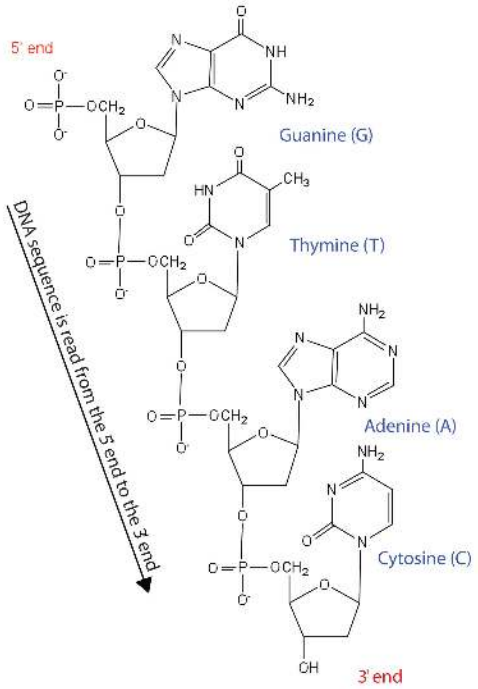


Figure **7.10.4** Structure of a segment of DNA. A similar segment of RNA would have OH groups on each C2′, and uracil would replace thymine.

Like proteins, nucleic acids have a primary structure that is defined as the sequence of their nucleotides. Unlike proteins, which have 20 different kinds of amino acids, there are only 4 different kinds of nucleotides in nucleic acids. For amino acid sequences in proteins, the convention is to write the amino acids in order starting with the N-terminal amino acid. In writing nucleotide sequences for nucleic acids, the convention is to write the nucleotides (usually using the one-letter abbreviations for the bases,

shown in Figure 7.10.4) starting with the nucleotide having a free phosphate group, which is known as the 5′ end, and indicate the nucleotides in order. For DNA, a lowercase *d* is often written in front of the sequence to indicate that the monomers are deoxyribonucleotides. The final nucleotide has a free OH group on the 3′ carbon atom and is called the *3′ end*. The sequence of nucleotides in the DNA segment shown in Figure 7.10.4 would be written 5′-dG-dT-dA-dC-3′, which is often further abbreviated to dGTAC or just GTAC.

Secondary Structure of DNA

The three-dimensional structure of DNA was the subject of an intensive research effort in the late 1940s to early 1950s. Initial work revealed that the polymer had a regular repeating structure. In 1950, Erwin Chargaff of Columbia University showed that the molar amount of adenine (A) in DNA was always equal to that of thymine (T). Similarly, he showed that the molar amount of guanine (G) was the same as that of cytosine (C). Chargaff drew no conclusions from his work, but others soon did.

At Cambridge University in 1953, James D. Watson and Francis Crick announced that they had a model for the secondary structure of DNA. Using the information from Chargaff's experiments (as well as other experiments) and data from the X ray studies of Rosalind Franklin (which involved sophisticated chemistry, physics, and mathematics), Watson and Crick worked with models that were not unlike a child's construction set and finally concluded that DNA is composed of two nucleic acid chains running antiparallel to one another—that is, side-by-side with the 5′ end of one chain next to the 3′ end of the other. Moreover, as their model showed, the two chains are twisted to form a double helix—a structure that can be compared to a spiral staircase, with the phosphate and sugar groups (the backbone of the nucleic acid polymer) representing the outside edges of the staircase. The purine and pyrimidine bases face the inside of the helix, with guanine always opposite cytosine and adenine always opposite thymine. These specific base pairs, referred to as complementary bases, are the steps, or treads, in our staircase analogy (Figure 7.10.5).

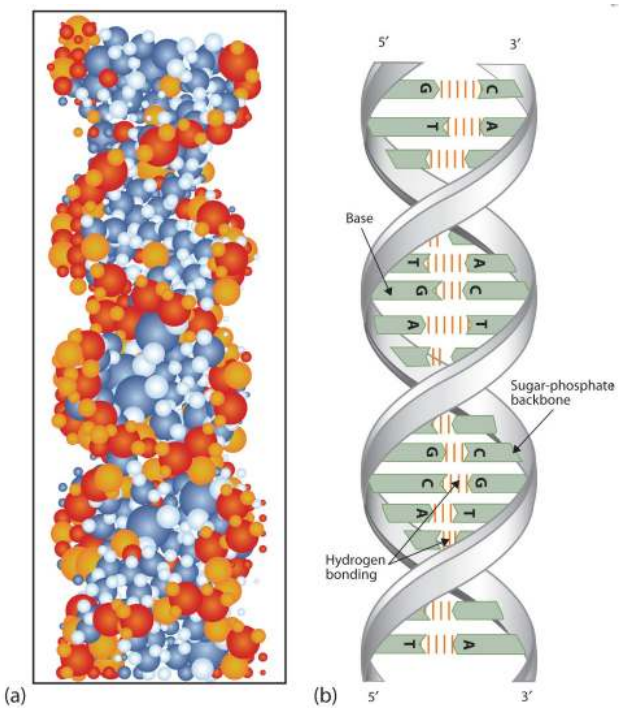


Figure 7.10.5 DNA Double Helix. (a) This represents a computer-generated model of the DNA double helix. (b) This represents a schematic representation of the double helix, showing the complementary bases.

The structure proposed by Watson and Crick provided clues to the mechanisms by which cells are able to divide into two identical, functioning daughter cells; how genetic data are passed to new generations; and even how proteins are built to required specifications. All these abilities depend on the pairing of complementary bases. Figure 7.10.6 shows the two sets of base pairs and illustrates two things. First, a pyrimidine is paired with a purine in each case, so that the long dimensions of both pairs are identical (1.08 nm).

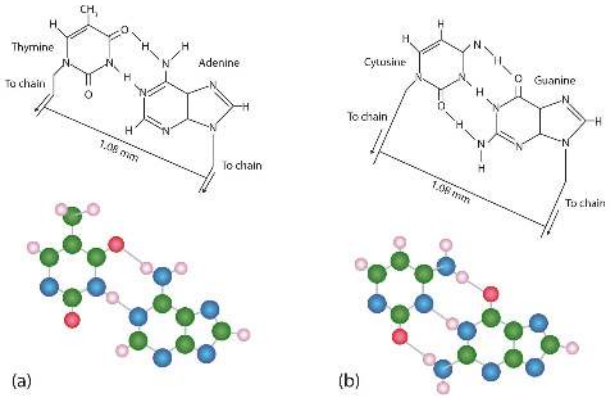


Figure **7.10.6** Complementary Base Pairing. Complementary bases engage in hydrogen bonding with one another: (a) thymine and adenine; (b) cytosine and guanine.

If two pyrimidines were paired or two purines were paired, the two pyrimidines would take up less space than a purine and a pyrimidine, and the two purines would take up more space, as illustrated in Figure **7.10.7**. If these pairings were ever to occur, the structure of DNA would be like a staircase made with stairs of different widths. For the two strands of the double helix to fit neatly, a pyrimidine must always be paired with a purine. The second thing you should notice in Figure **7.10.6** is that the correct pairing enables formation of three instances of hydrogen bonding between guanine and cytosine and two between adenine and thymine. The additive contribution of this hydrogen bonding imparts great stability to the DNA double helix.

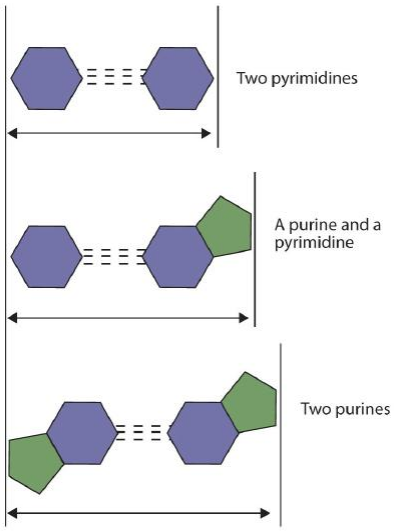


Figure **7.10.7** Difference in Widths of Possible Base Pairs

We previously stated that deoxyribonucleic acid (DNA) stores genetic information, while ribonucleic acid (RNA) is responsible for transmitting or expressing genetic information by directing the synthesis of thousands of proteins found in living organisms. But how do the nucleic acids perform these functions? Three processes are required: (1) *replication*, in which new copies of DNA are made; (2) *transcription*, in which a segment of DNA is used to produce RNA; and (3) *translation*, in which the information in RNA is translated into a protein sequence.

DNA: Self-Replication

New cells are continuously forming in the body through the process of cell division. For this to happen, the DNA in a dividing cell must be copied in a process known as replication. The complementary base pairing of the double helix provides a ready model for how genetic replication occurs. If the two chains of the double helix are pulled apart, disrupting the hydrogen bonding between base pairs, each chain can act as a *template*, or pattern, for the synthesis of a new complementary DNA chain.

The nucleus contains all the necessary enzymes, proteins, and nucleotides required for this synthesis. A short segment of DNA is “unzipped,” so that the two strands in the segment are separated to serve as templates for new DNA. DNA polymerase, an enzyme,

recognizes each base in a template strand and matches it to the complementary base in a free nucleotide. The enzyme then catalyzes the formation of an ester bond between the 5′ phosphate group of the nucleotide and the 3′ OH end of the new, growing DNA chain. In this way, each strand of the original DNA molecule is used to produce a duplicate of its former partner (Figure **7.10.8**). Whatever information was encoded in the original DNA double helix is now contained in each replicate helix. When the cell divides, each daughter cell gets one of these replicates and thus all of the information that was originally possessed by the parent cell.

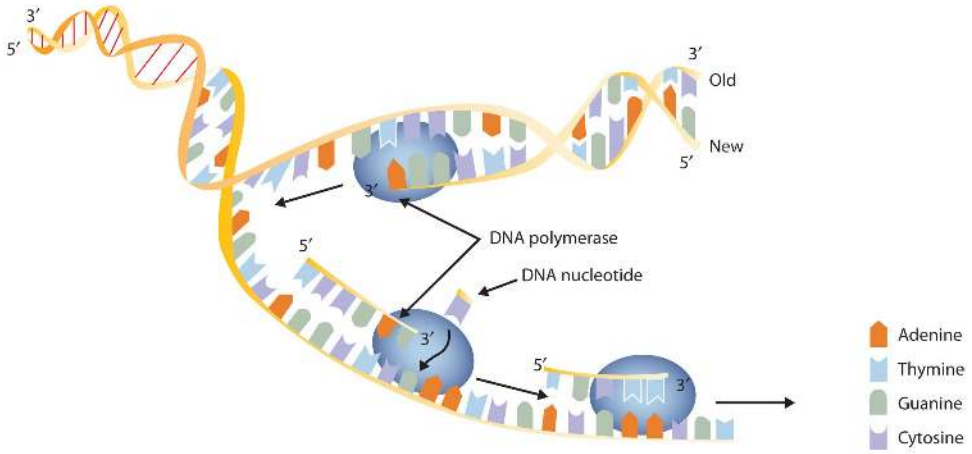


Figure **7.10.8** A Schematic Diagram of DNA Replication. DNA replication occurs by the sequential unzipping of segments of the double helix. Each new nucleotide is brought into position by DNA polymerase and is added to the growing strand by the formation of a phosphate ester bond. Thus, two double helixes form from one, and each consists of one old strand and one new strand, an outcome called *semiconservative replications*. (This representation is simplified; many more proteins are involved in replication.)

✔ Example 7.10.1

A segment of one strand from a DNA molecule has the sequence 5′-TCCATGAGTTGA-3′. What is the sequence of nucleotides in the opposite, or complementary, DNA chain?

Solution

Knowing that the two strands are antiparallel and that T base pairs with A, while C base pairs with G, the sequence of the complementary strand will be 3′-AGGTACTCAACT-5′.

? Exercise 7.10.1

A segment of one strand from a DNA molecule has the sequence 5′-CCAGTGAATTGCCTAT-3′. What is the sequence of nucleotides in the opposite, or complementary, DNA chain?

Answer

3′-GGTCACTTAACGGATA-5′.

Summary

- Nucleotides are composed of phosphoric acid, a pentose sugar (ribose or deoxyribose), and a nitrogen-containing base (adenine, cytosine, guanine, thymine, or uracil). Ribonucleotides contain ribose, while deoxyribonucleotides contain deoxyribose.
- DNA is the nucleic acid that stores genetic information. RNA is the nucleic acid responsible for using the genetic information in DNA to produce proteins.
- Nucleic acid sequences are written starting with the nucleotide having a free phosphate group (the 5′ end).
- Two DNA strands link together in an antiparallel direction and are twisted to form a double helix. The nitrogenous bases face the inside of the helix. Guanine is always opposite cytosine, and adenine is always opposite thymine.
- In DNA replication, each strand of the original DNA serves as a template for the synthesis of a complementary strand.
- DNA polymerase is the primary enzyme needed for replication.

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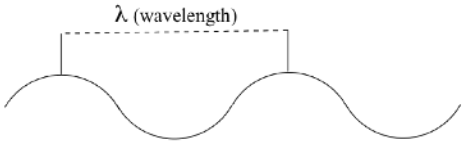
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8: Chemistry of color

The electromagnetic spectrum

Electromagnetic radiation, as you may recall from a previous chemistry or physics class, is composed of electrical and magnetic waves which oscillate on perpendicular planes. Visible light is electromagnetic radiation. So are the gamma rays that are emitted by spent nuclear fuel, the x-rays that a doctor uses to visualize your bones, the ultraviolet light that causes a painful sunburn when you forget to apply sun block, the infrared light that the army uses in night-vision goggles, the microwaves that you use to heat up your frozen burritos, and the radio-frequency waves that bring music to anybody who is old-fashioned enough to still listen to FM or AM radio.

Just like ocean waves, electromagnetic waves travel in a defined direction. While the speed of ocean waves can vary, however, the speed of electromagnetic waves – commonly referred to as the speed of light – is essentially a constant, approximately 300 million meters per second. This is true whether we are talking about gamma radiation or visible light. Obviously, there is a big difference between these two types of waves – we are surrounded by the latter for more than half of our time on earth, whereas we hopefully never become exposed to the former to any significant degree. The different properties of the various types of electromagnetic radiation are due to differences in their wavelengths, and the corresponding differences in their energies: *shorter wavelengths correspond to higher energy.*



High-energy radiation (such as gamma- and x-rays) is composed of very short waves – as short as 10^{-16} meter from crest to crest. Longer waves are far less energetic, and thus are less dangerous to living things. Visible light waves are in the range of 400 – 700 nm (nanometers, or 10^{-9} m), while radio waves can be several hundred meters in length.

The notion that electromagnetic radiation contains a quantifiable amount of energy can perhaps be better understood if we talk about light as a stream of *particles*, called **photons**, rather than as a wave. (Recall the concept known as 'wave-particle duality': at the quantum level, wave behavior and particle behavior become indistinguishable, and very small particles have an observable 'wavelength'). If we describe light as a stream of photons, the energy of a particular wavelength can be expressed as:

$$E = \frac{hc}{\lambda} \tag{4.1.1}$$

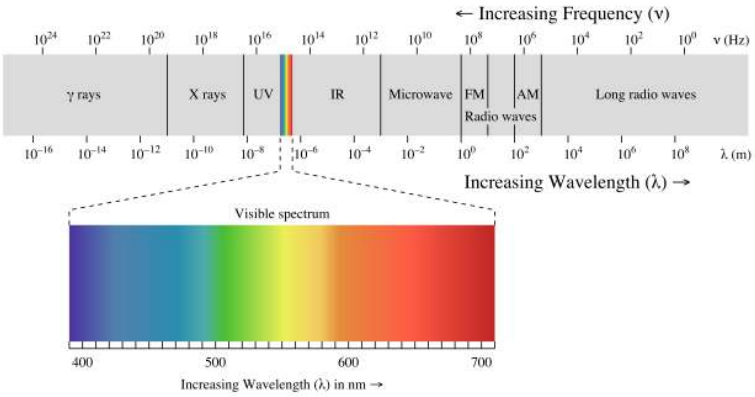
where E is energy in kJ/mol, **λ** (the Greek letter *lambda*) is wavelength in meters, *c* is 3.00 x 10^{8} m/s (the speed of light), and *h* is 3.99 x 10^{-13} kJ·s·mol^{-1}, a number known as **Planck's constant**.

Because electromagnetic radiation travels at a constant speed, each wavelength corresponds to a given frequency, which is the number of times per second that a crest passes a given point. Longer waves have lower frequencies, and shorter waves have higher frequencies. Frequency is commonly reported in hertz (Hz), meaning 'cycles per second', or 'waves per second'. The standard unit for frequency is s^{-1}.

When talking about electromagnetic waves, we can refer either to wavelength or to frequency - the two values are interconverted using the simple expression:

$$\lambda\nu = c \tag{4.1.2}$$

where **ν** (the Greek letter '*nu*') is frequency in s^{-1}. Visible red light with a wavelength of 700 nm, for example, has a frequency of 4.29 x 10^{14} Hz, and an energy of 40.9 kcal per mole of photons. The full range of electromagnetic radiation wavelengths is referred to as the **electromagnetic spectrum**.



(Image from Wikipedia commons)

Notice that visible light takes up just a narrow band of the full spectrum. White light from the sun or a light bulb is a mixture of all of the visible wavelengths. You see the visible region of the electromagnetic spectrum divided into its different wavelengths every time you see a rainbow: violet light has the shortest wavelength, and red light has the longest.

? Exercise 4.4

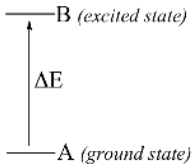
Visible light has a wavelength range of about 400-700 nm. What is the corresponding frequency range? What is the corresponding energy range, in kJ/mol of photons?

Solutions

Overview of a molecular spectroscopy experiment

In a spectroscopy experiment, electromagnetic radiation of a specified range of wavelengths is allowed to pass through a sample containing a compound of interest. The sample molecules absorb energy from some of the wavelengths, and as a result jump from a low energy 'ground state' to some higher energy 'excited state'. Other wavelengths are *not* absorbed by the sample molecule, so they pass on through. A detector on the other side of the sample records which wavelengths were absorbed, and to what extent they were absorbed.

Here is the key to molecular spectroscopy: *a given molecule will specifically absorb only those wavelengths which have energies that correspond to the energy difference of the transition that is occurring.* Thus, if the transition involves the molecule jumping from ground state A to excited state B, with an energy difference of **ΔE**, the molecule will specifically absorb radiation with wavelength that corresponds to **ΔE**, while allowing other wavelengths to pass through unabsorbed.



By observing which wavelengths a molecule absorbs, and to what extent it absorbs them, we can gain information about the nature of the energetic transitions that a molecule is able to undergo, and thus information about its structure.

These generalized ideas may all sound quite confusing at this point, but things will become much clearer as we begin to discuss specific examples.

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- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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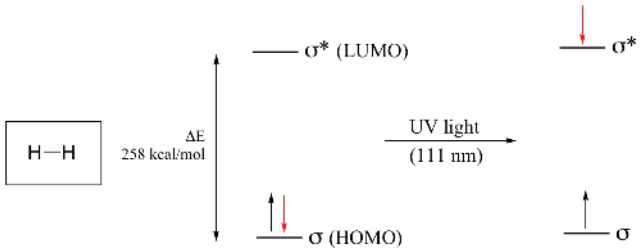
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8.1: Ultraviolet and visible spectroscopy

While interaction with infrared light causes molecules to undergo vibrational transitions, the shorter wavelength, higher energy radiation in the UV (200-400 nm) and visible (400-700 nm) range of the electromagnetic spectrum causes many organic molecules to undergo **electronic transitions**. What this means is that when the energy from UV or visible light is absorbed by a molecule, one of its electrons jumps from a lower energy to a higher energy molecular orbital.

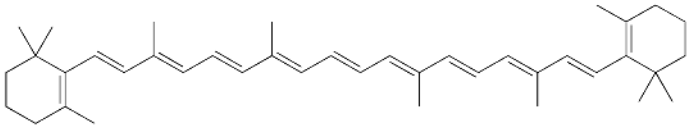
Electronic transitions

As you may recall from CHE 103, electrons in atoms are occupying atomic orbitals. Analogously, electrons in a molecule are occupying molecular orbitas. These orbitals are called HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital). In molecules, electrons can transition from HOMO to LUMO:



If the molecule is exposed to light of a wavelength with energy equal to **ΔE**, the HOMO-LUMO energy gap, this wavelength will be absorbed and the energy used to bump one of the electrons from the HOMO to the LUMO . For some molecules, these electron transitions occur in the UV-visible region of the electromagnetic spectrum. Molecules or parts of molecules that absorb light strongly in the UV-vis region are called **chromophores**. These electronic transitions Where UV-vis spectroscopy becomes useful to most organic and biological chemists is in the study of molecules with conjugated π systems.

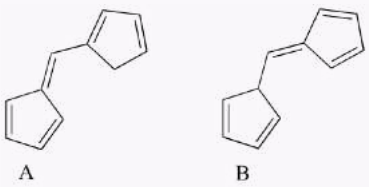
In molecules with extended pi systems, the HOMO-LUMO energy gap becomes so small that absorption occurs in the visible rather then the UV region of the electromagnetic spectrum. Beta-carotene, with its system of 11 conjugated double bonds, absorbs light with wavelengths in the blue region of the visible spectrum while allowing other visible wavelengths – mainly those in the red-yellow region - to be transmitted. This is why carrots are orange.



β-carotene

Exercise 4.9: What is the energy of the photons (in kJ/mol) of light with wavelength of 470 nm, the l_{max} of b-carotene?

Exercise 4.10: Which of the following molecules would you expect absorb at a longer wavelength in the UV region of the electromagnetic spectrum? Explain your answer.

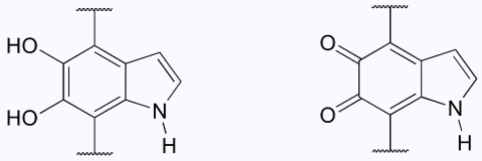


A B

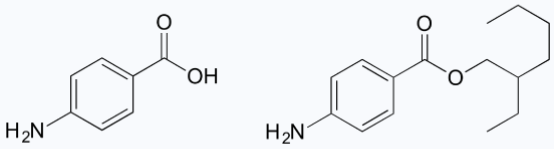
Solutions

Protecting yourself from sunburn

Human skin can be damaged by exposure to ultraviolet light from the sun. We naturally produce a pigment, called melanin, which protects the skin by absorbing much of the ultraviolet radiation. Melanin is a complex polymer, two of the most common monomers units of which are shown below.



common monomer units in melanin

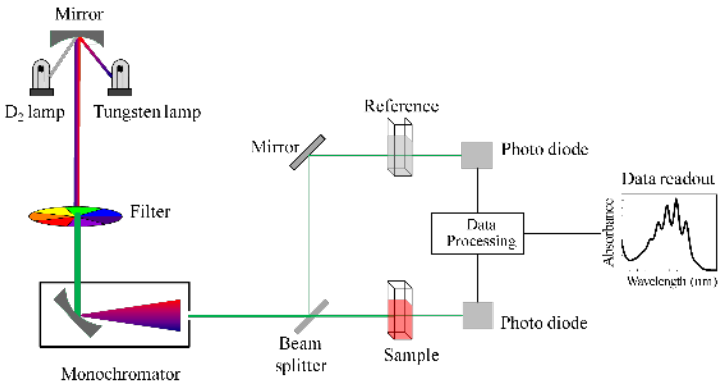


PABA Padimate-O

Overexposure to the sun is still dangerous, because there is a limit to how much radiation our melanin can absorb. Most commercial sunscreens claim to offer additional protection from both UV-A and UV-B radiation: UV-A refers to wavelengths between 315-400 nm, UV-B to shorter, more harmful wavelengths between 280-315 nm. PABA (*para*-aminobenzoic acid) was used in sunscreens in the past, but its relatively high polarity meant that it was not very soluble in oily lotions, and it tended to rinse away when swimming. Many sunscreens today contain, among other active ingredients, a more hydrophobic derivative of PABA called Padimate O.

Looking at UV-vis spectra

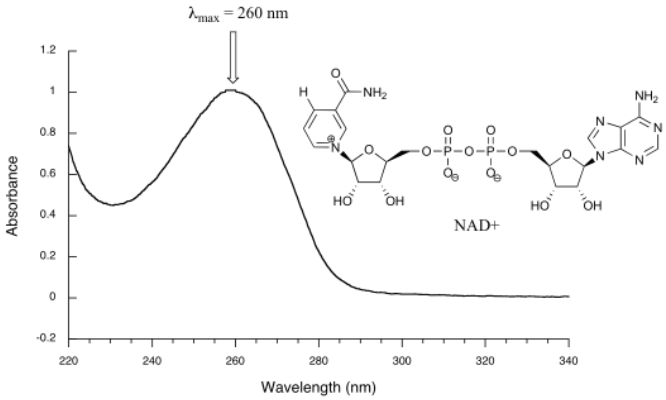
We have been talking in general terms about how molecules absorb UV and visible light – now let's look at some actual examples of data from a UV-vis absorbance spectrophotometer. The basic setup is the same as for IR spectroscopy: radiation with a range of wavelengths is directed through a sample of interest, and a detector records which wavelengths were absorbed and to what extent the absorption occurred.



Schematic for a UV-Vis spectrophotometer

(Image from Wikipedia Commons)

Below is the absorbance spectrum of an important biological molecule called nicotinamide adenine dinucleotide, abbreviated NAD^+. This compound absorbs light in the UV range due to the presence of conjugated pi-bonding systems.



Wavelength values on the x-axis are generally measured in nanometers (nm). Peaks in UV spectra tend to be quite broad, often spanning well over 20 nm at half-maximal height. Typically, there are two things that we look for and record from a UV-Vis spectrum. The first is λ_{max}, which is the wavelength at maximal light absorbance. As you can see, NAD^+ has $\lambda_{max} = 260\ nm$. We also want to record how much light is absorbed at λ_{max}. Here we use a unitless number called **absorbance**, abbreviated 'A'. To calculate absorbance at a given wavelength, the computer in the spectrophotometer simply takes the intensity of light at that wavelength *before* it passes through the sample (I_0), divides this value by the intensity of the same wavelength *after* it passes through the sample (I), then takes the $\log_{10}$ of that number:

$$A = \log \frac{I_0}{I} \tag{4.3.1}$$

You can see that the absorbance value at 260 nm (A_{260}) is about 1.0 in this spectrum.

Exercise 4.11: Express A = 1.0 in terms of percent transmittance (%T, the unit usually used in IR spectroscopy (and sometimes in UV-vis as well).

Solutions

Kahn Academy video tutorials on UV-Vis spectroscopy

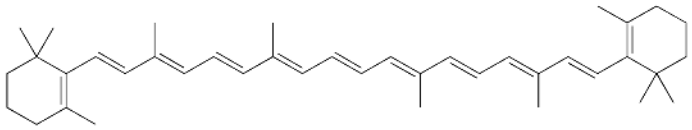
Contributors

- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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8.2: Effect of Conjugation

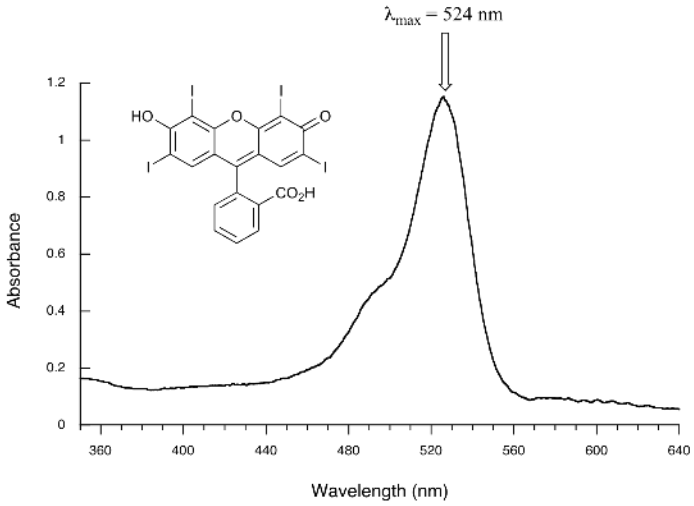
Conjugated systems or conjugated molecules contains an alternation of single and double bonds. For example, beta-carotene represents a conjugate system with 11 conjugated double bonds. Beta-carotene absorbs light with wavelengths in the blue region of the visible spectrum while allowing other visible wavelengths – mainly those in the red-yellow region - to be transmitted. This is why carrots are orange.



β-carotene

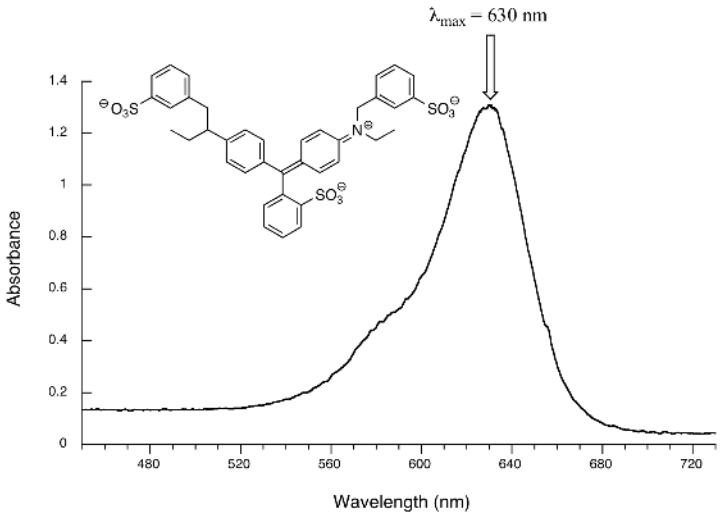
To understand the effect of conjugation, let's compare two typical food colorings. Food coloring Red #3 (less conjugated) and Blue #1 (more conjugated)

Here is the absorbance spectrum of the common food coloring Red #3:



Here, we see that the extended system of conjugated pi bonds causes the molecule to absorb light in the visible range. Because the λ_{max} of 524 nm falls within the green region of the spectrum, the compound appears red to our eyes.

Now, take a look at the spectrum of another food coloring, Blue #1:



Here, maximum absorbance is at 630 nm, in the orange range of the visible spectrum, and the compound appears blue.

We can observe that the more conjugation present in a molecule, the higher the maximum absorbance (λ_{max}) values. We say that the λ_{max} shifts towards longer wavelengths (lower energies, red shift). At the same time, the absorbance becomes more intense (higher values on the Y-axis).

Applications of UV spectroscopy in organic and biological chemistry

UV-vis spectroscopy has many different applications in organic and biological chemistry. One of the most basic of these applications is the use of the **Beer - Lambert Law** to determine the concentration of a chromophore. You most likely have performed a Beer – Lambert experiment in a previous chemistry lab. The law is simply an application of the observation that, within certain ranges, the absorbance of a chromophore at a given wavelength varies in a linear fashion with its concentration: the higher the concentration of the molecule, the greater its absorbance. If we divide the observed value of A at λ_{max} by the concentration of the sample (*c*, in mol/L), we obtain the **molar absorptivity**, or **extinction coefficient** (ε), which is a characteristic value for a given compound.

$\varepsilon = A/c$

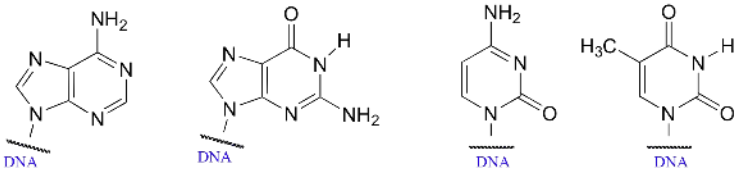
The absorbance will also depend, of course, on the **path length** - in other words, the distance that the beam of light travels though the sample. In most cases, sample holders are designed so that the path length is equal to 1 cm, so the units for molar absorptivity are mol * $L^{-1}cm^{-1}$. If we look up the value of e for our compound at λ_{max}, and we measure absorbance at this wavelength, we can easily calculate the concentration of our sample. As an example, for NAD^+ the literature value of ε at 260 nm is 18,000 mol * $L^{-1}cm^{-1}$. In our NAD^+ spectrum we observed A_{260} = 1.0, so using equation 4.4 and solving for concentration we find that our sample is 5.6 x 10^{-5} M.

Template:ExampleStart

The literature value of ε for 1,3-pentadiene in hexane is 26,000 mol * $L^{-1}cm^{-1}$ at its maximum absorbance at 224 nm. You prepare a sample and take a UV spectrum, finding that A_{224} = 0.850. What is the concentration of your sample?

Template:ExampleEnd

The bases of DNA and RNA are good chromophores:



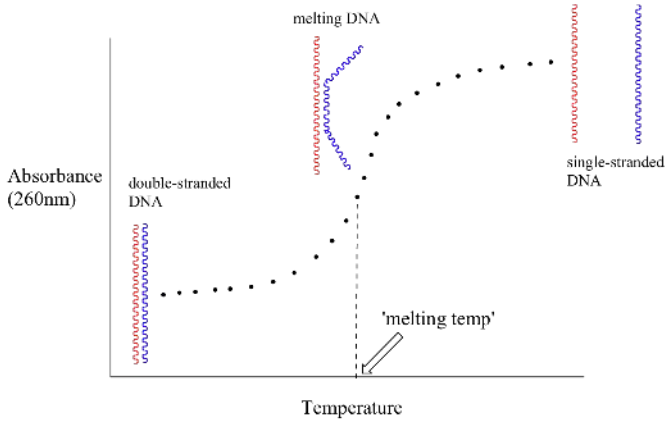
Biochemists and molecular biologists often determine the concentration of a DNA sample by assuming an average value of ε = 0.020 $ng^{-1} \times mL$ for double-stranded DNA at its λ_{max} of 260 nm (notice that concentration in this application is expressed in mass/volume rather than molarity: ng/mL is often a convenient unit for DNA concentration when doing molecular biology).

Template:ExampleStart

50 mL of an aqueous sample of double stranded DNA is dissolved in 950 mL of water. This diluted solution has a maximal absorbance of 0.326 at 260 nm. What is the concentration of the original (more concentrated) DNA sample, expressed in mg/mL?

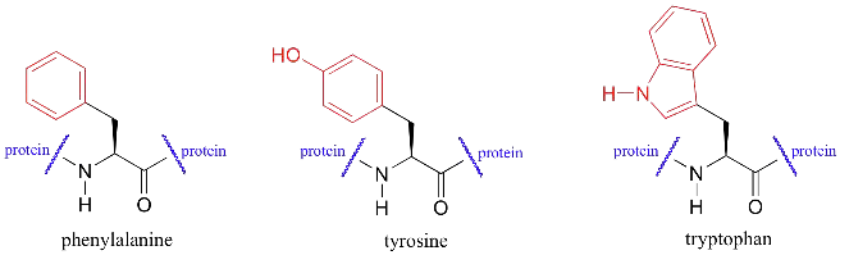
Template:ExampleEnd

Because the extinction coefficient of double stranded DNA is slightly lower than that of single stranded DNA, we can use UV spectroscopy to monitor a process known as DNA melting. If a short stretch of double stranded DNA is gradually heated up, it will begin to 'melt', or break apart, as the temperature increases (recall that two strands of DNA are held together by a specific pattern of hydrogen bonds formed by 'base-pairing').



As melting proceeds, the absorbance value for the sample increases, eventually reaching a high plateau as all of the double-stranded DNA breaks apart, or 'melts'. The mid-point of this process, called the 'melting temperature', provides a good indication of how tightly the two strands of DNA are able to bind to each other.

Proteins absorb light in the UV range due to the presence of the aromatic amino acids tryptophan, phenylalanine, and tyrosine, all of which are chromophores.



Biochemists frequently use UV spectroscopy to study conformational changes in proteins - how they change shape in response to different conditions. When a protein undergoes a conformational shift (partial unfolding, for example), the resulting change in the environment around an aromatic amino acid chromophore can cause its UV spectrum to be altered.

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8.3: Color and Constitution

Visible light is electromagnetic radiation having a rather narrow range of wavelengths (400-800 nm). A black substance absorbs *all* wavelengths of visible light. Selective absorption of visible light by a substance imparts color, but the color is not that of the light absorbed but instead of the residual light that the substance transmits or reflects. For example, a compound that absorbs in the region 435-480 nm removes blue light from the visible spectrum, and the residual light is recognized by the eye as being yellow. The relationship of the observed color to wavelength of light absorbed is shown in Table 28-1. It is customary to call the color observed the **complementary color** or the **subtraction color** to that absorbed.

Table 28-1: *Color and Wavelength*

Light absorbed		Complementary (subtraction) color seen
Wavelength (nm)	Color	
400–435	violet	green-yellow
435–480	blue	yellow
480–490	green-blue	orange
490–500	blue-green (cyan)	red
500–560	green	purple (magenta)
560–580	yellow-green	violet
580–595	yellow	blue
595–605	orange	green-blue
605–750	red	blue-green (cyan)

Figure 28-8.

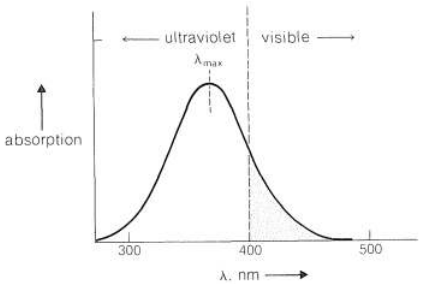


Figure 28-8: Absorption in the visible region by a colored substance that has λ_{max} in the ultraviolet.

Clearly, the color perceived, its brightness and its intensity, depends on the shape of the electronic spectral curve of the absorbing substance, which in turn depends on the chemical structure of the substance. A change in absorption from the blue to the red end of the spectrum corresponds to a *decrease* in the energy of the associated electronic transitions. We know also that this trend is associated with increasing conjugation of multiple bonds. For instance, 1,2-diphenylethene is colorless, whereas 1,10-diphenyl-1,3,5,7,9-decapentaene is yellow-orange:

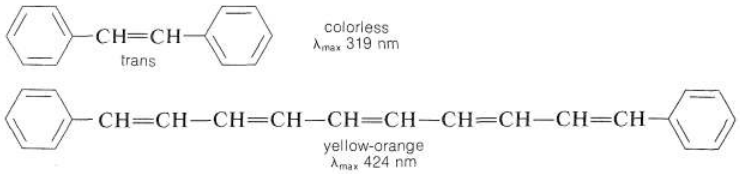


Figure 28-9, from which you can see that conjugation stabilizes both the ground state and the excited state but relatively more so the excited state. Thus the gap between the states narrows with increasing conjugation, and absorption shifts to longer wavelengths (also see Section 9-9B and 21-5C).

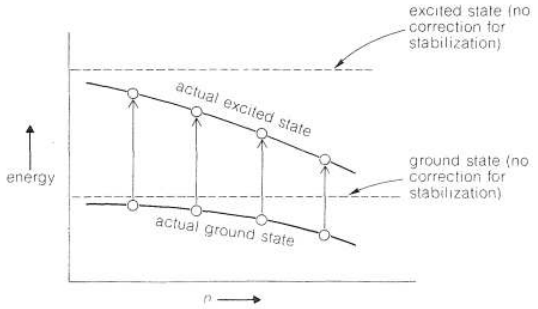


Figure 28-9: Schematic relationship between stabilization of ground and excited states of systems with n conjugated double bonds.

The effect of substituents on colors associated with conjugated systems is of particular interest in the study of dyes, because most dyes have relatively short conjugated systems and would not be intensely colored in the absence of substituent groups. (The plant pigments β-carotene, Section 2-1, and lycopene, often used as food coloring, are exceptions.)

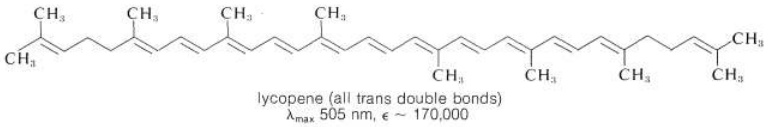
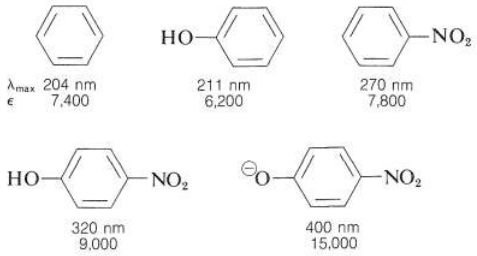


Figure 28-8. Its close relatives are benzene, benzenol, and nitrobenzene:



The conjugated π system common to all four compounds is that of the benzenoid ring, which is described as the absorbing **chromophore** (Section 22-3B). The hydroxyl and nitro substituents can be seen individually to shift the λ_{max} of the chromophore to longer wavelengths. However, the combined effect of the two substituents is much more dramatic, especially if the **OH** group is converted to the corresponding anion, 4-nitrobenzenolate. Now λ_{max} is shifted into the visible region, giving a yellow color, and because ϵ is large, the color is intense. Thus, properly chosen substituents can shift the main benzenoid absorption band from the ultraviolet into the visible region of the spectrum. Such substituents are often called **auxochromes**. They act by extending the conjugation of the chromophore and are particularly effective in causing large shifts towards the visible when one substituent is a π-electron donor and the other a π-electron acceptor. Thus, with the 4-nitrobenzenolate ion, interaction between the strongly electron-donating $-O^{\ominus}$ group and the strongly electron-accepting $-NO_2$ group provides significant stabilization:

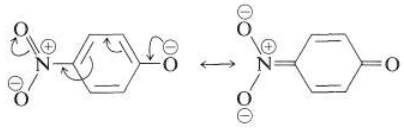
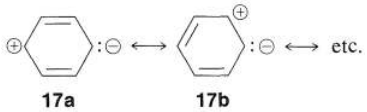


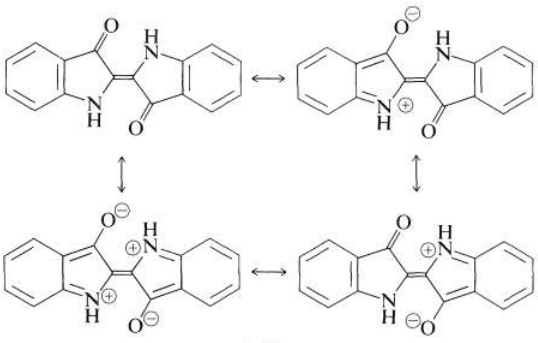
Figure 28-9). The narrowing of the energy gap is expected because excited electronic states have hybrid structures with much more important contributions from dipolar valence-bond forms than does the ground state (see Section 9-9B). Another way to look at the effect of substituents is to recall that excited singlet states of benzene will be stabilized by important contributions from resonance structures such as **17*a*** and **17*b***:



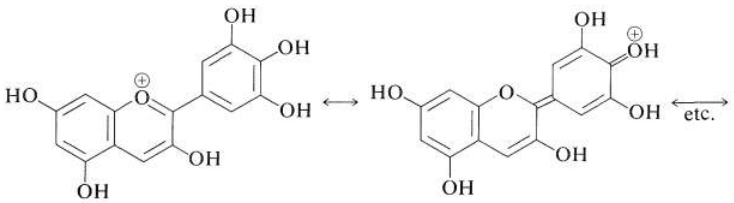
Hence, substitution of an electron-attracting group (such as NO_2) at one end of such a system and an electron-donating group (such as $O^{\ominus}$) at the other end should be particularly favorable for stabilization of the excited state (relative to the ground state, where **17*a***,

17*b*, etc., are of lesser importance). At the same time, we should *not* expect that two electron-attracting (or two electron-donating) groups at opposite ends would be nearly as effective.

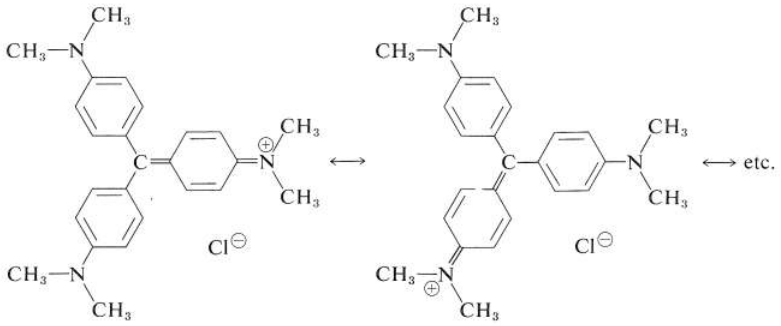
We hope you will understand from the foregoing discussion why it is that many intensely colored substances of natural or synthetic origin have conjugated structures with substituents, often cationic or anionic substituents, that can donate or accept electrons from the conjugated system. Such compounds provide us with many useful dyes, pigments, indicators, and food-coloring agents, as well as conferring color on plants and animals. A few examples follow:



indigo
(a deep-blue dye of natural and synthetic origin)



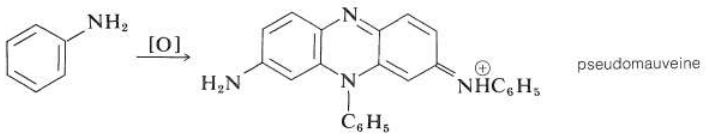
delphinidin
(member of a class of natural compounds, *anthocyanins*, that give color to flowers, leaves, fruits; they occur as glycosides)



Crystal Violet (synthetic dye)

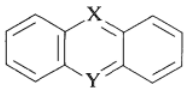
8.3.1: Dyes

Historically, the dye industry has been closely linked with the development of synthetic organic chemistry. Although dyes have been extracted from natural sources for centuries, it was not until 1856 that a synthetic dye was produced commercially. The previous year, William Henry Perkin - at age 17 - oxidized benzenamine (aniline) with potassium dichromate and isolated from the product (which was mostly aniline black; Section 23-11D) a purple compound that was excellent for dyeing silk. Perkin started commercial production of the dye under enormous difficulties. Because there was no organic chemical industry at the time, he had to design and build his own equipment as well as devise efficient syntheses for starting materials. His route to benzenamine stared with crude benzene from coal, which he nitrated and then reduced with iron and acid. He had to make the nitric acid (from nitrate salts and sulfuric acid) because concentrated nitric acid was not available. It was not until 1890 that the structure of Perkin's dye, called mauveine, was established by Otto Fischer. The dye was actually a mixture because the benzene used contained methylbenzene), but the product from the oxidation of benzenamine itself is structurally related to aniline black:

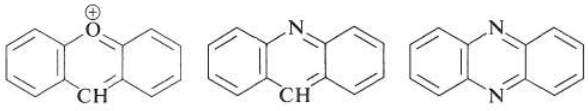


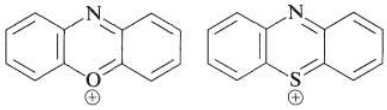
pseudomauveine

Although the mauveine dyes have been replaced with better dyes, they are representative of a group of useful dyes having the general structure



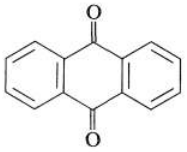
in which **X** and **Y** can be oxygen, nitrogen, sulfur, or carbon. The rings invariably carry substituents (hydroxyl or amino) that provide enhanced stabilization of the excited states. Examples of these ring systems follow:



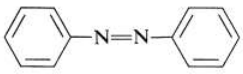


A large number of useful dyes are substituted triphenylmethane derivatives. Crystal Violet (Section 28-4) and phenolphthalein are excellent examples of this kind of dye.

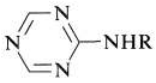
Other important dyes are derivatives of the following types of substances:



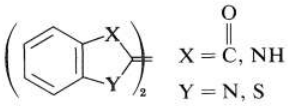
anthraquinone



azobenzene

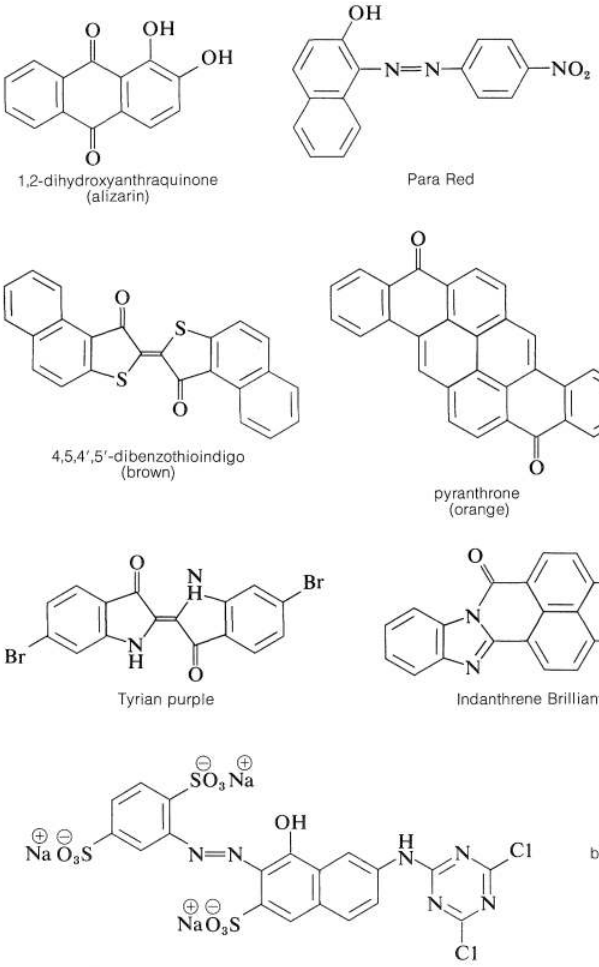


triazine



Examples are

https://chem.libretexts.org/@go/page/440332

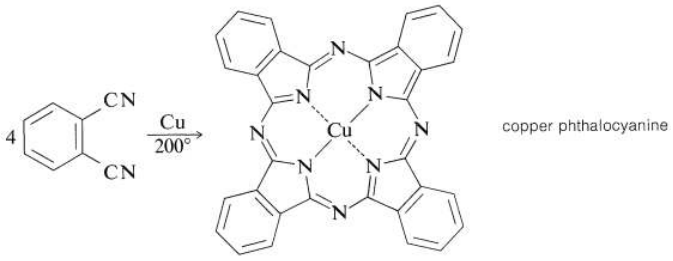


There is more to a successful dye than just an attractive color.[5] If it is to be useful, say for coloring fabrics, some simple means must be available for introducing the color into the fiber and then, usually of greater difficulty and importance, the color must be reasonably permanent - that is, resistant to normal laundry or cleaning procedures (wash-fast) and stable to light (light-fast). Here again, fundamentally important problems are involved. The scientific approach to improving wash-fastness of fabric dyes has to be based on a knowledge of the structural factors bearing on the intermolecular forces that determine solubilities. Light-fastness is connected with the photochemistry of organic compounds.

8.3.2: Pigments

The distinction between a dye and a pigment is that a dye actually is absorbed by the material to be colored, whereas a pigment is applied with a binding material to the surface. Pigments usually are highly insoluble substances. Many insoluble inorganic substances that would be wholly unsatisfactory as dyes are useful pigments.

Copper phthalocyanine is an example of a very important class of organic pigments. These are tetraazatetrabenzo derivatives of the porphyrin compounds discussed in Sections 20-9 and 25-8B. Copper phthalocyanine arises from condensation of four molecules of 1,2-benzenedicarbonitrile in the presence of copper metal at 200°:



[5]For a good account of dyes, see L. F. Fieser and M. Fieser, *Organic Chemistry*, D. C. Health & Co., Lexington, Mass., 1956, Chapter 36.

8.3.3: Contributors and Attributions

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8.4: Conjugation, Color, and the Chemistry of Vision

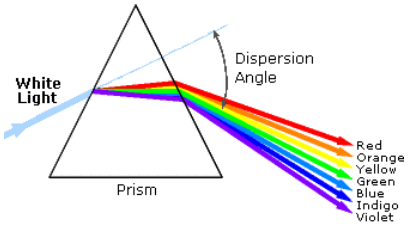
Objectives

After completing this section, you should be able to

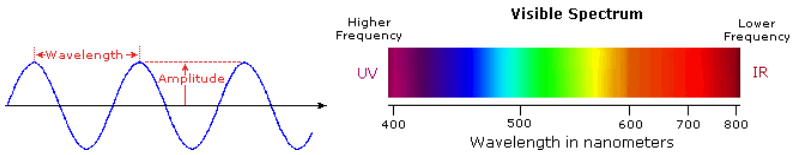
1. explain why some organic compounds have different colors based on compound structure and our perception of light.
2. state the relationship between frequency of light absorbed and the extent of conjugation in an extended pi electron system.

Introduction

An obvious difference between certain compounds is their color. Thus, quinone is yellow; chlorophyll is green; and aspirin is colorless. In this respect the human eye is functioning as a spectrometer analyzing the light reflected from the surface of a solid or passing through a liquid. Although we see sunlight (or white light) as uniform or homogeneous in color, it is actually composed of a broad range of radiation wavelengths in the ultraviolet (UV), visible and infrared (IR) portions of the spectrum. As shown on the image below, the component colors of the visible portion can be separated by passing sunlight through a prism, which acts to bend the light in differing degrees according to wavelength.

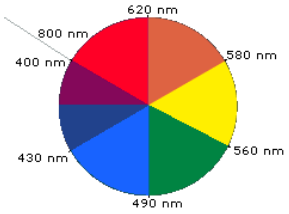


Visible wavelengths cover a range from approximately 400 to 800 nm. The longest visible wavelength is red and the shortest is violet. The wavelengths of what we perceive as particular colors in the visible portion of the spectrum are displayed and listed below.

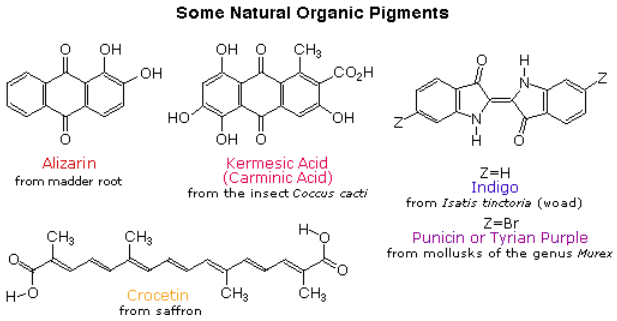


- **Violet:** 400 - 420 nm
- **Indigo:** 420 - 440 nm
- **Blue:** 440 - 490 nm
- **Green:** 490 - 570 nm
- **Yellow:** 570 - 585 nm
- **Orange:** 585 - 620 nm
- **Red:** 620 - 780 nm

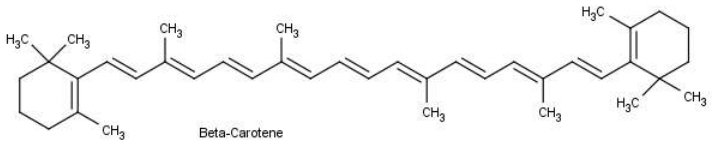
When white light passes through or is reflected by a colored substance, a characteristic portion of the mixed wavelengths is absorbed. The remaining light will then assume the complementary color to the wavelength(s) absorbed. This relationship is demonstrated by the color wheel shown below. Here, complementary colors are diametrically opposite each other. Thus, absorption of violet (400-440 nm) light renders a substance yellow, and absorption of 490-560 nm (green) light makes it red. Green is unique in that it can be created by absorption close to 400 nm as well as absorption near 800 nm.

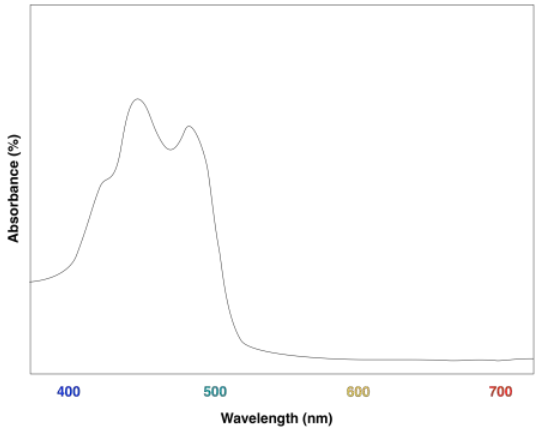


Early humans valued colored pigments, and used them for decorative purposes. Many of these were inorganic minerals, but several important organic dyes were also known. These included the crimson pigment, kermesic acid, the blue dye, indigo, and the yellow saffron pigment, crocetin. A rare dibromo-indigo derivative, punicin, was used to color the robes of the royal and wealthy. A common feature of all these colored compounds, displayed below, is a system of **extensively conjugated π-electrons**.

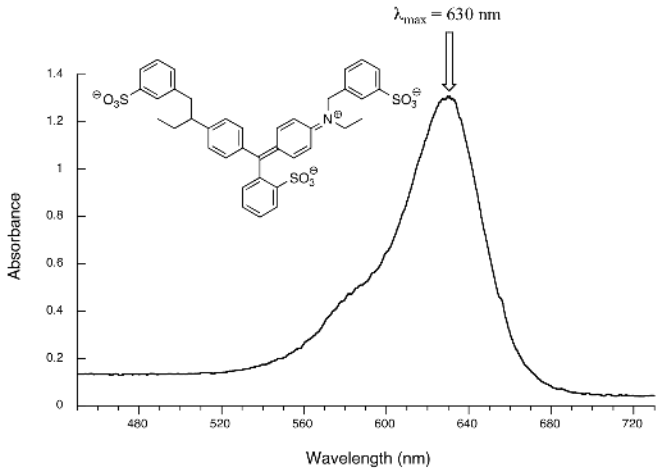


By understanding visible light, complementary colors, and adsorption the color of organic compounds can be understood. Beta-carotene, a compound found in carrots, is a deep orange color. Beta-carotene has 11 conjugated double bonds which places its λ_{max} at 455 nm which is within the blue region of the visible spectrum. The Beta-carotene compound absorbs blue from white light so it appears orange which is the the complementary color of blue.





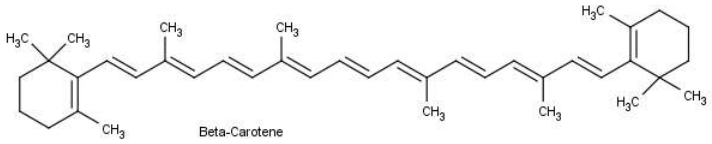
Another example is seen in the absorption spectrum of another food coloring, Blue #1:

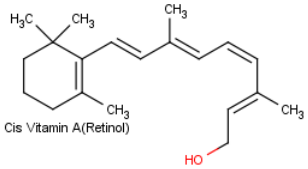


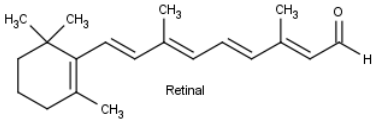
Blue #1 absorbs at a λ_{max} at 630 nm which is the color red in the visible spectrum. Blue is the complementary color of red.

Mechanism of Vision

Conjugation is also important in light sensitive compounds used for vision. Beta carotene, found in carrots and other natural products is cleaved into the liver and converted into Vitamin A, also known as retinol. Vitamin A is critical for vision because it is needed by the retina of eye. Retinol can be oxidized to an aldehyde called retinal which is also important for vision.





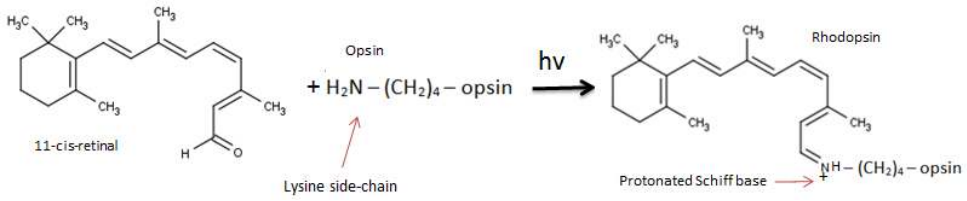


The eye is an extraordinarily sensitive instrument. Although its wavelength response is restricted to 400-800 nm, but its degree of sensitivity is such that a fully dark-adapted eye can clearly detect objects in light so dim as to correspond to a light input over the retina of only about 10,000 quanta per second - one light quantum per three minutes per receptor cell in the retina!

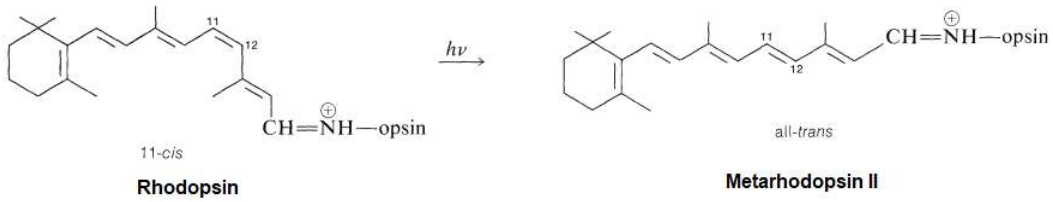
The retina is made up of two kinds of light-sensitive (photoreceptor) cells, known as rods and cones. The rods are the more sensitive and are responsible for vision in dim light. The cones are much fewer in number than the rods and provide detail and color vision in good light. The part of the retina that corresponds to the center of the visual field contains only cones. A red pigment called **rhodopsin** is the photosensitive substance in the rod cells of the retina. It absorbs most strongly in the blue-green region of the visible spectrum (λ_{max} = 500nm) and is essentially unaffected by the far-red end of the spectrum. Cone vision appears to involve a different pigment called **iodopsin**, which absorbs farther toward the red than does rhodopsin.

Rhodopsin, is made up of a protein (opsin) and retinal. Opsin does not absorb visible light, but when it is bonded with 11-cis-retinal to from rhodopsin, the new molecule has a very broad absorption band in the visible region of the spectrum. Rhodopsin is formed

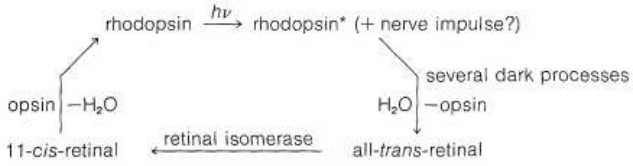
by an an imine (Schiff base) functional group formed between the aldehyde group of the retinal and the side-chain amino function of a lysine unit of opsin.



Opsin itself is colorless, whereas 11-cis-retinal absorbs strongly at 370 nm. The combination of opsin with 11-cis-retinal produces a remarkable shift of λ_{max} to longer wavelengths (430 nm to 620 nm, depending on the species). Light striking the retina changes the color of rhodopsin from red to yellow. The primary photochemical event in this process was established by G. Wald (Nobel Laureate in Physiology and Medicine, 1967), who showed that light absorption led to a change of configuration about the C_{11}-C_{12} double bond of the retinal moiety fo rhodopsin from *cis* to *trans* to form a compound called metarhodopsin II. The new form of trans-retinal does not fit as well into the opsin protein, and so a series of geometry changes in the protein begins. As the protein changes its geometry, it initiates a cascade of biochemical reactions that result in changes in charge so that a large potential difference builds up across the neuron membranes. This potential difference is passed along to an adjoining nerve cell as an electrical impulse. The nerve cell carries this impulse to the brain, where the visual information is interpreted.

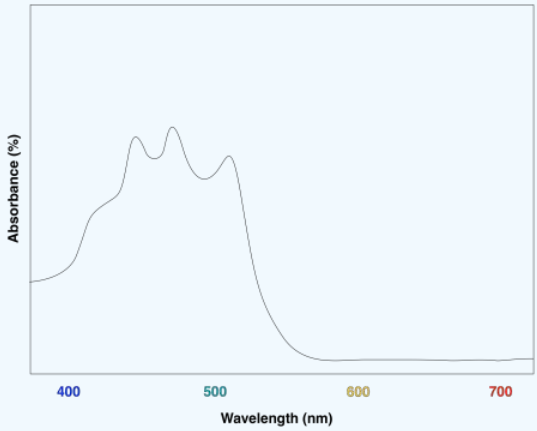


Metarhodopsin II can then be recycled back to rhodopsin by first cleaving to form all-*trans*-retinal and the isomerization back to 11-*cis*-retinal by the enzyme retinal isomerase. Finally, 11-*cis*-retinal is once again coupled with opsin to form rhodopsin.



? Exercise 8.4.1

Lycopene is conjugated compound found in tomatoes. What colors correspond to the UV-Vis absorption maxima of lycopene? What color do we see when we look at lycopene?



Answer

The absorption maxima of lycopene are regions of blue and green in the visible spectrum. Lycopene would be expected to appears orange and red.

? Exercise 8.4.2

Asprin has a λ_{max} of 220 nm. Briefly explain why Asprin appears white.

Answer

Asprin absorbs in the ultraviolet portion of the electromagnetic spectrum. Asprin cannot remove any colors from white light by absorption so the compound itself appears white. Many compounds with a relatively small amount of conjugation appear white because they only absorb in the ultraviolet and not the visible region.

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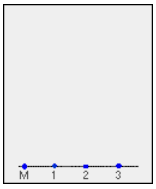
8.5: Paper Chromatography

Chromatography is used to separate mixtures of substances into their components. All forms of chromatography work on the same principle. They all have a stationary phase (a solid, or a liquid supported on a solid) and a mobile phase (a liquid or a gas). The mobile phase flows through the stationary phase and carries the components of the mixture with it. Different components travel at different rates. We'll look at the reasons for this further down the page. In paper chromatography, the stationary phase is a very uniform absorbent paper. The mobile phase is a suitable liquid solvent or mixture of solvents.

Producing a paper chromatogram

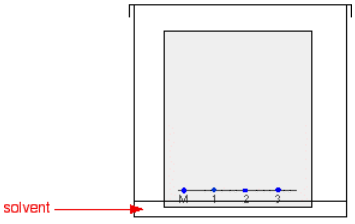
You probably used paper chromatography as one of the first things you ever did in chemistry to separate out mixtures of colored dyes - for example, the dyes which make up a particular ink. That's an easy example to take, so let's start from there.

Suppose you have three blue pens and you want to find out which one was used to write a message. Samples of each ink are spotted on to a pencil line drawn on a sheet of chromatography paper. Some of the ink from the message is dissolved in the minimum possible amount of a suitable solvent, and that is also spotted onto the same line. In the diagram, the pens are labeled 1, 2 and 3, and the message ink as M.



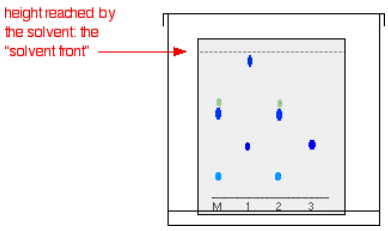
The paper is suspended in a container with a shallow layer of a suitable solvent or mixture of solvents in it. It is important that the solvent level is below the line with the spots on it. The next diagram doesn't show details of how the paper is suspended because there are too many possible ways of doing it and it clutters the diagram. Sometimes the paper is just coiled into a loose cylinder and fastened with paper clips top and bottom. The cylinder then just stands in the bottom of the container.

The reason for covering the container is to make sure that the atmosphere in the beaker is saturated with solvent vapour. Saturating the atmosphere in the beaker with vapour stops the solvent from evaporating as it rises up the paper.



As the solvent slowly travels up the paper, the different components of the ink mixtures travel at different rates and the mixtures are separated into different colored spots.

The diagram shows what the plate might look like after the solvent has moved almost to the top.



It is fairly easy to see from the final chromatogram that the pen that wrote the message contained the same dyes as pen 2. You can also see that pen 1 contains a mixture of two different blue dyes - one of which might be the same as the single dye in pen 3.

R_f values

Some compounds in a mixture travel almost as far as the solvent does; some stay much closer to the base line. The distance travelled relative to the solvent is a constant for a particular compound as long as you keep everything else constant - the type of paper and the exact composition of the solvent, for example.

The distance travelled relative to the solvent is called the R_f value. For each compound it can be worked out using the formula:

$$R_f = \frac{\text{distance travelled by compound}}{\text{distance travelled by solvent}}$$

For example, if one component of a mixture travelled 9.6 cm from the base line while the solvent had travelled 12.0 cm, then the R_f value for that component is:

$$R_f = \frac{9.6}{12.0} = 0.80$$

In the example we looked at with the various pens, it wasn't necessary to measure R_f values because you are making a direct comparison just by looking at the chromatogram.

You are making the assumption that if you have two spots in the final chromatogram which are the same color and have travelled the same distance up the paper, they are most likely the same compound. It isn't necessarily true of course - you could have two similarly colored compounds with very similar R_f values. We'll look at how you can get around that problem further down the page.

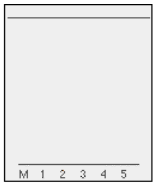
What if the substances you are interested in are colorless?

In some cases, it may be possible to make the spots visible by reacting them with something which produces a colored product. A good example of this is in chromatograms produced from amino acid mixtures.

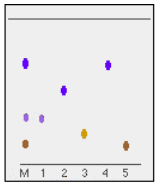
Suppose you had a mixture of amino acids and wanted to find out which particular amino acids the mixture contained. For simplicity we'll assume that you know the mixture can only possibly contain five of the common amino acids. A small drop of a solution of the mixture is placed on the base line of the paper, and similar small spots of the known amino acids are placed alongside it. The paper is then stood in a suitable solvent and left to develop as before. In the diagram, the mixture is M, and the known amino acids are labeled 1 to 5.

The position of the solvent front is marked in pencil and the chromatogram is allowed to dry and is then sprayed with a solution of ninhydrin. Ninhydrin reacts with amino acids to give colored compounds, mainly brown or purple.

The left-hand diagram shows the paper after the solvent front has almost reached the top. The spots are still invisible. The second diagram shows what it might look like after spraying with ninhydrin.



before spraying with ninhydrin



after spraying with ninhydrin

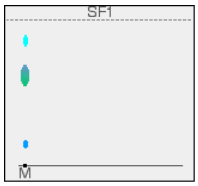
There is no need to measure the R_f values because you can easily compare the spots in the mixture with those of the known amino acids - both from their positions and their colors. In this example, the mixture contains the amino acids labeled as 1, 4 and 5. And what if the mixture contained amino acids other than the ones we have used for comparison? There would be spots in the mixture which didn't match those from the known amino acids. You would have to re-run the experiment using other amino acids for comparison.

Two way paper chromatography

Two way paper chromatography gets around the problem of separating out substances which have very similar R_f values. I'm going to go back to talking about colored compounds because it is much easier to see what is happening. You can perfectly well do this with colorless compounds - but you have to use quite a lot of imagination in the explanation of what is going on!

This time a chromatogram is made starting from a single spot of mixture placed towards one end of the base line. It is stood in a solvent as before and left until the solvent front gets close to the top of the paper.

In the diagram, the position of the solvent front is marked in pencil before the paper dries out. This is labeled as SF1 - the solvent front for the first solvent. We shall be using two different solvents.

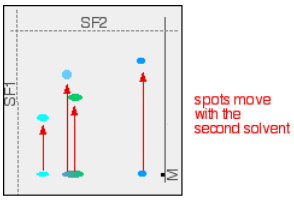


If you look closely, you may be able to see that the large central spot in the chromatogram is partly blue and partly green. Two dyes in the mixture have almost the same R_f values. They could equally well, of course, both have been the same color - in which case you couldn't tell whether there was one or more dye present in that spot.

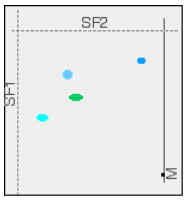
What you do now is to wait for the paper to dry out completely, and then rotate it through 90°, and develop the chromatogram again in a different solvent.

It is very unlikely that the two confusing spots will have the same R_f values in the second solvent as well as the first, and so the spots will move by a different amount.

The next diagram shows what might happen to the various spots on the original chromatogram. The position of the second solvent front is also marked.



You wouldn't, of course, see these spots in both their original and final positions - they have moved! The final chromatogram would look like this:



Two way chromatography has completely separated out the mixture into four distinct spots. If you want to identify the spots in the mixture, you obviously can't do it with comparison substances on the same chromatogram as we looked at earlier with the pens or amino acids examples. You would end up with a meaningless mess of spots. You can, though, work out the R_f values for each of the spots in both solvents, and then compare these with values that you have measured for known compounds under exactly the same conditions.

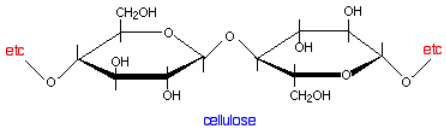
How does paper chromatography work?

Although paper chromatography is simple to do, it is quite difficult to explain compared with thin layer chromatography. The explanation depends to some extent on what sort of solvent you are using, and many sources gloss over the

problem completely. If you haven't already done so, it would be helpful if you could read the explanation for how thin layer chromatography works (link below). That will save me a lot of repetition, and I can concentrate on the problems.

The essential structure of paper

Paper is made of cellulose fibres, and cellulose is a polymer of the simple sugar, glucose.



cellulose

The key point about cellulose is that the polymer chains have -OH groups sticking out all around them. To that extent, it presents the same sort of surface as silica gel or alumina in thin layer chromatography.

It would be tempting to try to explain paper chromatography in terms of the way that different compounds are adsorbed to different extents on to the paper surface. In other words, it would be nice to be able to use the same explanation for both thin layer and paper chromatography. Unfortunately, it is more complicated than that!

The complication arises because the cellulose fibres attract water vapour from the atmosphere as well as any water that was present when the paper was made. You can therefore think of paper as being cellulose fibres with a very thin layer of water molecules bound to the surface.

It is the interaction with this water which is the most important effect during paper chromatography.

Paper chromatography using a non-polar solvent

Suppose you use a non-polar solvent such as hexane to develop your chromatogram.

Non-polar molecules in the mixture that you are trying to separate will have little attraction for the water molecules attached to the cellulose, and so will spend most of their time dissolved in the moving solvent. Molecules like this will therefore travel a long way up the paper carried by the solvent. They will have relatively high R_f values.

On the other hand, polar molecules will have a high attraction for the water molecules and much less for the non-polar solvent. They will therefore tend to dissolve in the thin layer of water around the cellulose fibres much more than in the moving solvent.

Because they spend more time dissolved in the stationary phase and less time in the mobile phase, they aren't going to travel very fast up the paper.

The tendency for a compound to divide its time between two immiscible solvents (solvents such as hexane and water which won't mix) is known as **partition**. Paper chromatography using a non-polar solvent is therefore a type of partition chromatography.

Paper chromatography using a water and other polar solvents

A moment's thought will tell you that partition can't be the explanation if you are using water as the solvent for your mixture. If you have water as the mobile phase and the water bound on to the cellulose as the stationary phase, there can't be any meaningful difference between the amount of time a substance spends in solution in either of them. All substances should be equally soluble (or equally insoluble) in both.

And yet the first chromatograms that you made were probably of inks using water as your solvent.

If water works as the mobile phase as well being the stationary phase, there has to be some quite different mechanism at work - and that must be equally true for other polar solvents like the alcohols, for example. Partition only happens between solvents which don't mix with each other. Polar solvents like the small alcohols do mix with water.

In researching this topic, I haven't found any easy explanation for what happens in these cases. Most sources ignore the problem altogether and just quote the partition explanation without making any allowance for the type of solvent you are using. Other sources quote mechanisms which have so many strands to them that they are far too complicated for this introductory level. I'm therefore not taking this any further - you shouldn't need to worry about this at UK A level, or its various equivalents.

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CHAPTER OVERVIEW

9: Nuclear Chemistry

9.1: Natural Radioactivity
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9.3: Half-Life and Radioisotopic Dating
9.4: Artificial Transmutation
9.5: Uses of Radioisotopes
9.6: Penetrating Power of Radiation
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9.9: Uses and Consequences of Nuclear Energy

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9.1: Natural Radioactivity

Learning Objectives

- Know the different sources of background radiation.
- Describe the biological impact of ionizing radiation
- List common sources of radiation exposure in the US.

Background Radiation

We are all exposed to a small amount of radiation in our daily lives. This **background radiation** comes from naturally occurring sources and from human-produced radiation. Exposure to x-rays and nuclear medicine isotopes, ground sources, and cosmic radiation account for almost half of the background exposure of the average American. Radon gas, formed from the decay of uranium and thorium isotopes, is responsible for a little over half the total amount of background radiation. See the table below for background sources.

***Table* 9.1.1** *Sources of Background Radiation*

radon	**54%**
consumer products	**3%**
nuclear medicine	**4%**
cosmic radiation	**8%**
terrestrial	**8%**
internal	**11%**
x-rays	**11%**
other	**1%**

The Problem of Radon

For many people, one of the largest sources of exposure to radiation is from radon gas (Rn-222). Radon-222 is an α emitter with a half–life of 3.82 days. It is one of the products of the radioactive decay series of U-238, which is found in trace amounts in soil and rocks. The radon gas that is produced slowly escapes from the ground and gradually seeps into homes and other structures above. Since it is about eight times more dense than air, radon gas accumulates in basements and lower floors, and slowly diffuses throughout buildings (Figure **9.1.1**).

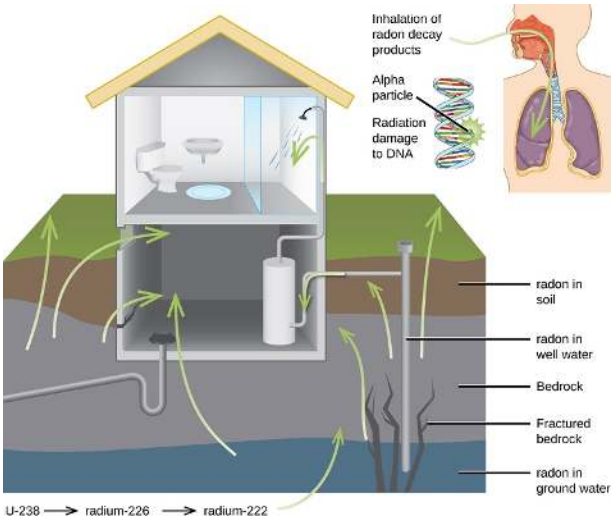


Figure **9.1.1**: Radon-222 seeps into houses and other buildings from rocks that contain uranium-238, a radon emitter. The radon enters through cracks in concrete foundations and basement floors, stone or porous cinderblock foundations, and openings for water and gas pipes.

Radon is found in buildings across the country, with amounts depending on where you live. The average concentration of radon inside houses in the US (1.25 pCi/L) is about three times the levels found in outside air, and about one in six houses have radon levels high enough that remediation efforts to reduce the radon concentration are recommended. Exposure to radon increases one's risk of getting cancer (especially lung cancer), and high radon levels can be as bad for health as smoking a carton of cigarettes a day. Radon is the number one cause of lung cancer in nonsmokers and the second leading cause of lung cancer overall. Radon exposure is believed to cause over 20,000 deaths in the US per year.

Measuring Radiation Exposure

Several different devices are used to detect and measure radiation, including Geiger counters, scintillation counters (scintillators), and radiation dosimeters (Figure **9.1.2**). Probably the best-known radiation instrument, the Geiger counter (also called the Geiger-Müller counter) detects and measures radiation. Radiation causes the ionization of the gas in a Geiger-Müller tube. The rate of ionization is proportional to the amount of radiation. A scintillation counter contains a scintillator—a material that emits light (luminesces) when excited by ionizing radiation—and a sensor that converts the light into an electric signal. Radiation dosimeters also measure ionizing radiation and are often used to determine personal radiation exposure. Commonly used types are electronic, film badge, thermoluminescent, and quartz fiber dosimeters.



Figure **9.1.2**: Devices such as (a) Geiger counters, (b) scintillators, and (c) dosimeters can be used to measure radiation. (credit c: modification of work by "osaMu"/Wikimedia commons).

Radiation Damage to Cells

The increased use of radioisotopes has led to increased concerns over the effects of these materials on biological systems (such as humans). All radioactive nuclides emit high-energy particles or electromagnetic waves. When this radiation encounters living cells, it can cause heating, break chemical bonds, or ionize molecules. The most serious biological damage results when these radioactive emissions fragment or ionize molecules. For example, alpha and beta particles emitted from nuclear decay reactions possess much higher energies than ordinary chemical bond energies. When these particles strike and penetrate matter, they produce ions and molecular fragments that are extremely reactive. The damage this does to biomolecules in living organisms can cause serious

malfunctions in normal cell processes, taxing the organism's repair mechanisms and possibly causing illness or even death (Figure 9.1.3).

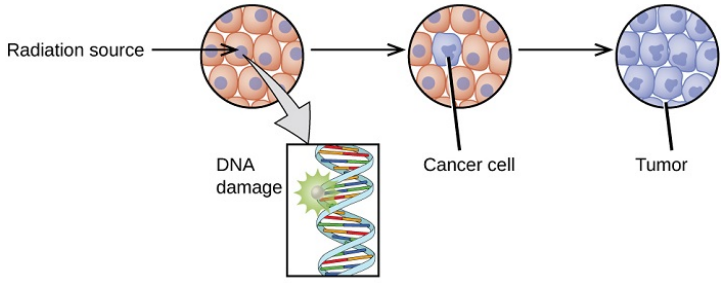


Figure 9.1.3: Radiation can harm biological systems by damaging the DNA of cells. If this damage is not properly repaired, the cells may divide in an uncontrolled manner and cause cancer.

Radiation can harm either the whole body (somatic damage) or eggs and sperm (genetic damage). Its effects are more pronounced in cells that reproduce rapidly, such as the stomach lining, hair follicles, bone marrow, and embryos. This is why patients undergoing radiation therapy often feel nauseous or sick to their stomach, lose hair, have bone aches, and so on, and why particular care must be taken when undergoing radiation therapy during pregnancy.

Ionizing vs. Nonionizing Radiation

There is a large difference in the magnitude of the biological effects of nonionizing radiation (for example, light and microwaves) and ionizing radiation, emissions energetic enough to knock electrons out of molecules (for example, α and β particles, γ rays, X-rays, and high-energy ultraviolet radiation) (Figure 9.1.4).

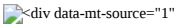


Figure 9.1.4: Lower frequency, lower-energy electromagnetic radiation is nonionizing, and higher frequency, higher-energy electromagnetic radiation is ionizing.

Energy absorbed from nonionizing radiation speeds up the movement of atoms and molecules, which is equivalent to heating the sample. Although biological systems are sensitive to heat (as we might know from touching a hot stove or spending a day at the beach in the sun), a large amount of nonionizing radiation is necessary before dangerous levels are reached. Ionizing radiation, however, may cause much more severe damage by breaking bonds or removing electrons in biological molecules, disrupting their structure and function. The damage can also be done indirectly, by first ionizing H_2O (the most abundant molecule in living organisms), which forms a H_2O^+ ion that reacts with water, forming a hydronium ion and a hydroxyl radical:

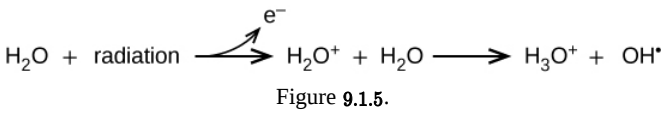


Figure 9.1.5.

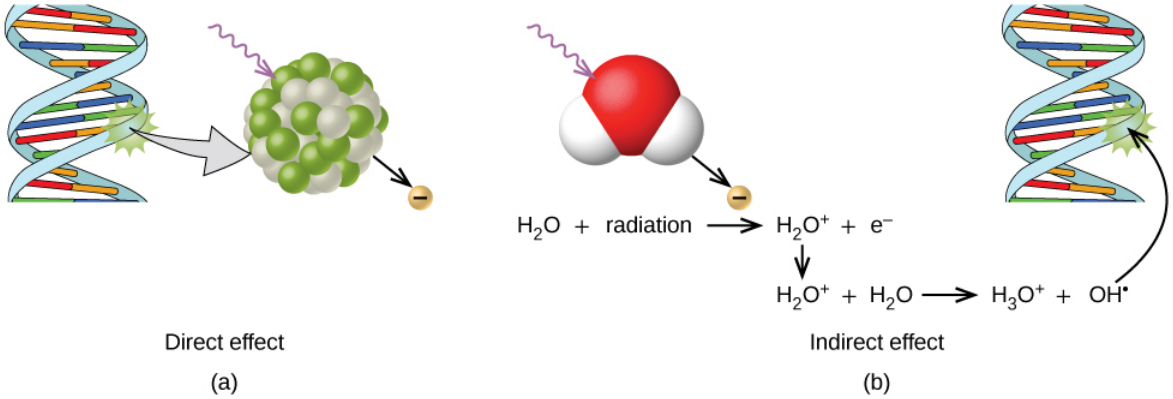


Figure 9.1.5: Ionizing radiation can (a) directly damage a biomolecule by ionizing it or breaking its bonds, or (b) create an H_2O^+ ion, which reacts with H_2O to form a hydroxyl radical, which in turn reacts with the biomolecule, causing damage indirectly.

The effects of radiation depend on the type, energy, and location of the radiation source, and the length of exposure. As shown in Figure **9.1.6**, the average person is exposed to background radiation, including cosmic rays from the sun and radon from uranium in the ground; radiation from medical exposure, including CAT scans, radioisotope tests, X-rays, and so on; and small amounts of radiation from other human activities, such as airplane flights (which are bombarded by increased numbers of cosmic rays in the upper atmosphere), radioactivity from consumer products, and a variety of radionuclides that enter our bodies when we breathe (for example, carbon-14) or through the food chain (for example, potassium-40, strontium-90, and iodine-131).

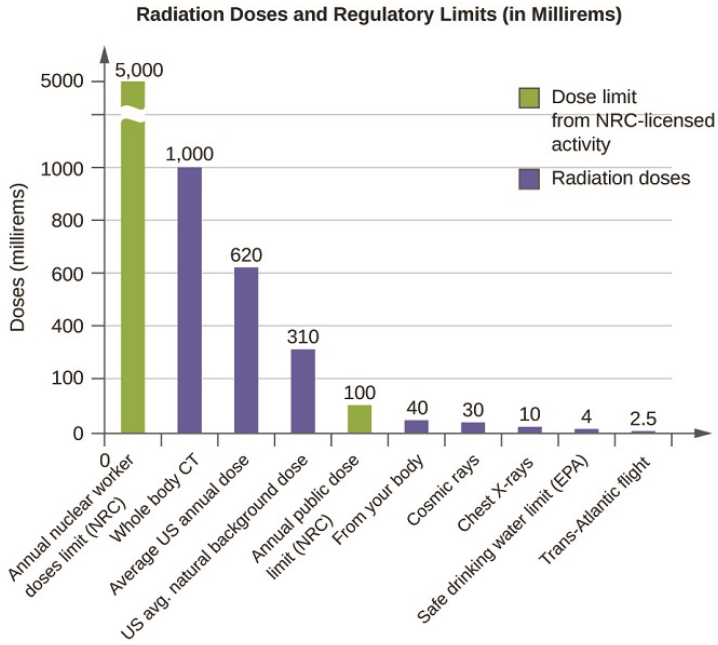


Figure **9.1.6** The total annual radiation exposure for a person in the US is about 620 mrem. The various sources and their relative amounts are shown in this bar graph. (source: U.S. Nuclear Regulatory Commission).

A short-term, sudden dose of a large amount of radiation can cause a wide range of health effects, from changes in blood chemistry to death. Short-term exposure to tens of rems of radiation will likely cause very noticeable symptoms or illness; a dose of about 500 rems is estimated to have a 50% probability of causing the death of the victim within 30 days of exposure. Exposure to radioactive emissions has a cumulative effect on the body during a person's lifetime, which is another reason why it is important to avoid any unnecessary exposure to radiation. Health effects of short-term exposure to radiation are shown in Table **9.1.2**.

Table **9.1.2** Health Effects of Radiation

Exposure (rem)	Health Effect	Time to Onset (without treatment)
5–10	changes in blood chemistry	—
50	nausea	hours
55	fatigue	—
70	vomiting	—
75	hair loss	2–3 weeks
90	diarrhea	—
100	hemorrhage	—
400	possible death	within 2 months
1000	destruction of intestinal lining	—
	internal bleeding	—
	death	1–2 weeks
2000	damage to central nervous system	—
	loss of consciousness;	minutes
	death	hours to days

It is impossible to avoid some exposure to ionizing radiation. We are constantly exposed to background radiation from a variety of natural sources, including cosmic radiation, rocks, medical procedures, consumer products, and even our own atoms. We can minimize our exposure by blocking or shielding the radiation, moving farther from the source, and limiting the time of exposure.

Summary

- Background radiation is defined and different sources of background radiation are listed.
- We are constantly exposed to radiation from a variety of naturally occurring and human-produced sources.
- Various devices, including Geiger counters, scintillators, and dosimeters, are used to detect and measure radiation, and monitor radiation exposure.
- Ionizing radiation is the most harmful because it can ionize molecules or break chemical bonds, which damages the molecule and causes malfunctions in cell processes. It can also create reactive hydroxyl radicals that damage biological molecules and disrupt physiological processes.

Contributors and Attributions

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9.2: Nuclear Equations

Learning Objectives

- Identify common particles and energies involved in nuclear reactions.
- Write and balance nuclear equations.

Changes of nuclei that result in changes in their atomic numbers, mass numbers, or energy states are nuclear reactions. To describe a nuclear reaction, we use an equation that identifies the nuclides involved in the reaction, their mass numbers and atomic numbers, and the other particles involved in the reaction.

Types of Particles in Nuclear Reactions

Many entities can be involved in nuclear reactions. The most common are protons, neutrons, alpha particles, beta particles, positrons, and gamma rays, as shown in Table **9.2.1**.

Table **9.2.1** A Summary of the Names, Symbols, Representations, and Descriptions of the Most Common Particles in Nuclear Reactions.

Name	Symbol(s)	Representation	Description
Alpha particle	^4_2He or $^4_2\alpha$		(High-energy) helium nuclei consisting of two protons and two neutrons
Beta particle	$^0_{-1}\text{e}$ or $^0_{-1}\beta$		(High-energy) electrons
Positron	$^0_{+1}\text{e}$ or $^0_{+1}\beta$		Particles with the same mass as an electron but with 1 unit of positive charge
Proton	^1_1H or ^1_1p		Nuclei of hydrogen atoms
Neutron	^1_0n		Particles with a mass approximately equal to that of a proton but with no charge
Gamma ray	γ		Very high-energy electromagnetic radiation

Balancing Nuclear Reactions

A balanced chemical reaction equation reflects the fact that during a chemical reaction, bonds break and form, and atoms are rearranged, but the total numbers of atoms of each element are conserved and do not change. A balanced nuclear reaction equation indicates that there is a rearrangement during a nuclear reaction, but of subatomic particles rather than atoms. Nuclear reactions also follow conservation laws, and they are balanced in two ways:

1. The sum of the mass numbers of the reactants equals the sum of the mass numbers of the products.
2. The sum of the charges of the reactants equals the sum of the charges of the products.

If the atomic number and the mass number of all but one of the particles in a nuclear reaction are known, we can identify the particle by balancing the reaction. For instance, we could determine that $^{17}_8\text{O}$ is a product of the nuclear reaction of $^{14}_7\text{N}$ and ^4_2He if we knew that a proton, ^1_1H, was one of the two products. Example **9.2.1** shows how we can identify a nuclide by balancing the nuclear reaction.

Nuclear Decay Processes

Radioactive decay involves the emission of a particle and/or energy as one atom changes into another. In most instances, the atom changes its identity to become a new element. There are four different types of emissions that occur.

Alpha Emission

Alpha (α) decay involves the release of helium ions from the nucleus of an atom. This ion consists of two protons and two neutrons and has a $2+$ charge. Release of an α-particle produces a new atom that has an atomic number two less than the original atom and an atomic weight that is four less. A typical alpha decay reaction is the conversion of uranium-238 to thorium:

$$^{238}_{92}\text{U} \rightarrow {}^{234}_{90}\text{Th} + {}^{4}_{2}\alpha^{+}$$

We see a decrease of two in the atomic number (uranium to thorium) and a decrease of four in the atomic weight (238 to 234). Usually the emission is not written with atomic number and weight indicated since it is a common particle whose properties should be memorized. Quite often the alpha emission is accompanied by gamma (γ) radiation, a form of energy release. Many of the largest elements in the periodic table are alpha-emitters.

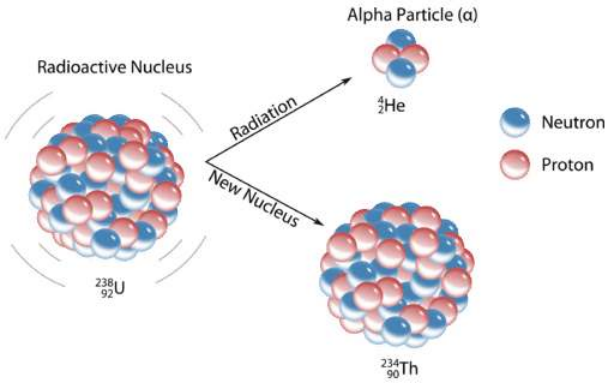


Figure **9.2.1** *Emission of an alpha particle from the nucleus.*

Chemists often use the names **parent isotope** and **daughter isotope** to represent the original atom and the product other than the alpha particle. In the previous example,

$$^{238}_{92}\text{U}$$

is the parent isotope, and

$$^{234}_{90}\text{Th}$$

is the daughter isotope. When one element changes into another in this manner, it undergoes **radioactive decay**.

Example 9.2.1

Write the nuclear equation that represents the radioactive decay of radon-222 by alpha particle emission and identify the daughter isotope.

Solution

Radon has an atomic number of 86, so the parent isotope is represented as

$$^{222}_{86}\text{Rn}$$

We represent the alpha particle as

$$^{4}_{2}\text{He}$$

Use subtraction (222 − 4 = 218 and 86 − 2 = 84) to identify the daughter isotope as polonium:

$$^{222}_{86}\text{Rn} \rightarrow {}^{4}_{2}\text{He} + {}^{218}_{84}\text{Th}$$

Exercise 9.2.1

Write the nuclear equation that represents radioactive decay of polonium-208 by alpha particle emission and identify the daughter isotope.

Answer

$$^{208}_{80}\text{Po} \rightarrow {}^{4}_{2}\text{He} + {}^{204}_{82}\text{Pb}$$

$$^{204}_{82}\text{Pb}$$

Beta Emission

Beta (β) **decay** is a more complicated process. Unlike the α-emission, which simply expels a particle, the β-emission involves the transformation of a neutron in the nucleus to a proton and an electron. The electron is then ejected from the nucleus. In the process,the atomic number increases by one while the atomic weight stays the same. As is the case with α-emissions, β-emissions are often accompanied by γ-radiation.

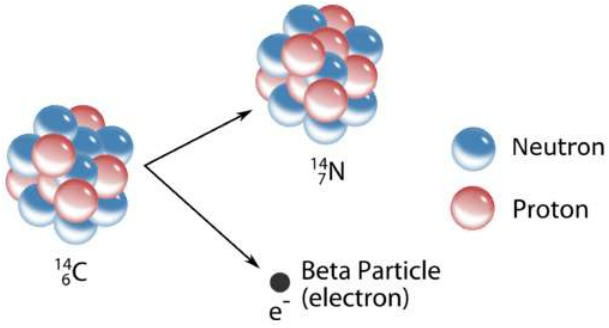


Figure 9.2.2 *Beta emission.*

A typical beta decay process involves carbon-14, often used in radioactive dating techniques. The reaction forms nitrogen-14 and an electron:

$$^{14}_{6}\text{C} \rightarrow {}^{14}_{7}\text{N} + {}^{0}_{-1}\text{e}$$

Again, the beta emission is usually simply indicated by the Greek letter β; memorization of the process is necessary in order to follow nuclear calculations in which the Greek letter β appears without further notation.

Example 9.2.2

Write the nuclear equation that represents the radioactive decay of boron-12 by beta particle emission and identify the daughter isotope. A gamma ray is emitted simultaneously with the beta particle.

Solution

The parent isotope is $^{4}_{2}\text{He}$

while one of the products is $^{0}_{-1}\text{e}$

So that the mass and atomic numbers have the same value on both sides, the mass number of the daughter isotope must be 12, and its atomic number must be 6. The element having an atomic number of 6 is carbon. Thus the complete nuclear equation is as follows:

$$^{12}_{5}\text{B} \rightarrow {}^{12}_{6}\text{C} + {}^{0}_{-1}\text{e} + \gamma$$

The daughter isotope is carbon-12.

? Exercise 9.2.2

Write the nuclear equation that represents the radioactive decay of rubidium-87 by beta particle emission and identify the daughter isotope.

Answer

$$^{87}_{37}\text{Rb} \rightarrow {}^{87}_{38}\text{Sr} + {}^{0}_{-1}\text{e}$$

$$^{87}_{38}\text{Sr}$$

Gamma Emission

Gamma (γ) radiation is simply energy. It may be released by itself or more commonly in association with other radiation events. There is no change of atomic number of atomic weight in a simple γ-emission. Often, an isotope may produce γ-radiation as a result of a transition in a metastable isotope. This type of isotope may just "settle", with a shifting of particles in the nucleus. The composition of the atom is not altered, but the nucleus could be considered more "comfortable" after the shift. This shift increases the stability of the isotope from the energetically unstable (or "metastable") isotope to a more stable form of the nucleus. Gamma (γ) emission can occur virtually instantaneously, as it does in the alpha decay of uranium-238 to thorium-234, where the asterisk denotes an excited state:

$$^{238}_{92}\text{U} \rightarrow \underset{\substack{\text{excited}\\ \text{nuclear}\\ \text{state}}}{^{234}_{90}\text{Th}^{*}} + {}^{4}_{2}\alpha \xrightarrow{\text{relaxation}} {}^{234}_{90}\text{Th} + {}^{0}_{0}\gamma \tag{9.2.1}$$

If we disregard the decay event that created the excited nucleus, then

$$^{234}_{88}\text{Th}^{*} \rightarrow {}^{234}_{88}\text{Th} + {}^{0}_{0}\gamma \tag{9.2.2}$$

or more generally,

$$^{A}_{Z}\text{X}^{*} \rightarrow {}^{A}_{Z}\text{X} + {}^{0}_{0}\gamma \tag{9.2.3}$$

Gamma emission can also occur after a significant delay. For example, technetium-99*m* has a half-life of about 6 hours before emitting a γ ray to form technetium-99 (the *m* is for metastable). Because γ rays are energy, their emission does not affect either the mass number or the atomic number of the daughter nuclide. Gamma-ray emission is therefore the only kind of radiation that does not necessarily involve the conversion of one element to another, although it is almost always observed in conjunction with some other nuclear decay reaction.

Positron Emission

A **positron** is a positive electron (a form of antimatter). This rare type of emission occurs when a proton is converted to a neutron and a positron in the nucleus, with ejection of the positron. The atomic number will decrease by one while the atomic weight does not change. A positron is often designated by β^{+}.

Carbon-11 emits a positron to become boron-11:

$$^{11}_{6}\text{C} \rightarrow {}^{11}_{5}\text{B} + {}^{0}_{+1}\beta$$

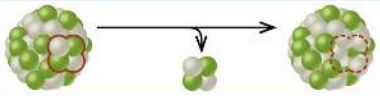
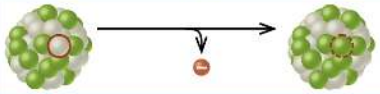
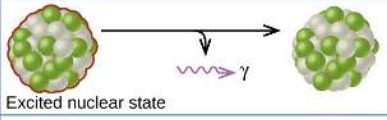
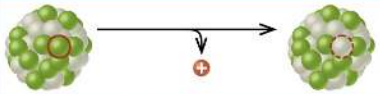
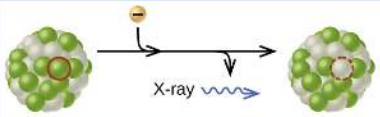
Electron Capture

An alternate way for a nuclide to increase its neutron to proton ratio is by a phenomenon called electron capture. In electron capture, an electron from an inner orbital is captured by the nucleus of the atom and combined with a proton to form a neutron. For example, silver-106 undergoes electron capture to become palladium-106.

$$^{106}_{47}\text{Ag} + {}^{0}_{-1}\text{e} \rightarrow {}^{106}_{46}\text{Pd}$$

Note that the overall result of electron capture is identical to positron emission. The atomic number decreases by one while the mass number remains the same.

Table **9.2.2** Different Types of Decay and Changes in Atomic and Mass Numbers.

Type	Nuclear equation	Representation	Change in mass/atomic numbers
Alpha decay	${}^{A}_{Z}X \rightarrow {}^{4}_{2}He + {}^{A-4}_{Z-2}Y$		A: decrease by 4 Z: decrease by 2
Beta decay	${}^{A}_{Z}X \rightarrow {}^{0}_{-1}e + {}^{A}_{Z+1}Y$		A: unchanged Z: increase by 1
Gamma decay	${}^{A}_{Z}X \rightarrow {}^{0}_{0}\gamma + {}^{A}_{Z}Y$		A: unchanged Z: unchanged
Positron emission	${}^{A}_{Z}X \rightarrow {}^{0}_{+1}e + {}^{A}_{Y-1}Y$		A: unchanged Z: decrease by 1
Electron capture	${}^{A}_{Z}X + {}^{0}_{-1}e \rightarrow {}^{A}_{Y-1}Y$		A: unchanged Z: decrease by 1

Following are the equations of several nuclear reactions that have important roles in the history of nuclear chemistry:

- The first naturally occurring unstable element that was isolated, polonium, was discovered by the Polish scientist Marie Curie and her husband Pierre in 1898. It decays, emitting α particles:

$$^{212}_{84}\text{Po} \longrightarrow {}^{208}_{82}\text{Pb} + {}^{4}_{2}\text{He}$$

- The first nuclide to be prepared by artificial means was an isotope of oxygen, ^{17}O. It was made by Ernest Rutherford in 1919 by bombarding nitrogen atoms with α particles:

$$^{14}_{7}\text{N} + {}^{4}_{2}\alpha \longrightarrow {}^{17}_{8}\text{O} + {}^{1}_{1}\text{H}$$

- James Chadwick discovered the neutron in 1932, as a previously unknown neutral particle produced along with ^{12}C by the nuclear reaction between ^{9}Be and ^{4}He:

$$^{9}_{4}\text{Be} + {}^{4}_{2}\text{He} \longrightarrow {}^{12}_{6}\text{C} + {}^{1}_{0}\text{n}$$

- The first element to be prepared that does not occur naturally on the earth, technetium, was created by bombardment of molybdenum by deuterons (heavy hydrogen, $^{2}_{1}\text{H}$), by Emilio Segre and Carlo Perrier in 1937:

$$^{2}_{1}\text{H} + {}^{97}_{42}\text{Mo} \longrightarrow 2{}^{1}_{0}\text{n} + {}^{97}_{43}\text{Tc}$$

- The first controlled nuclear chain reaction was carried out in a reactor at the University of Chicago in 1942. One of the many reactions involved was:

$$^{235}_{92}\text{U} + {}^{1}_{0}\text{n} \longrightarrow {}^{87}_{35}\text{Br} + {}^{146}_{57}\text{La} + 3{}^{1}_{0}\text{n}$$

Summary

- Nuclei can undergo reactions that change their number of protons, number of neutrons, or energy state.
- Many different particles can be involved in nuclear reactions. The most common are protons, neutrons, positrons (which are positively charged electrons), electrons, alpha (α) particles (which are high-energy helium nuclei), beta (β) particles (which are high-energy electrons), and gamma (γ) rays (which compose high-energy electromagnetic radiation).
- As with chemical reactions, nuclear reactions are always balanced. When a nuclear reaction occurs, the total mass (number) and the total charge remain unchanged.

Contributors and Attributions

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9.3: Half-Life and Radioisotopic Dating

Learning Objectives

- Define *half-life*.
- Determine the amount of radioactive substance remaining after a given number of half-lives.
- Define a radioactive decay series.

Whether or not a given isotope is radioactive is a characteristic of that particular isotope. Some isotopes are stable indefinitely, while others are radioactive and decay through a characteristic form of emission. As time passes, less and less of the radioactive isotope will be present, and the level of radioactivity decreases. An interesting and useful aspect of radioactive decay is **half life**. which is the amount of time it takes for one-half of a radioactive isotope to decay. The half-life of a specific radioactive isotope is constant; it is unaffected by conditions and is independent of the initial amount of that isotope.

For example, cobalt-60, an isotope that emits gamma rays used to treat cancer, has a half-life of 5.27 years (Figure **9.3.1**). In a given cobalt-60 source, since half of the $^{60}_{27}\text{Co}$ nuclei decay every 5.27 years, both the amount of material and the intensity of the radiation emitted is cut in half every 5.27 years. (Note that for a given substance, the intensity of radiation that it produces is directly proportional to the rate of decay of the substance and the amount of the substance.) This is as expected for a process following first-order kinetics. Thus, a cobalt-60 source that is used for cancer treatment must be replaced regularly to continue to be effective.

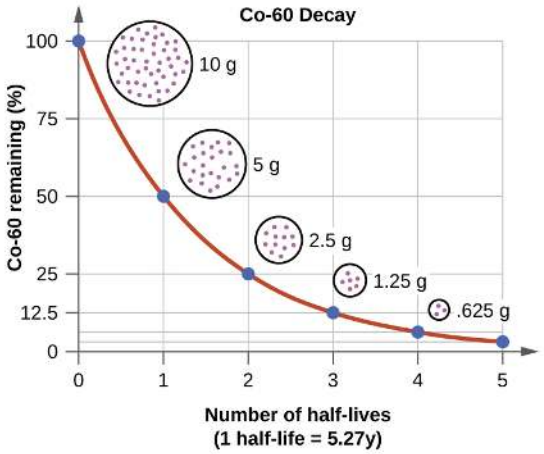


Figure **9.3.1** For cobalt-60, which has a half-life of 5.27 years, 50% remains after 5.27 years (one half-life), 25% remains after 10.54 years (two half-lives), 12.5% remains after 15.81 years (three half-lives), and so on.

We can determine the amount of a radioactive isotope remaining after a given number half-lives by using the following expression:

$$\textit{amount remaining} = \textit{initial amount} \times \left(\frac{1}{2}\right)^{n}$$

where *n* is the number of half-lives. This expression works even if the number of half-lives is not a whole number.

Example 9.3.1:

The half-life of fluorine-20 is 11.0 s. If a sample initially contains 5.00 g of fluorine-20, how much remains after 44.0 s?

Solution

If we compare the time that has passed to the isotope's half-life, we note that 44.0 s is exactly 4 half-lives, so using the previous expression, $n = 4$. Substituting and solving results in the following:

$$\textit{amount remaining} = 5.00g \times \left(\frac{1}{2}\right)^{4}$$
$$\textit{amount remaining} = 5.00g \times \left(\frac{1}{16}\right)$$
$$\textit{amount remaining} = 0.313g$$

Less than one-third of a gram of fluorine-20 remains.

Exercise 9.3.1

The half-life of titanium-44 is 60.0 y. A sample of titanium contains 0.600 g of titanium-44. How much remains after 240.0 y?

Answer

0.0375 g

Example 9.3.2

If there are 60 grams of **Np**-240 present, how much **Np**-240 will remain after 4 hours? (**Np**-240 has a half-life of 1 hour)

Solution

Np-240 with a half life of only 1 hour.

Amount of Np-240 present	Amount of time passed
60 g	0 (this is the amount before any time has passed)
30 g	1 hour (1 half-life)
15 g	2 hours (2 half-lives)
7.5 g	3 hours
3.75 g	4 hours

After 4 hours, only **3.75 g** of our original **60 g** sample would remain the radioactive isotope **Np**-240.

Exercise 9.3.2

A sample of **Ac**-225 originally contained 80 grams and after 50 days only 2.55 grams of the original **Ac**-225 remain. What is the half life of **Ac**-225?

Answer

10 days.

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. For example: the half-life of $^{209}_{83}\mathrm{Bi}$ is 1.9×10^{19} years; $^{239}_{94}\mathrm{Ra}$ is 24,000 years; $^{222}_{86}\mathrm{Rn}$ is 3.82 days; and element-111 (Rg for roentgenium) is 1.5×10^{-3} seconds. The table below illustrates half-lives for several selected elements.

Table **9.3.1**: Table of Selected Half-lives

Element	Mass Number (A)	Half-life	Element	Mass Number (A)	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	5730 years
Americium	245	25 minutes	Carbon	16	740 milliseconds

Uranium Decay Series

The naturally occurring radioactive isotopes of the heaviest elements fall into chains of successive disintegrations, or decays, and all the species in one chain constitute a radioactive family, or radioactive decay series. Three of these series include most of the naturally radioactive elements of the periodic table. They are the uranium series, the actinide series, and the thorium series. (Figure **9.3.2**). In all three series, the end-product is a stable isotope of lead.

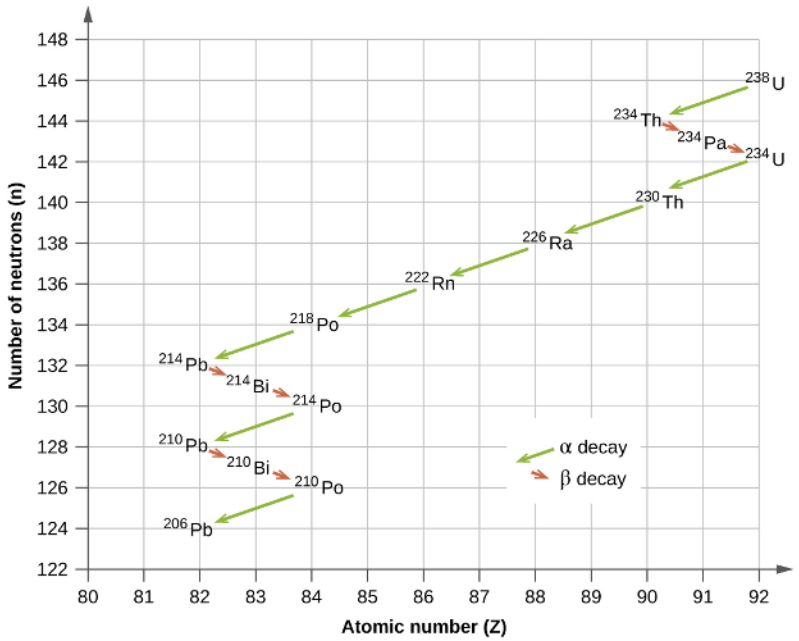


Figure **9.3.2** Uranium-238 undergoes a radioactive decay series consisting of 14 separate steps before producing stable lead-206. This series consists of eight α decays and six β decays.

Radioactive Dating

Radioactive dating *is a process by which the approximate age of an object is determined through the use of certain radioactive nuclides*. For example, carbon-14 has a half-life of 5,730 years and is used to measure the age of organic material. The ratio of carbon-14 to carbon-12 in living things remains constant while the organism is alive because fresh carbon-14 is entering the organism whenever it consumes nutrients. When the organism dies, this consumption stops, and no new carbon-14 is added to the organism. As time goes by, the ratio of carbon-14 to carbon-12 in the organism gradually declines, because carbon-14 radioactively decays while carbon-12 is stable. Analysis of this ratio allows archaeologists to estimate the age of organisms that were alive many thousands of years ago. For example, with the half-life of $^{14}_{6}\text{C}$ being 5730 years, if the $^{14}_{6}\text{C}:\ ^{12}_{6}\text{C}$ ratio in a wooden object found in an archaeological dig is half what it is in a living tree, this indicates that the wooden object is 5730 years old.

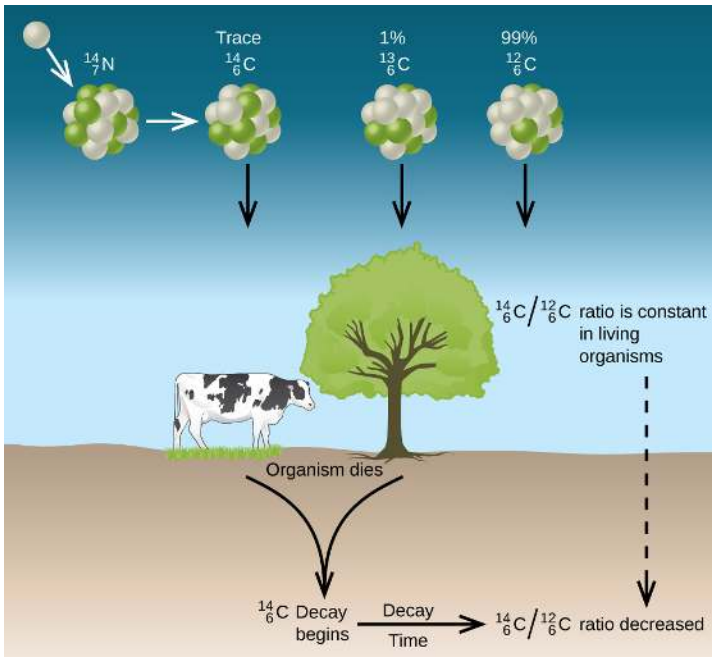


Figure **9.3.3**: Along with stable carbon-12, radioactive carbon-14 is taken in by plants and animals, and remains at a constant level within them while they are alive. After death, the C-14 decays and the C-14:C-12 ratio in the remains decreases. Comparing this ratio to the C-14:C-12 ratio in living organisms allows us to determine how long ago the organism lived (and died). (CC-BY 4.0; OpenStax).

C-14 dating does have limitations. For example, a sample can be C-14 dating if it is approximately 100 to 50,000 years old. Before or after this range, there is too little of the isotope to be detected. Substances must have obtained C-14 from the atmosphere. For this reason, aquatic samples cannot be effectively C-14 dated. Lastly, accuracy of C-14 dating has been affected by atmosphere nuclear weapons testing. Fission bombs ignite to produce more C-14 artificially. Samples tested during and after this period must be checked against another method of dating (isotopic or tree rings).

To calculate the age of a substance using isotopic dating, use the equation below:

$$\text{how old (time)} = n \times t_{1/2}$$

where n is the number of half-lives and $t_{1/2}$ is the half-life (in time).

Example 9.3.3

How long will it take for 18.0 grams of Ra-226 to decay to leave a total of 2.25 grams? Ra-226 has a half-life of 1600 years.

Solution

18.0g ⇒ 9.0g ⇒ 4.5g ⇒ 2.25g, this is three half-lives

$$\text{how old (time)} = 3 \times 1600\,years$$

This decay process takes 4800 years to occur.

Willard Libby

A National Historic Chemical Landmark -American Chemical Society

Dedicated at the University of Chicago on October 10, 2016.

In 1946, Willard Libby proposed an innovative method for dating organic materials by measuring their content of carbon-14, a newly discovered radioactive isotope of carbon. Known as radiocarbon dating, this method provides objective age estimates for carbon-based objects that originated from living organisms. The “radiocarbon revolution” made possible by Libby’s discovery



greatly benefited the fields of archaeology and geology by allowing practitioners to develop more precise historical chronologies across geography and cultures.

Willard F. Libby (right), the physical chemist who conceived of radiocarbon dating, with graduate student Ernest Anderson.

University of Chicago Photographic Archive, apf1-03868, Special Collections Research Center, University of Chicago Library.

Go to Link below for more details

www.acs.org/content/acs/en/education/whatischemistry/landmarks/radiocarbon-dating.html



Libby's anti-coincidence counter. The circular arrangement of Geiger counters (center) detected radiation in samples while the thick metal shields on all sides were designed to reduce background radiation.
University of Chicago Photographic Archive, apf1-03874, Special Collections Research Center, University of Chicago Library.

Radioactive Dating Using Nuclides Other than Carbon-14

Radioactive dating can also use other radioactive nuclides with longer half-lives to date older events. 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 4.5×10^9 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 4 billion years. This radioactivity approach can be used to detecting fake wine vintages too.

Isotopes with shorter half-lives are used to date more recent samples. For example, tritium ($t_{1/2}$ =12.3 years) can date samples within an age range of 1-100 years. Chemists and geologists use tritium dating to determine the age of water (ocean and fresh). In addition, tritium dating can be useful in determining the age of wines and brandies.

K-40 decays by positron emission and electron capture to form Ar-40 with a half-life of 1.25 billion years. If a rock sample is crushed and the amount of Ar-40 gas that escapes is measured, determination of the Ar-40:K-40 ratio yields the age of the rock. Other methods, such as rubidium-strontium dating (Rb-87 decays into Sr-87 with a half-life of 48.8 billion years), operate on the same principle. To estimate the lower limit for the earth's age, scientists determine the age of various rocks and minerals, making the assumption that the earth is older than the oldest rocks and minerals in its crust. As of 2014, the oldest known rocks on earth are the Jack Hills zircons from Australia, found by uranium-lead dating to be almost 4.4 billion years old.

Summary

- Natural radioactive processes are characterized by a half-life, the time it takes for half of the material to decay radioactively.
- The amount of material left over after a certain number of half-lives can be determined using the following expression:

$$amount\ remaining = initial\ amount \times \left(\frac{1}{2}\right)^n$$

  where *n* is the number of half-lives.

- **C**-14 dating procedures have been used to determine the age of organic artifacts. Its half-life is approximately 5700 years.

Contributors and Attributions

- TextMap: Beginning Chemistry (Ball et al.)
-
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- Elizabeth R. Gordon (Furman University)
- American Chemical Society-Chemical Landmarks

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9.4: Artificial Transmutation

Learning Objective

- Describe the synthesis of transuranium nuclides.

After the discovery of radioactivity, the field of nuclear chemistry was created and developed rapidly during the early twentieth century. A slew of new discoveries in the 1930s and 1940s, along with World War II, combined to usher in the Nuclear Age in the mid-twentieth century. Science learned how to create new substances, and certain isotopes of certain elements were found to possess the capacity to produce unprecedented amounts of energy, with the potential to cause tremendous damage during war, as well as produce enormous amounts of power for society's needs during peace.

Synthesis of Nuclides

Nuclear transmutation is the conversion of one nuclide into another. It can occur by the radioactive decay of a nucleus, or the reaction of a nucleus with another particle. The first manmade nucleus was produced in Ernest Rutherford's laboratory in 1919 by a transmutation reaction, the bombardment of one type of nuclei with other nuclei or with neutrons. Rutherford bombarded nitrogen atoms with high-speed α particles from a natural radioactive isotope of radium and observed protons resulting from the reaction:

$$^{14}_{7}\mathrm{N} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{17}_{8}\mathrm{O} + {}^{1}_{1}\mathrm{H}$$

The $^{17}_{8}\mathrm{O}$ and $^{1}_{1}\mathrm{H}$ nuclei that are produced are stable, so no further (nuclear) changes occur.

To reach the kinetic energies necessary to produce transmutation reactions, devices called particle accelerators are used. These devices use magnetic and electric fields to increase the speeds of nuclear particles. In all accelerators, the particles move in a vacuum to avoid collisions with gas molecules. When neutrons are required for transmutation reactions, they are usually obtained from radioactive decay reactions or from various nuclear reactions occurring in nuclear reactors. The Chemistry in Everyday Life feature that follows discusses a famous particle accelerator that made worldwide news.

CERN Particle Accelerator

Located near Geneva, the CERN ("Conseil Européen pour la Recherche Nucléaire," or European Council for Nuclear Research) Laboratory is the world's premier center for the investigations of the fundamental particles that make up matter. It contains the 27-kilometer (17 mile) long, circular Large Hadron Collider (LHC), the largest particle accelerator in the world (Figure **9.4.1**). In the LHC, particles are boosted to high energies and are then made to collide with each other or with stationary targets at nearly the speed of light. Superconducting electromagnets are used to produce a strong magnetic field that guides the particles around the ring. Specialized, purpose-built detectors observe and record the results of these collisions, which are then analyzed by CERN scientists using powerful computers.



Figure **9.4.1**: A small section of the LHC is shown with workers traveling along it. (credit: Christophe Delaere)

In 2012, CERN announced that experiments at the LHC showed the first observations of the Higgs boson, an elementary particle that helps explain the origin of mass in fundamental particles. This long-anticipated discovery made worldwide news

and resulted in the awarding of the 2013 Nobel Prize in Physics to François Englert and Peter Higgs, who had predicted the existence of this particle almost 50 years previously.

Prior to 1940, the heaviest-known element was uranium, whose atomic number is 92. Now, many artificial elements have been synthesized and isolated, including several on such a large scale that they have had a profound effect on society. One of these—element 93, neptunium (Np)—was first made in 1940 by McMillan and Abelson by bombarding uranium-238 with neutrons. The reaction creates unstable uranium-239, with a half-life of 23.5 minutes, which then decays into neptunium-239. Neptunium-239 is also radioactive, with a half-life of 2.36 days, and it decays into plutonium-239. The nuclear reactions are:

$$^{238}_{92}\text{U} + ^{1}_{0}\text{n} \longrightarrow ^{239}_{92}\text{U} \tag{9.4.1}$$

$$^{239}_{92}\text{U} \longrightarrow ^{239}_{93}\text{Np} + ^{0}_{-1}\text{e} \quad t_{\frac{1}{2}} \quad \text{half-life} = 23.5\ \text{min} \tag{9.4.2}$$

$$^{239}_{93}\text{Np} \longrightarrow ^{239}_{94}\text{Pu} + ^{0}_{-1}\text{e} \quad t_{\frac{1}{2}} \quad \text{half-life} = 2.36\ \text{days} \tag{9.4.3}$$

Plutonium is now mostly formed in nuclear reactors as a byproduct during the decay of uranium. Some of the neutrons that are released during U-235 decay combine with U-238 nuclei to form uranium-239; this undergoes β decay to form neptunium-239, which in turn undergoes β decay to form plutonium-239 as illustrated in the preceding three equations. It is possible to summarize these equations as:

$$^{238}_{92}\text{U} + ^{1}_{0}\text{n} \longrightarrow ^{239}_{92}\text{U} \xrightarrow{\beta^-} ^{239}_{93}\text{Np} \xrightarrow{\beta^-} ^{239}_{94}\text{Pu}$$

Heavier isotopes of plutonium—Pu-240, Pu-241, and Pu-242—are also produced when lighter plutonium nuclei capture neutrons. Some of this highly radioactive plutonium is used to produce military weapons, and the rest presents a serious storage problem because they have half-lives from thousands to hundreds of thousands of years.

Although they have not been prepared in the same quantity as plutonium, many other synthetic nuclei have been produced. Nuclear medicine has developed from the ability to convert atoms of one type into other types of atoms. Radioactive isotopes of several dozen elements are currently used for medical applications. The radiation produced by their decay is used to image or treat various organs or portions of the body, among other uses.

The elements beyond element 92 (uranium) are called transuranium elements. As of this writing, 22 transuranium elements have been produced and officially recognized by IUPAC; several other elements have formation claims that are waiting for approval. Some of these elements are shown in Table **9.4.1**.

Table **9.4.1** Preparation of Some of the Transuranium Elements

Name	Symbol	Atomic Number	Reaction
americium	Am	95	$^{239}_{94}\text{Pu} + ^{1}_{0}\text{n} \longrightarrow ^{240}_{95}\text{Am} + ^{0}_{-1}\text{e}$
curium	Cm	96	$^{239}_{94}\text{Pu} + ^{4}_{2}\text{He} \longrightarrow ^{242}_{96}\text{Cm} + ^{1}_{0}\text{n}$
californium	Cf	98	$^{242}_{96}\text{Cm} + ^{4}_{2}\text{He} \longrightarrow ^{245}_{98}\text{Cf} + ^{1}_{0}\text{n}$
einsteinium	Es	99	$^{238}_{92}\text{U} + 15\,^{1}_{0}\text{n} \longrightarrow ^{253}_{99}\text{Es} + 7\,^{0}_{-1}\text{e}$
mendelevium	Md	101	$^{253}_{99}\text{Es} + ^{4}_{2}\text{He} \longrightarrow ^{256}_{101}\text{Md} + ^{1}_{0}\text{n}$
nobelium	No	102	$^{246}_{96}\text{Cm} + ^{12}_{6}\text{C} \longrightarrow ^{254}_{102}\text{No} + 4\,^{1}_{0}\text{n}$
rutherfordium	Rf	104	$^{249}_{98}\text{Cf} + ^{12}_{6}\text{C} \longrightarrow ^{257}_{104}\text{Rf} + 4\,^{1}_{0}\text{n}$
seaborgium	Sg	106	$^{206}_{82}\text{Pb} + ^{54}_{24}\text{Cr} \longrightarrow ^{257}_{106}\text{Sg} + 3\,^{1}_{0}\text{n}$ $^{249}_{98}\text{Cf} + ^{18}_{8}\text{O} \longrightarrow ^{263}_{106}\text{Sg} + 4\,^{1}_{0}\text{n}$
meitnerium	Mt	107	$^{209}_{83}\text{Bi} + ^{58}_{26}\text{Fe} \longrightarrow ^{266}_{109}\text{Mt} + ^{1}_{0}\text{n}$

Summary

- It is possible to produce new atoms by bombarding other atoms with nuclei or high-speed particles.
- The products of transmutation reactions can be stable or radioactive.

- A number of artificial elements, including technetium, astatine, and the transuranium elements, have been produced in this way.

Contributors and Attributions

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9.5: Uses of Radioisotopes

Learning Objectives

- Understand how radiation is used in agriculture and various industries.
- Understand the difference between diagnostic and therapeutic radiation.

Radioactive isotopes have the same chemical properties as stable isotopes of the same element, but they emit radiation, which can be detected. If we replace one (or more) atom(s) with radioisotope(s) in a compound, we can track them by monitoring their radioactive emissions. This type of compound is called a radioactive tracer (or radioactive label). Radioisotopes are used to follow the paths of biochemical reactions or to determine how a substance is distributed within an organism.

Radioisotopes in Industry and Agriculture

Radioisotopes (radioactive isotopes or radionuclides or radioactive nulcides) are used in two major ways: either for their radiation alone (irradiation, nuclear batteries) or for the combination of chemical properties and their radiation (tracers, biopharmaceuticals).

Tracer Applications

Radioactive isotopes are effective tracers because their radioactivity is easy to detect. A **tracer** is a substance that can be used to follow the pathway of that substance through some structure. For instance, leaks in underground water pipes can be discovered by running some **tritium (H-3)**-containing water through the pipes and then using a Geiger counter to locate any radioactive tritium subsequently present in the ground around the pipes. (Recall that tritium is a radioactive isotope of hydrogen.)

Tracers are used in diverse ways to study the mechanisms of chemical reactions in plants and animals. These include labeling fertilizers in studies of nutrient uptake by plants and crop growth, investigations of digestive and milk-producing processes in cows, and studies on the growth and metabolism of animals and plants.

For example, the radioisotope **C-14** was used to elucidate the details of how photosynthesis occurs. The overall reaction is:

$$6\,CO_2(g) + 6\,H_2O(l) \longrightarrow C_6H_{12}O_6(s) + 6\,O_2(g),$$

but the process is much more complex, proceeding through a series of steps in which various organic compounds are produced. In studies of the pathway of this reaction, plants were exposed to CO_2 containing a high concentration of $^{14}_{6}C$. At regular intervals, the plants were analyzed to determine which organic compounds contained carbon-14 and how much of each compound was present. From the time sequence in which the compounds appeared and the amount of each present at given time intervals, scientists learned more about the pathway of the reaction.

Phosphorus-32 is used in plant sciences for tracking a plant's uptake of fertilizer from the roots to the leaves. The phosphorus-32-labelled fertilizer is given to the plant hydroponically or via water in the soil and the usage of the phosphorus can be mapped from the emitted beta radiation. The information gathered by mapping the fertilizer uptake show how the plant takes up and uses the phosphorus from fertilizer.

Irradiation of Food and Mail

Co-60 (gamma source) and x-rays are use to irradiate many foods in the United States. Ionizing radiation can be used to kill food borne illnesses like salmonella and e coli. Irradiating food can also prolong shelf-life, delay ripening, and destroy insects. In addition, gamma/x-ray can sterilize foods making refrigeration unnecessary. Often, sterilized food is served to hospital patients who have impaired immune systems.

In the United States, irradiation of food is regulated by the FDA (Food and Drug Administration). Foods that have been irradiated must display the symbol called the radura on their packaging. Some foods that could display this symbol are: meats (beef, pork, chicken), shrimp, lobster, fruits, vegetables, shellfish, and spices. Contrary to the belief of some people, irradiation of food *does not* make the food itself radioactive.



Figure **9.5.1** The preservation of strawberries with Ionizing Radiation.

In the fall of 2001, anthrax laced letters *(*Figure **9.5.2**) were sent to various new agencies and two United States senators. Anthrax is an infectious disease caused by bacteria. It exists naturally in some soils and can be isolated in a laboratory.

Figure **9.5.2** Anthrax-laced letter that was sent to Senator Tom Daschle. Image taken from: https://upload.wikimedia.org/wikiped...hle_letter.jpg

To combat this form of bioterrorism, the United States Postal Service(USPS)and the Federal Bureau of Investigation (FBI) installed x-ray generators to irradiate suspicious looking mail sent to some governmental facilities. X-rays will kill the majority of this bacteria and some viruses as well. Once irradiated, mail (packages and letters) might change in color, texture, and smell. This ionizing radiation chemically alters the composition of the mail's paper component. The x-rays do not leave the mail radioactive.

Smoke Detectors

Americium-241, an α emitter with a half-life of 458 years, is used in tiny amounts in ionization-type smoke detectors (Figure **9.5.3**). The α emissions from Am-241 ionize the air between two electrode plates in the ionizing chamber. A battery supplies a potential that causes movement of the ions, thus creating a small electric current. When smoke enters the chamber, the movement of the ions is impeded, reducing the conductivity of the air. This causes a marked drop in the current, triggering an alarm.

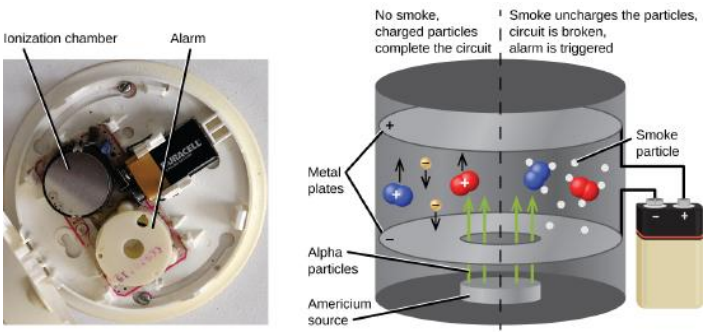


Figure **9.5.3** Inside a smoke detector, Am-241 emits α particles that ionize the air, creating a small electric current. During a fire, smoke particles impede the flow of ions, reducing the current and triggering an alarm. (credit a: modification of work by "Muffet"/Wikimedia Commons)

Other Applications

Commercial applications of radioactive materials are equally diverse . They include determining the thickness of films, paper, and thin metal sheets by exploiting the penetration power of various types of radiation(Figure **9.5.4**). Flaws in metals used for structural purposes can be detected using high-energy gamma rays from cobalt-60 in a fashion similar to the way X-rays are used to examine the human body. In one form of pest control, flies are controlled by sterilizing male flies with γ radiation so that females breeding with them do not produce offspring.

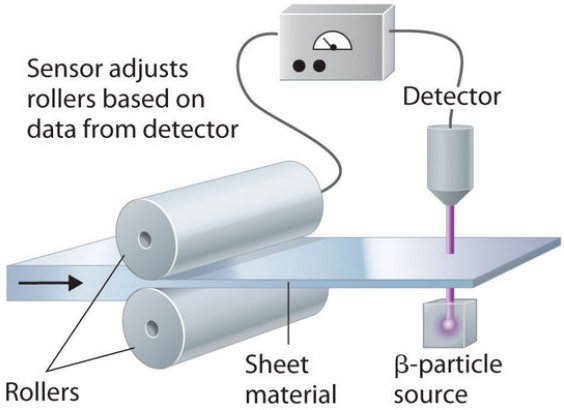


Figure **9.5.4** Using radiation to control the thickness of a material. Because the amount of radiation absorbed by a material is proportional to its thickness, radiation can be used to control the thickness of plastic film, tin foil, or paper. As shown, a beta emitter is placed on one side of the material being produced and a detector on the other. An increase in the amount of radiation that reaches the detector indicates a decrease in the thickness of the material and vice versa. The output of the detector can thus be used to control the thickness of the material.

Radioisotopes in Medicine

Radioactive tracers are also used in many medical applications, including both diagnosis and treatment. They are used to measure engine wear, analyze the geological formation around oil wells, and much more.

Radioisotopes have revolutionized medical practice, where they are used extensively. Over 10 million nuclear medicine procedures and more than 100 million nuclear medicine tests are performed annually in the United States.

Diagnostic Medical Applications

Diagnostic medical applications involve testing for a disease or condition. In nuclear medicine, this could involve using PET scans, or isotopic studies. The radiation involved for each of these types of tools will vary in mrem or mSv amounts.

PET Scanning

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. Watch this informational video on how this technique works.

PET Scan



***Video* 9.5.1** *PET scans: What to expect.*

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

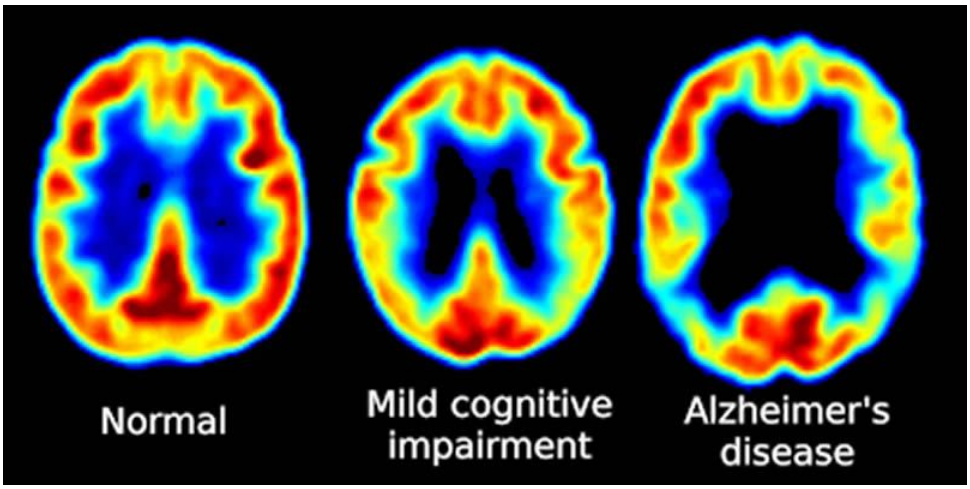


Figure **9.5.5** Mild cognitive impairment (MCI) is a state between normal ageing and dementia, where someone's mind is functioning less well than would be expected for their age. This image is for illustrative purposes only. (Public Domain; Center For Functional Imaging, Lawrence Berkeley National Laboratory. Alzheimer's Disease Neuroimaging Initiative (ADNI).

PET Scanning, is used to image the physiological aspects of the body rather than the anatomy (Figures **9.5.5** and **9.5.6**). It images the function of the body rather than the form, such as where tagged molecules go and how they are used. For instance, if you were to image the brain of a deceased person, nothing would show up on a PET scan opposed to a CAT scan, as the brain is no longer functional. Pet Scanning is very useful in imaging tumors, which can be done when patients are injected with certain tracers. Often times PET scanners are used in collaboration with CAT scanners to create a composite image that shows both the function and form

of the body. The animation below is a whole-body PET scan using the radioisotope of ^{18}F ($t_{1/2}$ = 110 min). Using this tracer, doctors can determine if cancer has metastasized by looking at the metabolic activity of glucose.

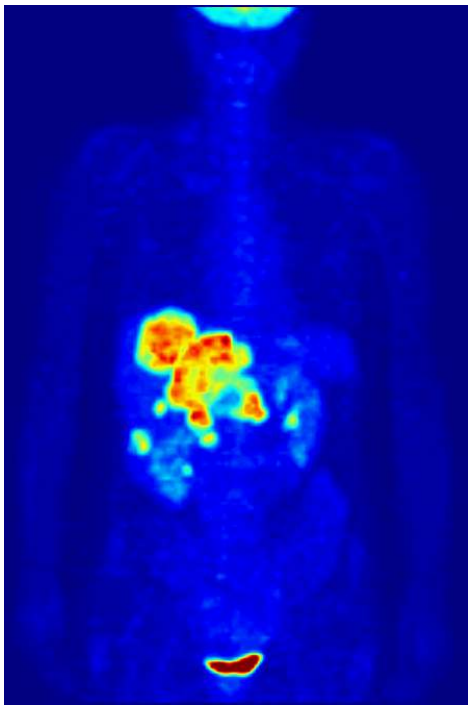


Figure 9.5.6 A whole body analysis by a PET scan. (Public Domain; Jens Maus, http://jens-maus.de/)

Other Isotopic Tests

Radioisotopes have revolutionized medical practice, where they are used extensively. Over 10 million nuclear medicine procedures and more than 100 million nuclear medicine tests are performed annually in the United States. Four typical examples of radioactive tracers used in medicine are technetium-99 ($^{99}_{43}Tc$), thallium-201 ($^{201}_{81}Tl$), iodine-131 ($^{131}_{53}I$), and sodium-24 ($^{24}_{11}Na$). Damaged tissues in the heart, liver, and lungs absorb certain compounds of technetium-99 preferentially. After it is injected, the location of the technetium compound, and hence the damaged tissue, can be determined by detecting the γ rays emitted by the Tc-99 isotope. Thallium-201 (Figure 9.5.7) becomes concentrated in healthy heart tissue, so the two isotopes, Tc-99 and Tl-201, are used together to study heart tissue. Iodine-131 concentrates in the thyroid gland, the liver, and some parts of the brain. It can therefore be used to monitor goiter and treat thyroid conditions, such as Grave's disease, as well as liver and brain tumors. Salt solutions containing compounds of sodium-24 are injected into the bloodstream to help locate obstructions to the flow of blood.



Figure 9.5.7 Administering thallium-201 to a patient and subsequently performing a stress test offer medical professionals an opportunity to visually analyze heart function and blood flow. (credit: modification of work by "Blue0ctane"/Wikimedia Commons)

Small doses of **I**-131 (too small to kill cells) are 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.

Some isotopes that are used to diagnose diseases are shown in Table **9.5.1**. All of these nuclear isotopes release one form of ionizing radiation (either/add particle or ray). In addition, each isotopic application would involve a specific amount of mrem/mSv radiation.

Table **9.5.1** Selected Radioisotopes Used in Diagnostic Nuclear Medicine

Symbol-mass	Half-Life ($t_{1/2}$)	Application
Xe-133	5.27 days	Lung imaging
H-3	12.26 years	Analyzing total body water
Tl-201	73 hours	Stress tests for heart problems
Fe-59	44.5 days	Detection of anemia
Gd-153	242 days	Analyzing bone density
Cr-51	27.8 days	Determining blood volume
C-11	20.4 minutes	Brain scans
Tc-99m	6.0 hours	Heart, lung, kidney, bone marrow, brain, or bone marrow imaging
Pu-238	86 years	Powering pacemakers
I-131	8.0 days	Imaging Thyroid

The “m” in Tc-99m stands for “metastable,” indicating that this is an unstable, high-energy state of Tc-99. Metastable isotopes emit γ radiation to rid themselves of excess energy and become (more) stable.

Keep in mind that x-rays, CT scans, PET scans, and isotopic studies involve ionizing radiation. In contrast, MRI (magnetic resonance imaging) and ultrasounds do not utilize ionizing forms of radiation.

Therapeutic Radiation

There are many techniques used to treat cancer. Surgery can be used to remove cancerous tumors inside or on the body. With chemotherapy, ingested or injected chemicals are used to kill rapidly dividing cells (cancerous and noncancerous). Other cancer treatment methods include immunotherapy, stem cell replacement, hormone therapy, and targeted therapy.

Radiation therapy and Chemotherapy: Two different treatment procedures

Patients diagnosed with cancer might be required to do chemotherapy or radiation therapy. Sometimes, both of these methods are used for a patient. In this picture, a female patient is receiving chemotherapy through an IV. She is participating in cooling therapy while receiving her treatment. By placing her hands and feet in cooling devices, this will lower her chances of losing her finger and toenails. Cold cap therapy is also now available for chemotherapy patients. Wearing this type of device could enable a patient to keep his/her hair during chemotherapy.



Figure **9.5.8** *(CC BY 2.0; Jenny Mealing).*

Current therapeutic radiation applications involve the use of gamma, x-rays, or protons. Recently, some research facilities are investigating the use of alpha and beta tagged molecules to kill cancer cells. These radioisotopes will first locate a cancer related molecule on a tumor cell. Then, the alpha or beta tagged species will inject its radiation into the tumor. Sr-89 (beta emitter) and Ra-223 (alpha emitter) have been used in clinical research trials of certain types of bone cancers.

Radiation Therapy is used as a treatment to control malignant cells within cancer patients. Oncologists (specialists that deal with cancer) utilize radiation frequently to help slow or cure the spread of cancer within individuals. Radiation is specifically applied to malignant tumors in order to shrink them in size. Medical professionals, mainly radiation oncologists, administer a variety of dosages to patient, contingent to the patients current health, as well as other treatments such as chemotherapy, success of surgery, etc.

External Beam Therapy (Photon and Proton Therapy)

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. The video below illustrates the basic preparation and administration of external beam therapy.

Radiation Therapy



***Video* 9.5.2** *Targeting cancer - Radiation therapy treatment process.*

Photon EBT utilizes either x-ray or gamma rays. An x-ray source would require a linear accelerator to produce high energy electrons. In contrast, a gamma source incorporates a radioactive isotope (like Co-60). Keep in mind both of these technologies use ionizing radiation. As a result, cancer patients must be monitored throughout their life to ensure they do not develop other cancers, like leukemia. EBT is used to treat the following diseases as well as others:

- Breast cancer
- Colorectal cancer
- Head and neck cancer
- Lung cancer
- Prostate cancer

The majority of radiation patients receive photon EBT. The smaller size of this machine makes this therapy an option for all sizes of hospitals and cancer treatment centers. Photon EBT equipment costs approximately three million dollars. The size and the price of this technology enables smaller facilities to keep their patients closer to home during treatment

Another method of radiation treatment involving protons is not as commonly used in the United States. **Photon therapy** requires a cyclotron to generate proton beams (recall, a proton is an ionized H-1 isotope). Unlike x-ray or gamma rays (photon therapy), protons are extremely heavy.

At this time, research facilities are working on miniaturizing proton generators. An ideal technology would reduce the cost from hundreds of millions of dollars to about twenty to thirty million per device. This would make proton therapy more available and convenient for patients.



***Video*9.5.3** *Proton therapy versus radiation therapy*

There are many advantages to choosing proton therapy over photon therapy. Unlike photon radiation, proton beams will only penetrate to the depth of the tumor and not pass through the entire body. This reduces the overall toxicity dose. In addition, fewer treatments are required for proton therapy patients than photon therapy.Unfortunately, proton therapy is more expensive than photon therapy and less common. Once approved by a facility and medical insurance, a patient may have to move temporarily to a larger city to receive treatment. Some forms of cancer have never been clinically treated with proton therapy (namely, breast cancer). Patients desiring proton therapy might not be able to receive type of therapy due to lack of research.

Brachtherapy

Brachytherapy involves placing ionizing pellets(seeds) or rods directly at the tumor. Photons (in the form of x-ray or gamma ray) are produced inside the body and will penetrate throughout this particular area localizing the radiation. Pellets are surgically implanted while rods can be temporarily inserted to produce radiation internally. With pellets/seeds, the patient will remain radioactive as long as these devices remain inside the body. People undergoing this type of radiotherapy need to be aware of their constant emission of radiation. Radiation that is administered through rods connected to a photon device will disperse energy immediately and not leave the patient radioactive.

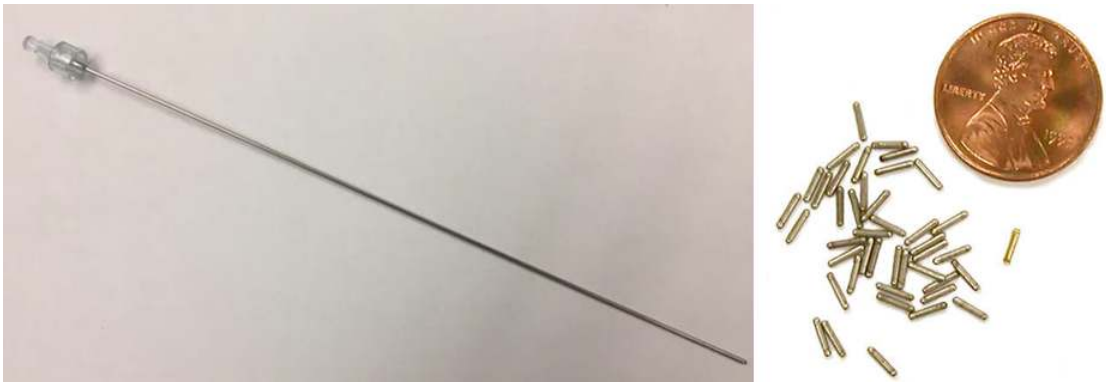


Figure **9.5.9** The picture on the left shows a brachytherapy rod. This device would be connected to a gamma source and connected inside a human body. The second images shows radioactive pellets or seeds that can be surgically implanted near a tumor. Note how small the pellets are when compared to an American penny. Image taken from: https://c1.staticflickr.com/8/7254/7...74d83b7058.jpg

Brachytherapy is widely used in the treatment of cancers involving reproductive organs. Because the radiation is isolated internally, patients are less likely to experience side effects when receiving this type of treatment. Cancers that have been treated with brachytherapy are shown below:

- Prostate
- Breast
- Esophageal
- Lung
- Uterine
- Anal/Rectal
- Sarcomas
- Head and neck

Table **9.5.2** list commonly used radionuclides for brachtherapy.

Table **9.5.2** Commonly Used Radiation Sources (radionuclides) for Brachytherapy.

Radionuclide	Type	Half-life
Cesium-131 (^{131}Cs)	Electron Capture, ε	9.7 days
Cesium-137 (^{137}Cs)	β^-- particles, γ-rays	30.17 years
Cobalt-60 (^{60}Co)	β^-- particles, γ-rays	5.26 years
Iridium-192 (^{192}Ir)	γ-rays	73.8 days
Iodine-125 (^{125}I)	Electron Capture, ε	59.6 days
Palladium-103 (^{103}Pd)	Electron Capture, ε	17.0 days
Ruthenium-106 (^{106}Ru)	β^-- particles	1.02 years
Radium-226 (^{226}Ra)	β^-- particles	1599 years

Side Effects of Radiation Therapy

Patients receiving radiation therapy can experience a variety of side effects. For example, sterility could occur if reproductive organs are irradiated. Skin that has been irradiated can appear dry and feel itchy. Some patients will loose sensation in the irradiated area. Radiation can affect the production of white and red blood cells. A reduction of white blood cells results in immunity disorders. Red blood cell lose causes anemia. Gastrointestinal issues such as diarrhea and nausea are common during radiation therapy. Some patients will lose hair as well. Lastly, dry mouth and tooth decay are prevalent during radiation treatments.

Medications are available to alleviate symptoms of radiation therapy. Narcotics can be prescribed to help alleviate intense pain. Prescription medications like zofran (Figure **9.5.10**) and phenergan can help with nausea. Special mouthwashes have been formulated to reduce dry mouth and cavities.

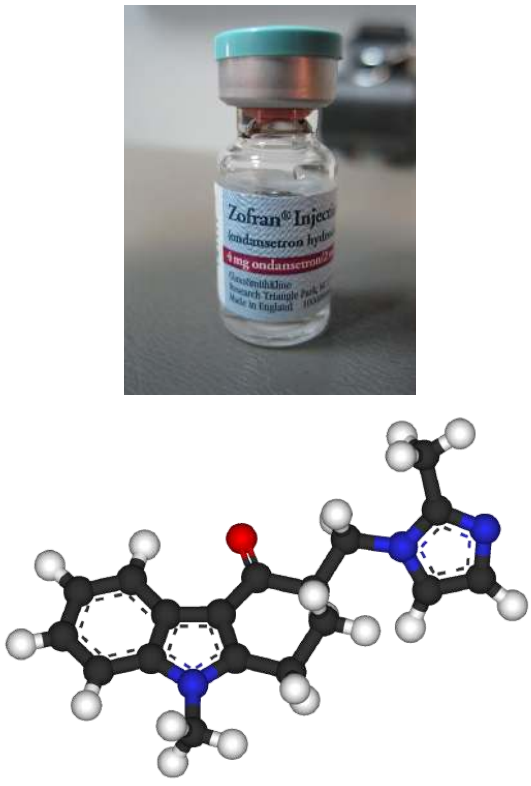


Figure **9.5.10**(left) *Zofran is a medication used to prevent nausea and vomiting caused by cancer chemotherapy, radiation therapy, or surgery. (right) A vial of Zofran 4 mg containing ondansetron for intravenous injection. This medicine is a controlled substance and is used for nausea. Images used with permision (left: Public domain; Fvasconcellos and right: CC BY 3.0; Intropin)*

Hair loss is a side effect of radiation, but only locally

Radiation therapy can cause hair loss, but hair is only lost in the area being treated. For instance, radiation to your head may cause you to lose some or all the hair on your head (even eyebrows and lashes), but if you get treatment to your hip, you won't lose the hair on your head.

Summary

- Compounds known as radioactive tracers can be used to follow reactions, track the distribution of a substance, diagnose and treat medical conditions, and much more.
- Other radioactive substances are helpful for controlling pests, visualizing structures, providing fire warnings, and for many other applications.
- Hundreds of millions of nuclear medicine tests and procedures, using a wide variety of radioisotopes with relatively short half-lives, are performed every year in the US.
- Radiation therapy uses high-energy radiation to kill cancer cells by damaging their DNA. The radiation used for this treatment may be delivered externally or internally.

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9.6: Penetrating Power of Radiation

Learning Objective

- Compare qualitatively the ionizing and penetration power of alpha particles (α), beta particles (β), and gamma rays (γ).

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. In most cases, radiation will damage a single (or very small number) of cells by breaking the cell wall or otherwise preventing a cell from reproducing.

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 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. In general, the greater mass present the greater the ionizing power and the lower the penetration power.

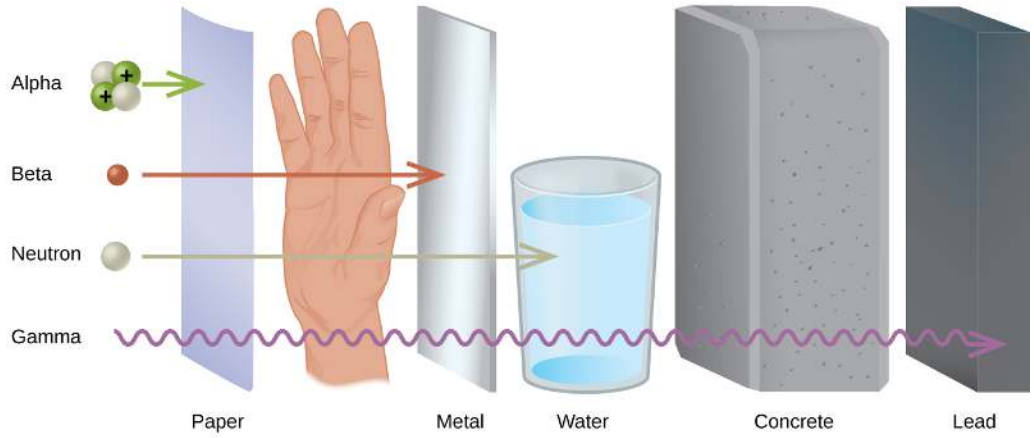


Figure **9.6.1**: The ability of different types of radiation to pass through material is shown. From least to most penetrating, they are alpha < beta < neutron < gamma. (CC BY-SA 4.0; OpenStax).

Comparing only the three common types of ionizing radiation, **alpha particles** have the greatest mass. 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. Alpha particles have the least penetration power and can be stopped by a thick sheet of paper or even a layer of clothes. 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.

A comparison of Alpha particles, beta particles and gamma rays is given in Table 9.6.1.

Table 9.6.1 Comparison of Penetrating Power,Ionizing Power and Shielding of Alpha and Beta Particles, and Gamma Rays.

Particle	Symbol	Mass	Penetrating Power	Ionizing Power	Shielding
Alpha	α	4amu	Very Low	Very High	Paper Skin
Beta	β	1/2000amu	Intermediate	Intermediate	Aluminum
Gamma	γ	0 (energy only)	Very High	Very Low	2 inches lead

The safest amount of radiation to the human body is zero. It isn't possible to be exposed to no ionizing radiation so the next best goal is to be exposed to as little as possible. The two best ways to minimize exposure is to limit time of exposure and to increase distance from the source.

Summary

- Types of radiation differ in their ability to penetrate material and damage tissue, with alpha particles the least penetrating but potentially most damaging and gamma rays the most penetrating.
- The two best ways to minimize exposure is to limit time of exposure and to increase distance from the source.

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9.7: Energy from the Nucleus

Learning Objectives

- Explain where nuclear energy comes from.
- Describe the difference between fission and fusion.
- Know key examples of nuclear fission and nuclear fusion.

A combination of radiochemistry and radiation chemistry is used to study nuclear reactions such as fission and fusion. Some early evidence for nuclear fission was the formation of a short-lived radioisotope of barium which was isolated from neutron irradiated uranium (^{139}Ba, with a half-life of 83 minutes and ^{140}Ba, with a half-life of 12.8 days, are major fission products of uranium). **Nuclear fission** is the splitting of an atomic nucleus. In nuclear weapons and reactors, neutrons hit unstable nuclei to form smaller atoms. **Nuclear Fusion** is the bringing together of two atomic nuclei to form a larger atom. Figure **9.7.1** illustrates the difference between nuclear fission and nuclear fusion.

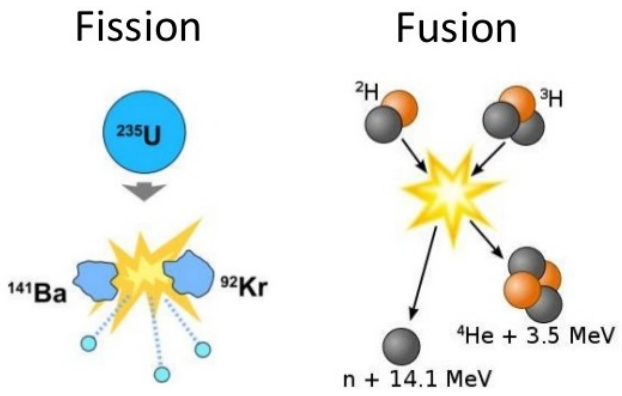


Figure **9.7.1** Nuclear fission occurs with one large nuclear is split into two or more smaller nuclei (left) . Nuclear fusion happens when two small nuclei combine to make a larger nucleus (right) .

Einstein and the Equivalence of Mass and Energy

Nuclear changes occur with a simultaneous release of energy. Where does this energy come from? If we could precisely measure the masses of the reactants and products of a nuclear reaction, we would notice that the amount of mass drops slightly in the conversion from reactants to products. Consider the following nuclear equation, in which the molar mass of each species is indicated to four decimal places:

$$^{235}_{235.0439}\text{U} \rightarrow ^{139}_{138.9088}\text{Ba} + ^{94}_{93.9343}\text{Kr} + ^{2\times1}_{2\times1.0087}\text{n}$$

If we compare the mass of the reactant (235.0439) to the masses of the products (sum=234.8605) we notice a mass difference of -0.1834 g or -0.0001834 kg. Where did this mass go?

According to Albert Einstein's theory of relativity, energy (E) and mass (m) are related by the following equation:

$$E = mc^2$$

where c is the speed of light, or

$$c = 3.00 \times 10^8\, m/s$$

In the course of the chemical reaction for uranium, the mass difference is converted to energy, which is given off by the reaction:

$$E = (-0.0001834\, kg)(3.00 \times 10^8\, m/s)^2 = -1.65 \times 10^{13} J = -1.65 \times 10^{10} kJ$$

(For the units to work out, mass must be expressed in units of kilograms.) That is, 16.5 billion kJ of energy is given off every time 1 mol of uranium-235 undergoes this nuclear reaction. This is an extraordinary amount of energy. Compare it to combustion

reactions of hydrocarbons, which give off about 650kJ/mol of energy for every CH_2 unit in the hydrocarbon-on the order of *hundreds* of kilojoules per mole. Nuclear reactions give off *billions* of kilojoules per mole.

If this energy could be properly harvested, it would be a significant source of energy for our society. **Nuclear energy** involves the controlled harvesting of energy from fission reactions. The reaction can be controlled because the fission of uranium-235 (and a few other isotopes, such as plutonium-239) can be artificially initiated by injecting a neutron into a uranium nucleus. The overall nuclear equation, with energy included as a product, is then as follows:

$$^{235}\mathrm{U} + \mathrm{mtd} + +3^{1}$$

Thus by the careful addition of extra neutrons into a sample of uranium, we can control the fission process and obtain energy that can be used for other purposes. (Artificial or induced radioactivity, in which neutrons are injected into a sample of matter that subsequently cause fission, was first demonstrated in 1934 by Irène Joliot-Curie and Frédéric Joliot, the daughter and son-in-law of Marie Curie.)

Binding Energy

The forces that bind nucleons together in an atomic nucleus are much greater than those that bind an electron to an atom through electrostatic attraction. This is evident by the relative sizes of the atomic nucleus and the atom (10^{-15} and 10^{-10}m, respectively). The energy required to pry a nucleon from the nucleus is therefore much larger than that required to remove (or ionize) an electron in an atom. In general, all nuclear changes involve large amounts of energy per particle undergoing the reaction. This has numerous practical applications.

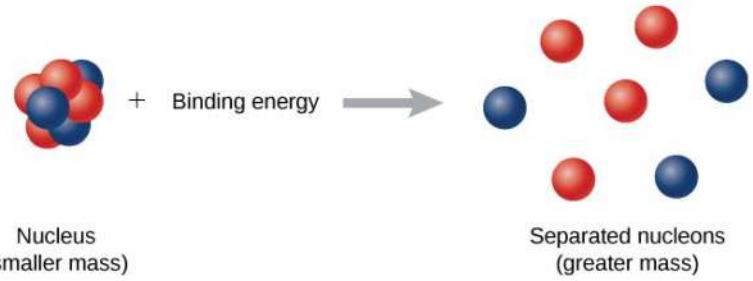


Figure **9.7.2***The binding energy is the energy required to break a nucleus into its constituent protons and neutrons. A system of separated nucleons has a greater mass than a system of bound nucleons.*

As shown in figure **9.7.2**, energy is put into the system to break apart the nucleus. The amount of energy required is called the total **binding energy** (BE), E_b. The binding energy is equal to the amount of energy released in forming the nucleus, and is therefore given by

$$E_b = (\Delta m)c^2. \tag{9.7.1}$$

In nuclear physics, one of the most important experimental quantities is the *binding energy per nucleon (BEN)*, which is defined by

$$BEN = \frac{E_b}{A} \tag{9.7.2}$$

This quantity is the average energy required to remove an individual nucleon (proton or neutron) from a nucleus—analogous to the ionization energy of an electron in an atom. If the BEN is relatively large, the nucleus is relatively stable. BEN values are estimated from nuclear scattering experiments.

Figure **9.7.3** shows the relative binding energies for various isotopes. Of these elements, fission requires heavy, unstable nuclei. This means selected atoms would have low binding energies and would have large atomic masses. Nuclei that are larger than Fe-56 may undergo fission. Uranium-238 and uranium-235 both have lower binding energies with heavy masses-.

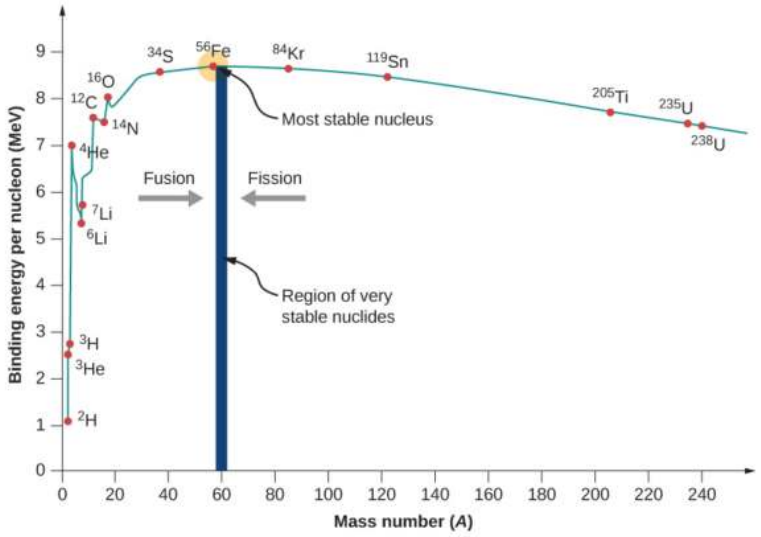


Figure **9.7.3** In this graph of binding energy per nucleon for stable nuclei, the BEN is greatest for nuclei with a mass near ^{56}Fe. Therefore, fusion of nuclei with mass numbers much less than that of Fe, and fission of nuclei with mass numbers greater than that of Fe, are exothermic processes. (CC BY. OpenStax).

These two isotopes would be suitable for splitting based on these requirements. Of these two isotopes, only uranium-235 is readily fissionable. This is due to odd neutron count contributing to additional instability. Another fissionable isotope not shown in Figure **9.7.3** is plutonium-239. This is a synthetic isotope produced by transmutation and decay reactions. Like uranium-235, it has low binding energy, high mass, and an odd number of neutrons. U-235 and Pu-239 are used in atomic bombs (fission based) and nuclear reactors.

Positively charged centers of atoms make nuclear fusion extremely difficult. For this reason, smaller atoms are suitable for fusion reactions. In addition, these particular isotopes need to have low binding energies in order to undergo fusion. Atoms that possess these two qualities are H-2 and H-3. For fusion to occur, extreme temperatures are required to fuse these deuterium and tritium together.

As we will see, the BEN-versus-*A* graph implies that nuclei divided or combined release an enormous amount of energy. This is the basis for a wide range of phenomena, from the production of electricity at a nuclear power plant to sunlight.

Nuclear Fission

In both fission and fusion, large amounts of energy are given off in the form of heat, light, and gamma radiation. Italian physicist, Enrico Fermi, performed the first fission reaction in 1934. He was unaware that he had split a uranium atom into two smaller nuclei. Nuclear fission of heavy elements was discovered on December 17, 1938 by German Otto Hahn and his assistant Fritz Strassmann, and explained theoretically in January 1939 by Lise Meitner (Figure **9.7.4**) and her nephew Otto Robert Frisch. Frisch named the process "fission" by analogy with biological fission of living cells.

Figure **9.7.4** *Austrian physicist, Lise Meitner of U-238.*

Image take from: https://upload.wikimedia.org/wikiped...ner12crop2.J

Since then, fission has been observed in many other isotopes, including most actinide isotopes that have an odd number of neutrons. A typical nuclear fission reaction is shown in Figure **9.7.5**.

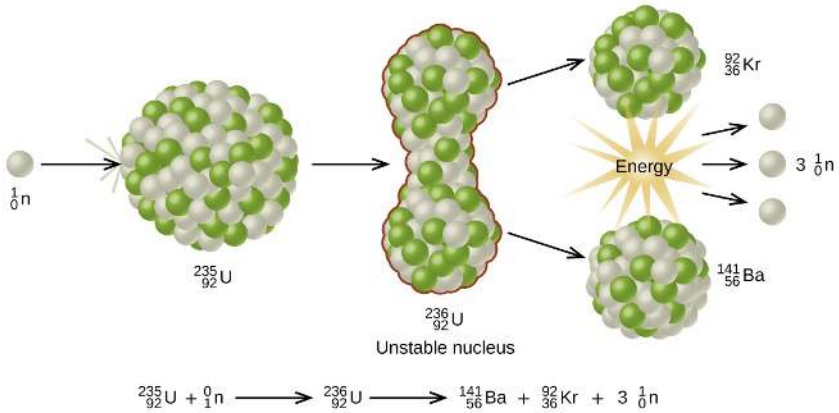


Figure **9.7.5** When a slow neutron hits a fissionable U-235 nucleus, it is absorbed and forms an unstable U-236 nucleus. The U-236 nucleus then rapidly breaks apart into two smaller nuclei (in this case, Ba-141 and Kr-92) along with several neutrons (usually two or three), and releases a very large amount of energy.

Among the products of Meitner, Hahn, and Strassman's fission reaction were barium, krypton, lanthanum, and cerium, all of which have nuclei that are more stable than uranium-235. Since then, hundreds of different isotopes have been observed among the products of fissionable substances.

Fission has been used in nuclear weapons and powers all nuclear reactors. Approximately fifty-five countries worldwide possess fission technology in the form of research or energy reactors. Less than ten of these countries have fission weapons.

A tremendous amount of energy is produced by the fission of heavy elements. For instance, when one mole of U-235 undergoes fission, the products weigh about 0.2 grams less than the reactants; this "lost" mass is converted into a very large amount of energy, about 1.8×10^{10} kJ per mole of U-235. Nuclear fission reactions produce incredibly large amounts of energy compared to chemical reactions. The fission of 1 kilogram of uranium-235, for example, produces about 2.5 million times as much energy as is produced by burning 1 kilogram of coal.

Nuclear Chain Reaction

As described earlier, when undergoing fission U-235 produces two "medium-sized" nuclei, and two or three neutrons. These neutrons may then cause the fission of other uranium-235 atoms, which in turn provide more neutrons that can cause fission of even more nuclei, and so on. If this occurs, we have a nuclear chain reaction (Figure **9.7.6**). On the other hand, if too many neutrons escape the bulk material without interacting with a nucleus, then no chain reaction will occur.

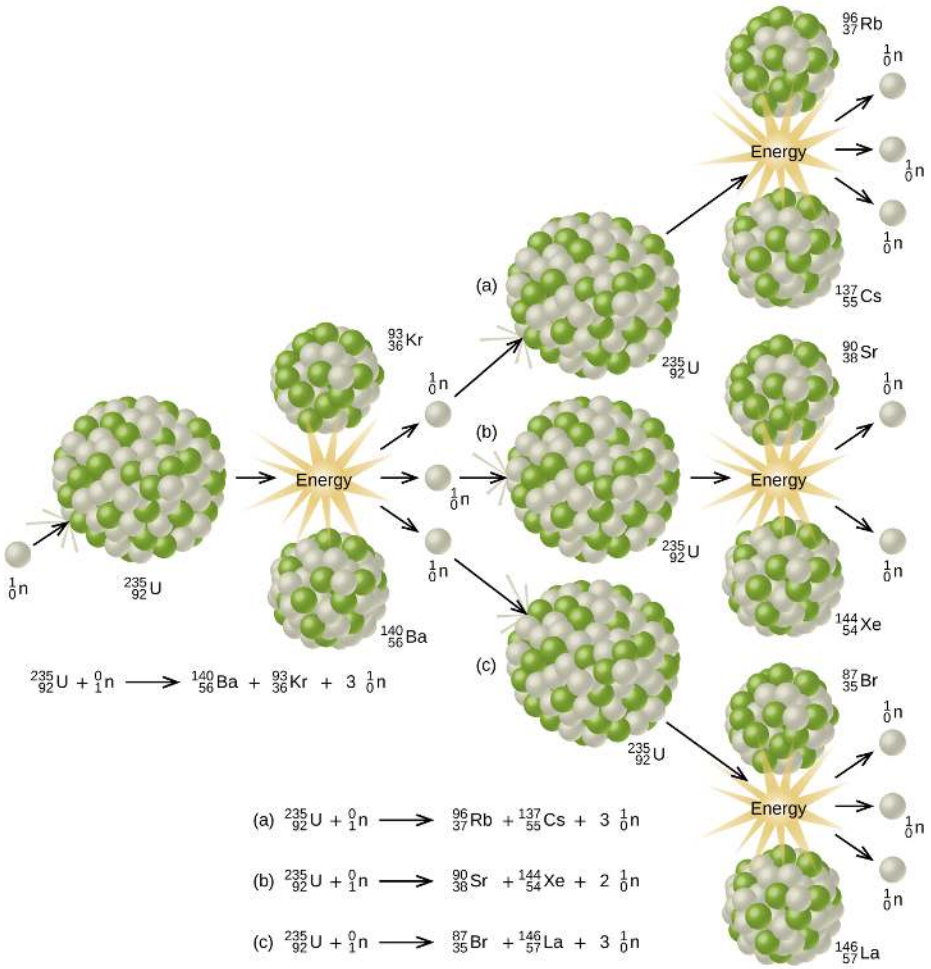


Figure **9.7.6** The fission of a large nucleus, such as U-235, produces two or three neutrons, each of which is capable of causing fission of another nucleus by the reactions shown. If this process continues, a nuclear chain reaction occurs.

Material that can sustain a nuclear fission chain reaction is said to be fissile or fissionable. (Technically, fissile material can undergo fission with neutrons of any energy, whereas fissionable material requires high-energy neutrons.) Nuclear fission becomes self-sustaining when the number of neutrons produced by fission equals or exceeds the number of neutrons absorbed by splitting nuclei plus the number that escape into the surroundings. The amount of a fissionable material that will support a self-sustaining chain reaction is a critical mass. An amount of fissionable material that cannot sustain a chain reaction is a subcritical mass. An amount of material in which there is an increasing rate of fission is known as a supercritical mass. The critical mass depends on the type of material: its purity, the temperature, the shape of the sample, and how the neutron reactions are controlled (Figure **9.7.7**).

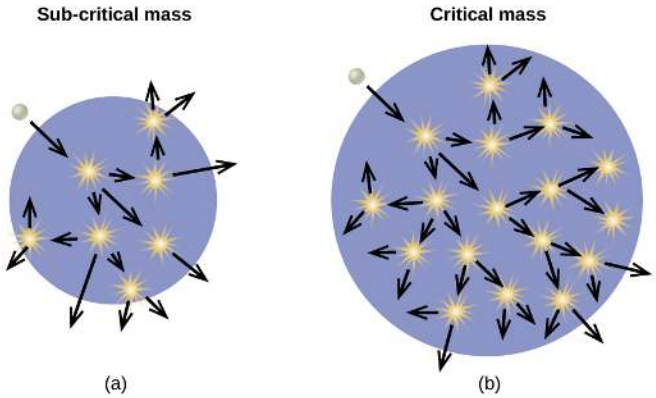


Figure **9.7.7** (a) In a subcritical mass, the fissile material is too small and allows too many neutrons to escape the material, so a chain reaction does not occur. (b) In a critical mass, a large enough number of neutrons in the fissile material induce fission to create a chain reaction.

Thermonuclear Reactions

Thermonuclear fusion is a way to achieve nuclear fusion by using extremely high temperatures. There are two forms of thermonuclear fusion: *uncontrolled*, in which the resulting energy is released in an uncontrolled manner, as it is in thermonuclear weapons ("hydrogen bombs") and in most stars; and *controlled*, where the fusion reactions take place in an environment allowing some or all of the energy released to be harnessed for constructive purposes. The discussion below is limited to the fusion process that powers the sun and the stars.

The prime energy producer in the sun is the fusion of hydrogen to form helium, which occurs at a solar-core temperature of 14 million kelvin. The net result is the fusion of four protons into one alpha particle, with the release of two positrons, two neutrinos (which changes two of the protons into neutrons), and energy (Figure **9.7.8**).

This is a net reaction of a more complicated series of events:

$$4\,{}^{1}_{1}\mathrm{H} \longrightarrow {}^{4}_{2}\mathrm{He} + 2\,{}^{1}_{0}\mathrm{n}$$

A helium nucleus has a mass that is 0.7% less than that of four hydrogen nuclei; this lost mass is converted into energy during the fusion. This reaction produces about 3.6×10^{11} kJ of energy per mole of ${}^{4}_{2}\mathrm{He}$ produced. This is somewhat larger than the energy produced by the nuclear fission of one mole of U-235 (1.8×10^{10} kJ), and over 3 million times larger than the energy produced by the (chemical) combustion of one mole of octane (5471 kJ).

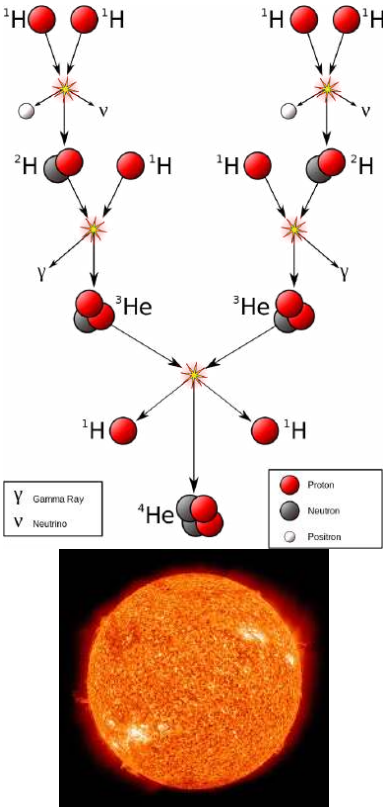


Figure **9.7.8** Nuclear fusion producing helium (left). The Sun is a main-sequence star, and thus generates its energy by nuclear fusion of hydrogen nuclei into helium (right).

Summary

- Nuclear energy comes from tiny mass changes in nuclei as radioactive processes occur.
- In fission, large nuclei break apart and release energy; in fusion, small nuclei merge together and release energy.
- The continues process whereby neutrons produced from the initial fission of a large nucleus like U-235 cause further fission of another nucleus.
- In a critical mass, a large enough number of neutrons in the fissile material induce fission to create a chain reaction.
- The most important fusion process in nature is the one that powers the stars. The net result is the fusion of four protons into one alpha particle, with the release of two positrons, two neutrinos (which changes two of the protons into neutrons), and energy

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- TextMap: Beginning Chemistry (Ball et al.)
- Marisa Alviar-Agnew (Sacramento City College)
- Wikipedia

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9.8: Nuclear Bombs

Learning Objectives

- Describe the key features of an atomic bomb.
- Define nuclear fallout.

World war two brought about many advances in weaponry. The Nazis used the immense science ability of their newly conquered countries to attempt to create super weapons to keep the new territory. The weapons included new tanks like the feared Tiger Tank, or the highly advanced Luftwaffe air force. However, the one weapon the Nazi's really wanted to hold was the atomic bomb. The problem that the Nazi's began to have though was that many of the great minds they once had left the country and came to the United States. Also, in the end Allied troops got to Hitler and his scientists just before they could complete any atomic bombs. The U.S. also wanted to create an atom bomb, and for the same reasons. The Manhattan Project was started to form this new weapon.

The Manhattan Project was successful in the United States because of the vast resources that could be pulled together for the project. The great minds worked under the University of Chicago football field to try and create fission. A plant in Tennessee had the sole purpose of producing enough uranium for atomic bomb testing. Finally, New Mexico was the epicenter of the whole operation. This is where the bombs were constructed and tested. The resources needed were immense. There had to be enough fuel for the bomb, and everything required to make it. There had to be housing and food for all the scientists. Maybe most importantly, there had to be enough money to support the project. The Unites States was able to effectively use all of these resources, while the Germans did not have the resources, and didn't use them as effectively. Finally, after years of hard work an atomic bomb test took place of July 16, 1945. The bomb was held together in some parts by just tape, yet it was a huge success. The problem was that the war in Europe was already over, so President Truman had to decide whether or not to use the bomb on Japan.

The war in the Pacific was a lot different than the war in Europe. In Europe, you landed once and fought your way through to Berlin to defeat the Nazi's. However, in the Pacific Japan controlled hundreds of Islands before you got to the mainland. The invasion would have cost huge amounts of American lives and resources. As a result, when the bomb had a successful test President Truman said he hardly hesitated to approve of the usage of the atomic bomb on Japan.

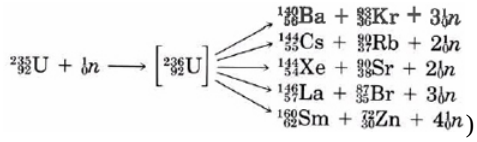
The first atomic bomb was dropped on Hiroshima on August 6, 1945 by the Enola Gay. The bomb destroyed the city, killing almost 100,000 people. The city of Hiroshima was essentially leveled. Following this attack, on August 9, 1945 another atomic bomb was dropped on Nagasaki. The same effects were felt in this city. The United States was ready to drop another atomic bomb in the third week of August, 3 more in September, and 3 more in October if necessary. However, on August 15 Japan surrendered to the allies and World War Two was officially over.



Figure **9.8.1** (left) Hiroshima before the atomic bomb (right) Hiroshima after the atomic bomb

The Workings of the Atomic Bomb

A crucial feature of the fission of uranium without which an atom bomb is impossible is that fission *produces more neutrons than it consumes*. As can be seen from Eqs. (1), for every neutron captured by a $^{235}_{92}\mathrm{U}$ nucleus, between two and four neutrons are produced. Suppose now that we have a very large sample of the pure $^{235}_{92}\mathrm{U}$ isotope and a stray neutron enters this sample. As soon as it hits a $^{235}_{92}\mathrm{U}$ nucleus, fission will take place and about three neutrons will be produced. These in turn will fission three more $^{235}\mathrm{U}$ nuclei, producing a total of nine neutrons. A third repetition will produce 27 neutrons. a fourth 81. and so on. This process (which is called a *chain reaction*) escalates very rapidly. Within a few microseconds a very large number of nuclei fission, with the release of a tremendous amount of energy, and an atomic explosion results.



There are two reasons why a normal sample of uranium metal does not spontaneously explode in this way. In the first place natural uranium consists mainly of the isotope $^{238}_{92}\mathrm{U}$, while the fissionable isotope $^{235}_{92}\mathrm{U}$ comprises only 0.7 percent of the total. Most of the neutrons produced in a given fission process are captured by $^{238}_{92}\mathrm{U}$ nuclei without any further production of neutrons. The escalation of the fission process thus becomes impossible. However, even a sample of pure $^{235}\mathrm{U}$ will not always explode spontaneously. If it is sufficiently small, many of the neutrons will escape into the surroundings without causing further fission. The sample must exceed a **critical mass** before an explosion results. In an atomic bomb several pieces of fissionable material, all of which are below the critical mass, are held sufficiently far apart for no chain reaction to occur. When these are suddenly brought together, an atomic explosion results immediately.

Two types of atomic bombs were developed concurrently during the war: a relatively simple and a more complex . The gun-type design proved impractical to use with , and therefore a simpler gun-type called was developed that used , an that makes up only 0.7 percent of natural . Chemically identical to the most common isotope, , and with almost the same mass, it proved difficult to separate the two.

In parallel with the work on uranium was an effort to produce , which was discovered at the in 1940. After the feasibility of the world's first artificial nuclear reactor, the , was demonstrated in 1942 at the in the , the Project designed the at Oak Ridge and the production reactors at the in , in which uranium was irradiated and into plutonium. The plutonium was then chemically separated from the uranium, using the . The plutonium implosion-type weapon was developed in a concerted design and development effort by the Los Alamos Laboratory.

Isotopic Enrichment

A great deal of the five years of the Manhattan Project was spent in separating the 0.7 percent of $^{235}\mathrm{U}$ from the more abundant $^{238}\mathrm{U}$. Most of this work was performed at the at . This was done by preparing the gaseous compound $\mathrm{UF_6}$ and allowing it to effuse through a porous screen. Each effusion resulted in a gas which was slightly richer in the lighter isotope. Repeating this process eventually produced a compound rich enough in $^{235}\mathrm{U}$ for the purposes of bomb manufacture.

Synthesis of Plutonium

In parallel with the work on uranium was an effort to produce , which was discovered at the in 1940. Only the first bomb dropped on Japan used uranium. The second bomb used the artificial element *plutonium*, produced by the neutron bombardment of $^{238}\mathrm{U}$:

$$^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{239}_{94}\mathrm{Pu} + 2\,{}^{0}_{-1}\beta$$

Fission of Pu-239 occurs in much the same way as for U-235, giving a variety of products; for example,

$$^{239}_{94}\mathrm{Pu} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{90}_{38}\mathrm{Pu} + {}^{147}_{56}\mathrm{Ba} + 3\,{}^{1}_{0}\mathrm{n}$$

Again this is a highly exothermic reaction yielding about the same energy per mole (20 000 GJ $\mathrm{mol^{-1}}$) as $^{235}\mathrm{U}$.

This immense amount of energy released is the reason why plutonium and uranium were used. By comparison, 1 ton of TNT yields about 4 GJ $\mathrm{mol^{-1}}$ of energy. This means that the atomic bombs had about 5,000 times more energy than 1 ton of TNT, that is a huge amount of energy, and explains why the bomb was so effective and destructive.

Nuclear explosion



Video 9.8.1 *Nuclear explosion power comparison.*

Although the Fat Man atomic bomb was extremely powerful and destructive, it is not even close to the power of subsequent nuclear bombs. The atomic age was set forth by the United States on those two fateful days in August. In the subsequent years many other countries harnessed the power of nuclear weapons, including Russia, China, Britain, and France. The "high point" of the atomic age came with the explosion of the *Tsar Bomba* by Russia. This bomb was equal to 50 megatons of TNT, or 2,500 times more powerful than the Fat Man bomb. It was said that when the bomb was detonated the shock wave in the ground could be felt over 600 miles away (the bomb wasn't even detonated on the ground either, but rather in mid air!). The advance and use of nuclear weapons seemed to be growing at an extraordinarily fast pace. However, countries stepped up and signed various treaties, including the Nuclear Non-Proliferation Treaty, to stop the increase in nuclear weapons and hopefully the use of any more in the future.

Bomb Construction

At Los Alamos, New Mexico, J. Robert Oppenheimer, and his research group were given the task of assembling and testing the fission bomb. Both types of fuel that were manufactured (U-235 and Pu-239) would be placed separately into two different bomb designs. The smaller of the two bombs would contain U-235 and was code-named "Little Boy." The larger bomb, which housed Pu-239, was named "Fat Man." Of the two, only the Pu-239 bomb would be tested before it was dropped in wartime.

The basic design of the U-235 bomb is shown in the figure below. To prevent the spontaneous detonation of an atomic bomb, the fissile U-235 is kept in a subcritical configuration. It is then rapidly assembled into a supercritical mass using conventional explosives. Once the bomb has achieved this mass, any neutron introduced into it will be likely to initiate a chain reaction. The mechanism for "Little Boy" was a gun that fired one subcritical piece of U-235 into another to form a supercritical mass (Figure **9.8.2**). The pieces had to be assembled within a time less than the average time between appearances of spontaneous neutrons from either U-235 or cosmic radiation. A conventional explosive in an artillery barrel could fire the U-235 mass at speeds of a few millimeters per second, fast enough to prevent a fizzle caused by a spontaneous neutron setting off a premature chain reaction.

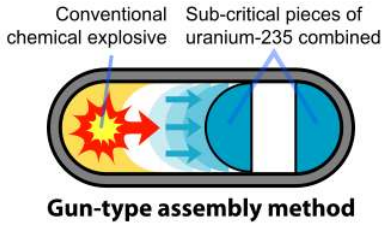


Figure 9.8.2: Little Boy: Gun-Type Device. (Public Domain).

Originally, the gun-type mechanism was planned for both the U-235 and Pu-239 weapons. However, a problem arose with the Pu-239 bomb that required a different assembly mechanism because of the small amount of Pu-240 that is produced with the Pu-239 in the reactor. Pu-240 emits large numbers of neutrons spontaneously: 1,030 neutrons per gram per second compared with 0.0004 neutrons per gram per second for U-235. Even at a concentration of 1% Pu-240 in the fissile Pu-239, the required mass of Pu emits

52,000 neutrons per second or one neutron every 20 microseconds. Thus, it is very probable that a neutron from Pu-240 will initiate a premature chain reaction during the critical last 100 microseconds of the critical mass in a gun-type assembly. This problem was discovered in mid-1944, well after the start of the construction of the massive Hanford plutonium production facilities.

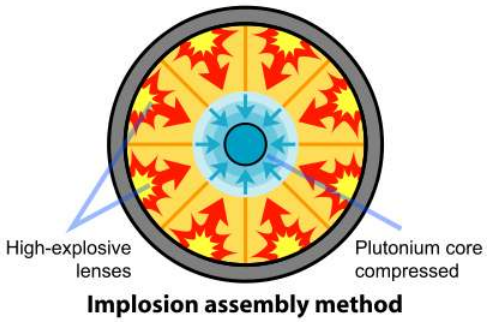


Figure 9.8.3: Fat Man: Implosion-type bomb. (Public Domain).

The removal of the Pu-240 was impractical. So the scientists and engineers looked for a faster method of assembling the plutonium. A mechanism based on implosion provided the solution to this problem. In this design, the fissile material is shaped into a single sphere with a mass slightly less than critical (Figure 9.8.3). Layers of carefully shaped high explosives surround the sphere. When the explosives are detonated, the force of the shock wave compresses the fissile material into a smaller volume, forming a supercritical mass. This method of assembly is much faster than the gun-type mechanism and thus eliminates the problems resulting from spontaneous neutron emission of Pu-240. The spherical mass resulted in a pumpkin-shaped weapon called "Fat Man".

Example 9.8.1

Watch the from the 23-minute mark through the 32-minute mark of the third installment of the History Channel's Manhattan Project and answer the questions below.



1. What were the problems with the two different types of fuel that were to be used in the fission weapons?
2. What was the configuration or set-up of the Pu-239 bomb?
3. The combination of electromagnetic separation and gaseous diffusion enriched enough U-235 to produce how many bombs?
4. Why was the U-235 bomb never tested?
5. When was the construction of the U-235 completed?
6. How much did Truman know about the nuclear bombs when FDR was alive?
7. Who was selected to pilot the plane for the nuclear weapons?
8. What island would serve as a base to house the nuclear bombs before delivering them to their targets?

In July 1945, the United States had enough fissile material for one uranium and two plutonium weapons. The scientists and engineers felt confident that the gun-type assembly mechanism for Little Boy would function properly. Besides, they did not have

the material for a test device. They were less confident about the implosion mechanism on the plutonium weapon and felt that a test was necessary. On July 16, 1945, the first nuclear device, known as "The Gadget", was placed on a 100-foot tower and successfully detonated in the Alamogordo Desert, 200 miles south of Los Alamos (Figure 9.8.4).

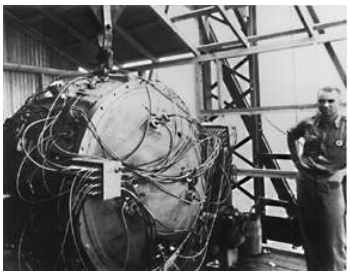


Figure 9.8.4: The Gadget at the Trinity Test Site, 1945. Courtesy of the U.S. Department of Defense

As the war with Japan continued and a costly allied invasion loomed as a real possibility, President Truman approved the use of nuclear weapons against selected Japanese targets. The U.S. Army Air Force received orders to use these weapons anytime after August 3, 1945. On August 6, "Little Boy" was dropped on Hiroshima (Figure 9.8.5).



Figure 9.8.5: Little Boy - The only U-235 weapons constructed during WWII. Courtesy of the U.S. Department of Defense

Little Boy was a uranium weapon containing 141.4 pounds of fissionable material containing 82.7% U-235. Only about two pounds fissioned, releasing an energy equivalent to 15-16,000 tons of TNT. The immediate effects of the blast killed an estimated 70,000 people, and by the end of 1945 an additional 20,000 to 70,000 deaths occurred, many due to lack of adequate medical resources.

Three days later, "Fat Man" destroyed a large part of Nagasaki (Figure 9.8.6). Fat Man contained 13.6 pounds of Pu-239, of which only 2 pounds underwent fission. The explosive yield was equivalent to about 22,000 tons of TNT. Fat man resulted in 35,000 immediate deaths. By the end of 1945, at least 70,000 people perished in this event.

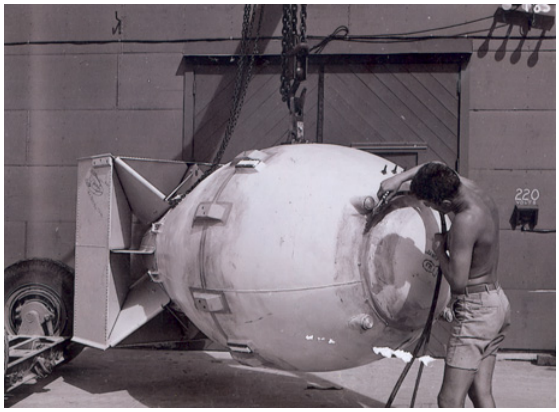


Figure* 9.8.6*: *Fat Man – One of many Pu-239 nuclear weapons constructed during WWII. Courtesy of the U.S. Department of Defense*

Example 9.8.2

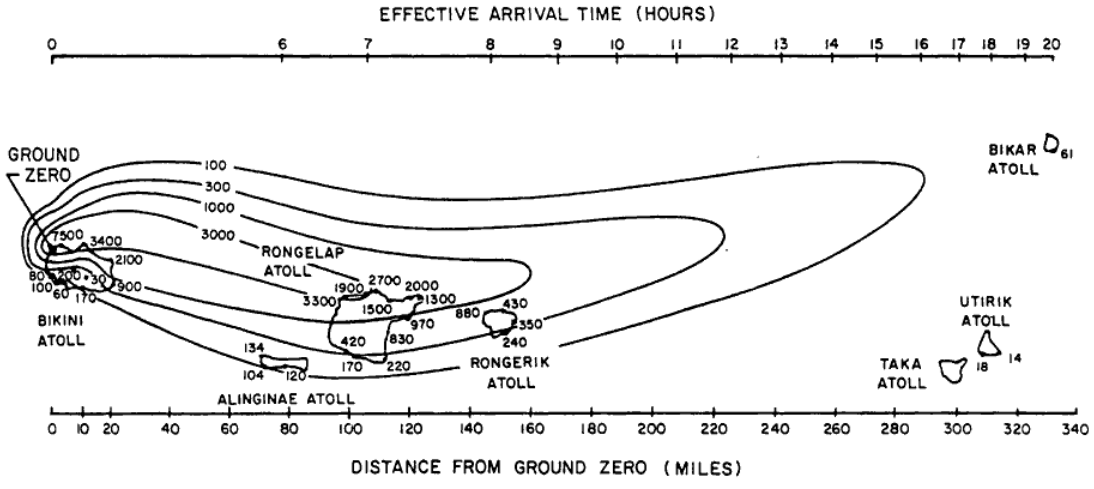
Start the video below at the 23:20 mark and stop it at the 29-minute setting. Then, answer the questions below:



9. When and where was the first nuclear bomb tested?
10. Was the bomb placed on the ground?
11. What were scientists afraid the first nuclear bomb would do?
12. What did Edward Teller (father of the fusion bomb) apply to his skin before the bomb was ignited? Why did he do this?
13. What did the bomb do to the tower and the surrounding sand?
14. In the photograph, where did General Grove focus his attention?

Nuclear Fallout

Nuclear fallout refers to the radioactive material that "falls out" of the atmosphere after a nuclear explosion (reactor or bomb). It consists of dust and radioactive particles that can contaminate an area with radioactivity and pose a huge health hazard to biological organisms. It can contaminate the animal food chain which can have drastic effects on the affected region. Weather has a huge impact on fallout, wind currents can spread radioactive fallout either over a large area, such as in the case of *Castle Bravo*, or not.



alt

Figure 9.8.2: The 450 km (280 mi) fallout plume from 15 Mt shot Castle Bravo, 1954. (Pubic Domain; United States Department of Energy via Wikipedia)

In regards to nuclear reactions, fission produces more fallout products that fusion. Intense heat of the latter type of reactions reduces the amount and type of radioisotopes produced. Although more powerful, fusion is a "cleaner" type of nuclear reaction. By increasing the fission component of a fusion weapon, bombs can be designed to generate more fallout products.Of the different

types of isotopes that fission produces, the most worrisome are Sr-90, Cs-137,and I-131. The first of these isotopes has a half-life of 28.8 years and decays by gamma and beta emission. Once ingested or inhaled, Sr-90 deposits in teeth, bone,and bone marrow. Sr-90 exposure can lead to bone cancer and/or leukemia. Cs-137 ($t_{1/2}$ = 30.17 years) emits beta and gamma radiation. This ionizing radiation deposits in soft tissues of the body. In addition, this particular radioisotope is water soluble and can easily contaminant food and water supplies. I-131 had a half-life over 8.1 days and undergoes gamma/beta decay. Once this fallout product enters the body, it attacks the thyroid gland. Extensive damage could affect heart rate, blood pressure, body temperature, and childhood growth. In addition, I-131 exposure could result in thyroid cancer.

Nuclear Fallout

Watch the fallout video and then answer the questions below:



Summary

- In an atomic bomb several pieces of fissionable material are held sufficiently far apart for no chain reaction to occur. When these are suddenly brought together, the critical mass is reached and an atomic explosion results immediately.
- The two fission bombs assembled at Los Alamos, New Mexico, by J. Robert Oppenheimer, and his research group were manufactured with two types of fuel namely, U-235 and Pu-239.
  - The smaller of the two bombs would contain U-235 and was code-named "Little Boy." This bomb was dropped in Hirsohima, Japan on Aug.6, 1945.
  - The larger bomb, which housed Pu-239, was named "Fat Man." This bomb was dropped in Nagazaki, Japan on Aug.9, 1945.
- Nuclear fallout refers to the radioactive material that "falls out" of the atmosphere after a nuclear explosion (reactor or bomb).

Contributors and Attributions

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9.9: Uses and Consequences of Nuclear Energy

Learning Objective

- Know the benefits and consequences of nuclear energy.

Nuclear Power Generation

The generation of electricity is critical for operation of businesses, health care delivery, schools, homes, and other areas requiring the use of electrical power. According to 2011 statistics, coal is used for 42% of the total power generated, with natural gas being employed for another 25%. Nuclear power plants are employed in about 19% of the cases, with renewable energy sources supplying the last 13%. All of these fuels are used to heat water to generate steam. The steam then turns a turbine to generate electricity.

Nuclear power plants use the energy from nuclear fission to produce electricity. **U-235** is the preferred nuclear fuel because when its atoms are split (fissioned), they not only emit heat and high energy radiation but also enough neutrons to maintain a chain reaction and provide energy to power a nuclear power plant. Uranium is found in rocks all over the world but is relatively rare and the supply is finite making it a nonrenewable energy source.

Uranium usually occurs in combination with small amounts of other elements and once it is mined, the U-235 must be extracted and processed before it can be used as a fuel in a nuclear power plant to generate electricity. The processed uranium is formed into fuel rods and then bundled into fuel assemblies. Fuel assemblies are stored onsite until they are needed by the reactor operators. At this stage, the uranium is only mildly radioactive, and essentially all radiation is contained within the metal tubes. When needed, the fuel is loaded into a reactor core (Figure **9.9.1**). Typically, about one third of the reactor core (40 to 90 fuel assemblies) is changed out every 12 to 24 months.

The most common type of reactors are the **pressurized water reactors** (PWR) (Figure **9.9.1**) in which water is pumped through the reactor core and heated by the fission process. The water is kept under high pressure inside the reactor so it does not boil. The heated water from the reactor passes through tubes inside the steam generator where the heat is transferred to water flowing around the tubes in the steam generator. The water in the steam generator boils and turns to steam. The steam is piped to the turbines. The force of the expanding steam drives the turbines, which spin a magnet in coil of wire – the generator– to produce electricity.

After passing through the turbines, the steam is converted back to water by circulating it around tubes carrying cooling water in the condenser. The condensed steam – now water – is returned to the steam generators to repeat the cycle.

The three water systems (condenser, steam generator, and reactor) are separate from each other and are not permitted to mix. Water in the reactor is radioactive and is contained within the containment structure whereas water in the steam generator and condenser is nonradioactive.

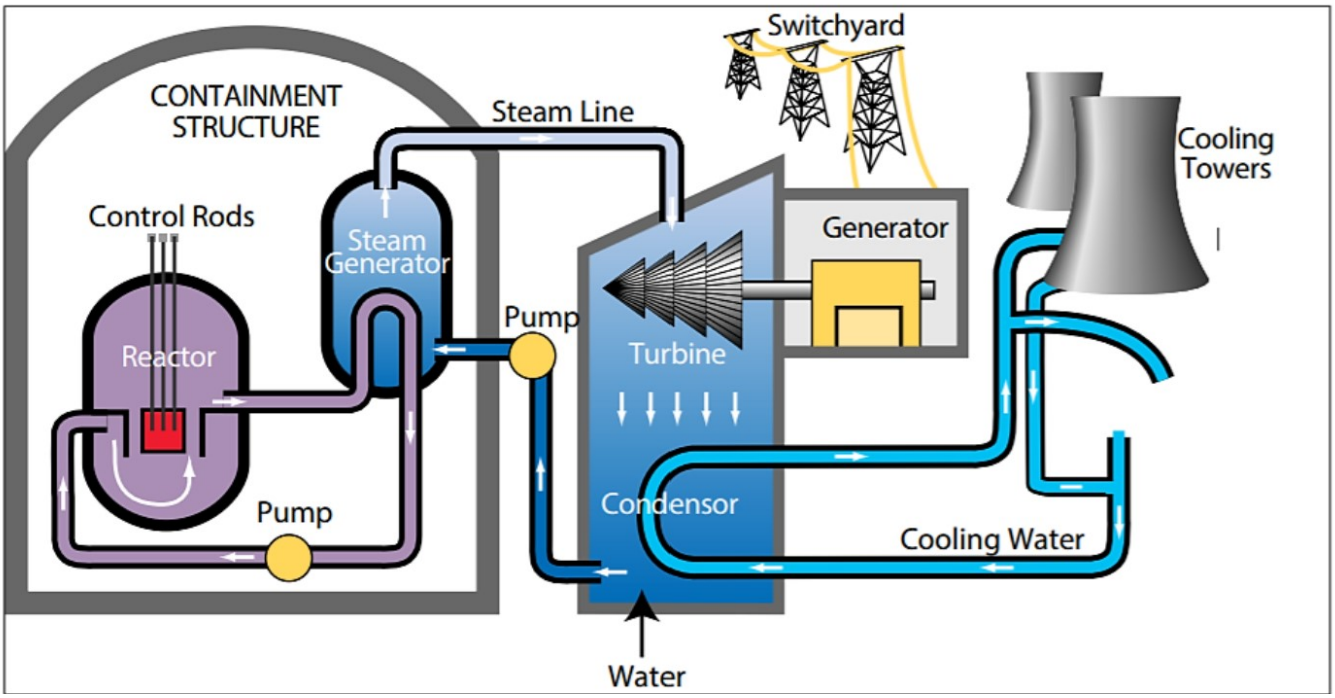


Figure **9.9.1:** *A schematic diagram of a pressurized water reactor (PWR), the most common type of nuclear reactor. Diagram from Tennessee Valley Authority (public domain). www.tva.com*

Benefits of Nuclear Energy

By using fission, nuclear power plants generate electricity without emitting air pollutants like those emitted by fossil fuel-fired power plants. This means that financial costs related to chronic health problems caused by air pollutants such as particulate material, carbon monoxide, nitrogen oxides and ozone among others are significantly reduced. In addition nuclear reactors do not produce carbon dioxide while operating which means that nuclear energy does not contribute to the global warming problem.

Another benefit of nuclear energy over fossil fuels especially coal is that uranium generates far more power per unit weight or volume. This means that less of it needs to be mined and consequently the damage to the landscapes is less especially when compared to the damage that results from coal mining such as mountaintop removal.

Nuclear power is also used to propel ships. The turbine can be connected to a propeller system. The rotating turbine shaft will turn the propeller to move the ship.



Figure **9.9.2** *Nuclear submarine.*

The Drawbacks of Nuclear Energy

The main environmental concern related to nuclear power is the creation of radioactive wastes such as uranium mill tailings, spent (used) reactor fuel, and other radioactive wastes. These materials can remain radioactive and dangerous to human health for thousands of years. Radioactive wastes are classified as low-level and high-level. By volume, most of the waste related to the nuclear power industry has a relatively low-level of radioactivity. **Uranium mill tailings** contain the radioactive element radium, which decays to produce **radon**, a radioactive gas. Most uranium mill tailings are placed near the processing facility or mill where they come from. Uranium mill tailings are covered with a barrier of material such as clay to prevent radon from escaping into the atmosphere, and they are then covered by a layer of soil, rocks, or other materials to prevent erosion of the sealing barrier.

Spent fuel rods contain a variety of products, consisting of unstable nuclei ranging in atomic number from 25 to 60, some transuranium elements, including plutonium and americium, and unreacted uranium isotopes. The unstable nuclei and the transuranium isotopes give the spent fuel a dangerously high level of radioactivity. The long-lived isotopes require thousands of years to decay to a safe level. The ultimate fate of the nuclear reactor as a significant source of energy in the United States probably rests on whether or not a politically and scientifically satisfactory technique for processing and storing the components of spent fuel rods can be developed.

The other types of **low-level radioactive waste** are the tools, protective clothing, wiping cloths, and other disposable items that get contaminated with small amounts of radioactive dust or particles at nuclear fuel processing facilities and power plants. These materials are subject to special regulations that govern their handling, storage, and disposal so they will not come in contact with the outside environment.

High-level radioactive waste consists of spent nuclear reactor fuel (i.e., fuel that is no longer useful for producing electricity). The spent reactor fuel is in a solid form consisting of small fuel pellets in long metal tubes called rods. Spent reactor fuel assemblies are initially stored in specially designed pools of water, where the water cools the fuel and acts as a radiation shield. Spent reactor fuel assemblies can also be stored in specially designed dry storage containers. An increasing number of reactor operators now store their older spent fuel in dry storage facilities using special outdoor concrete or steel containers with air cooling. There is currently no permanent disposal facility in the United States for high-level nuclear waste.

When a nuclear reactor stops operating, it must be **decommissioned**. This involves safely removing the reactor and all equipment that has become radioactive from service and reducing radioactivity to a level that permits other uses of the property. The U.S. Nuclear Regulatory Commission has strict rules governing nuclear power plant decommissioning that involve cleanup of radioactively contaminated plant systems and structures, and removal of the radioactive fuel.

A **nuclear meltdown**, or uncontrolled nuclear reaction in a nuclear reactor, can potentially result in widespread contamination of air and water. Some serious nuclear and radiation accidents have occurred worldwide. The most severe accident was the Chernobyl accident of 1986 in the then Soviet Union (now Ukraine) which killed 31 people directly and sickened or caused cancer in thousands more. The Fukushima Daiichi nuclear disaster (2011) in Japan (Figure **9.9.3**) was caused by a 9.0 magnitude earthquake that shut down power supply and a tsunami that flooded the plant's emergency power supply. This resulted in the release of radioactivity although it did not directly result in any deaths at the time of the disaster.

Another nuclear accident was the Three Mile Island accident (1979) in Pennsylvania, USA. This accident resulted in a near disastrous core meltdown that was due to a combination of human error and mechanical failure but did not result in any deaths and no cancers or otherwise have been found in follow up studies of this accident. While there are potentially devastating consequences to a nuclear meltdown, the likelihood of one occurring is extremely small. After every meltdown, including the 2011 Fukushima Daiichi disaster, new international regulations were put in place to prevent such an event from occurring again.



Figure **9.9.3** (a) After the accident, contaminated waste had to be removed, and (b) an evacuation zone was set up around the plant in areas that received heavy doses of radioactive fallout. (credit a: modification of work by "Live Action Hero"/Flickr)

The processes for mining and refining uranium ore and making reactor fuel require large amounts of energy. Nuclear power plants have large amounts of metal and concrete, which also require large amounts of energy to manufacture. If fossil fuels are used for mining and refining uranium ore or in constructing the nuclear plant, then the emissions from burning those fuels could be associated with the electricity that nuclear power plants generate.

Nuclear Reactor Design and Operation



***Video* 9.9.1** *The design and safe operation of a nuclear reactor.*

Summary

- The importance of nuclear power in generating electricity is described.
- The operation of a nuclear power plant is described.
- The drawbacks of nuclear energy is described.

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